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Polymer monolayers and Langmuir – Blodgett films. The influence of the chemical structure of the polymer and of external conditions on the formation and properties of organised planar assemblies

V V Arslanov

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Abstract. The current state of the problem of the preparation from polymers of planar mono- and multi-layer organised structures on the surface of a liquid or a solid is analysed. The structure and physicochemical properties of the corresponding monolayers and Langmuir – Blodgett films are examined and the characteristic features of the packing of the macromolecules on the surface of the liquid, questions concerning the stability of their monomolecular films, the compatibility of high- and low-molecular-mass compounds in the monolayers, and the influence of the degree of polymerisation, size, and orientation of the side group on the phase state of the monolayers are discussed. Much attention is devoted to the methods of preparation of Langmuir – Blodgett polymer films with a specified architecture and to the study of the characteristics of these monolayer ensembles and the prospects for their practical employment in molecular devices. The bibliography includes 306 references.

I. Introduction

The perfection of the objects and processes in living nature has long attracted the attention of natural scientists, stimulating an endeavour to use the principles underlying the functioning of biological systems for the development of devices for different purposes operating at the molecular level. Evidently, this approach is applicable not only to the traditional objects in molecular engineering, namely functional (molecular) electronics, ionics, photonics, etc., but also to a wider range of systems. In particular, the idea of embodying in molecular constructions based on the biosimulation concept of a most important principle, namely the self-regulation of biological systems, appears extremely attractive. For example, in order to ensure the specified properties, it is at present necessary to introduce pigments, inhibitors, antioxidants, and plasticisers into polymer coatings and plastics at concentrations which are so high that they alter significantly (as a rule, impair) the entire set of the fundamental characteristics of the materials. The creation of systems capable of recognising external influences at the molecular level and of responding to them adequately is one of the urgent problems in modern science. The achievement of rapid, local, and selective recognition and response opens the way to a reduction of material and energy expenditure on the neutralisation of undesirable influences on the system.

In a broad sense, these problems constitute the subject of the rapidly developing supramolecular chemistry, i.e. the 'constructional chemistry of intermolecular linkages' according to the definition of Jean-Marie Lehn — the 1987 Nobel Laureate in chemistry.[1] The scheme presented in Fig. 1 (see over) demonstrates the transition from molecular chemistry to molecular and supramolecular devices.[1] Within the framework of the present review, the supra- and poly-molecular chemical characteristics of organised assemblies are examined in parallel (and not consecutively) because recognition, transformation, migration, etc. processes, assigned in Fig. 1 to the field of supramolecular chemistry, are discussed in relation to organised planar structures.

On the basis of the foregoing, the creation of molecular (supramolecular) devices must include at least three main stages.

1. The construction or synthesis of organic molecules carrying a specific function. This problem of molecular chemistry, in which questions concerning the organisation of individual atoms, their binding to one another, and their disposition in a specific manner relative to one another in order to impart to the molecule the required steric structure are considered.

V V Arslanov Laboratory of the Adhesion of Polymers, Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, 117915 Moscow, Russian Federation. Fax (7-095) 952 75 14

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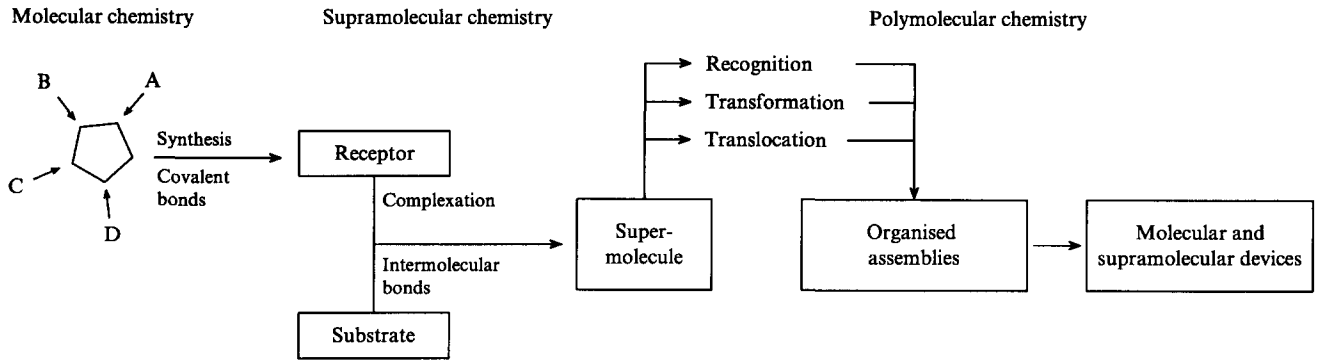


Figure 1. Transition from molecular to supramolecular chemistry.[1]

2. The creation of organised polymolecular assemblies. Evidently, the existing technological procedures for orienting materials, for example drawing, crystallisation, orientation in a flow, and epitaxial growth, are unsuitable for the preparation of assemblies of molecular dimensions. This problem is solved in two ways — primarily by self-assembly and forced organisation. The spontaneous formation of the nucleic acid double helix, which includes the recognition and selective pairing of bases, is a classical example of self-assembly. A second more recent example is the self-organisation of monolayers of alkylsiloxanes, aliphatic acids, dialkyl sulfides, dialkyl disulfides, and thiols on the surfaces of aluminium, silver, gold, silicon oxide, etc.[2-11] A higher level of this effect is illustrated in Fig. 2. A diphilic thiol and acid undergo selective adsorption and organisation on a mosaic surface consisting of sections of gold and aluminium oxide. Here too it is easy to identify two processes: the recognition of 'its own' support (Au for the thiol and Al_2O_3 for the acid) and self-organisation on the latter.

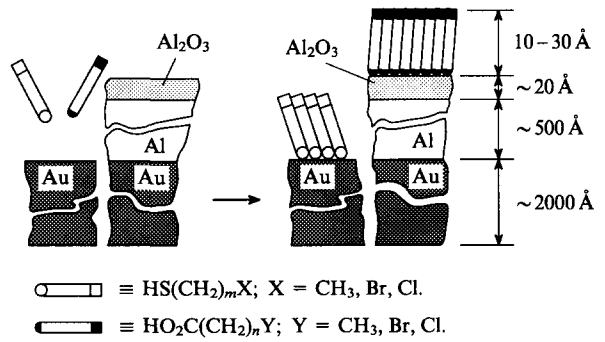


Figure 2. The formation of self-organised monolayers of diphilic molecules of an alkanethiol and a carboxylic acid on adsorption from solution on the surface of gold textured with aluminium oxide.[12]

The Langmuir–Blodgett method should be regarded as forced organisation, because the formation of a monolayer with a specified organisation on the surface of water and its transfer to a solid support require an energy expenditure.

Superlattices, i.e. nanometer layers of organic molecules with a specified alternation order with respect to their thickness, can be obtained only by the Langmuir–Blodgett method. It has been shown[13] that under these conditions the superlattices possess order also in the plane of the monolayers.

One may claim that the application of the Langmuir–Blodgett method always leads to the creation of molecular (supramolecular) constructions, the physical and chemical properties of which are largely determined by the cooperative nature of the behaviour of their constituent molecules.

3. The creation of molecular (supramolecular) devices. In order that a molecular construction should acquire the status of a device, it must be capable of performing a definite function. Solutions to this problem at a higher scale level are known — for example, in the existing devices for the storage and processing of information which employ only one physical effect and only one form of dynamic inhomogenity. The trend towards the miniaturisation of electronic instruments down to molecular devices entails the problem of the realisation and integration of various physical effects in one construction. However, being restricted solely by the 'safety tunnel', specifying the distances between molecular keys at 5–10 nm, such technology would make it possible to pack molecular electronic elements with a density of 10^{18} units per cm^3.[14]

Thus, in order to create molecular devices, it is necessary to seek molecular components capable of performing a specified function and suitable for incorporation into a system organised in a specific manner and formed by different types of polymolecular assemblies. The principal feature of these components and the devices formed from them consists in the fact that they perform their functions on the basis of the properties of molecules and supramolecules.[1] The nature of the components or functional groups introduced into the system determines the operations which can be performed by the molecular assemblies: energy, electron, and ion transfer, different types of chemical reactions, the recording, transmission, and storage of information, etc.

For low-molecular-mass diphilic compounds, studies involving all three stages indicated above are being actively prosecuted at the present time. One of the principal ways of carrying out the first of these (molecular chemistry) involves the grafting to the molecule carrying a definite physical functional group (tetracyanoquinodimethane, tetrathiafulvalene, thiophene, pyridine, dyes, etc.) of a hydrocarbon chain, which ensures the organisation of the monomolecular film on the surface of water.

In the case of polymer systems, this procedure is less appropriate in view of the limited set of macromolecules containing suitable functional groups. Therefore, in order to create monolayer-forming functional polymers, a different procedure is usually resorted to — side groups capable of responding to external influences are grafted onto the main hydrophobic chain. The polymerisation of functionalised monomers and their copolymerisation with inactive monomers, acting as spacer units in the polymer chain, are also employed.

The limited set of objects, the problem of the stability of the monolayers, and the complexity of the manipulations involved in the preparation of Langmuir–Blodgett films (LBF) are apparently the main causes of the appreciable lagging behind (especially in quantitative terms) of the research into high-molecular-mass mono- and multi-layer structures. On the other hand, the problem of the creation of molecular devices can hardly be solved without using high-molecular-mass compounds both in passive insulating layers and in active transforming and transmitting two-dimensional elements. However, the

studies on monolayers and LBF cannot be restricted to approaches traditional for low-molecular-mass compounds which have already been established as a result of attempts at the practical employment of the latter in molecular electronics, nonlinear optics, and other branches of engineering. The specific features of high-molecular-mass chemistry have given rise to a different range of fundamental questions and have influenced the applications of the corresponding monolayers and LBF.

A need has arisen for a more detailed consideration of the physical chemistry of the two-dimensional state of macromolecules and the establishment of a relation between the structure of polymers and their behaviour in a monolayer, the formation of multilayer, including alternating, high-molecular-mass assemblies, and for the study of the possibility of applying two-dimensional organised structures of high-molecular-mass compounds to traditional products of polymer chemistry—organic coatings, adhesives, and membranes (for example, for the preparation of materials with a specified gradient of a characteristic parameter). The theoretical interest in the phase behaviour of monolayers,[15] including high-molecular-mass monolayers, has arisen because certain approaches to the description of critical phenomena cannot be applied in the three-dimensional case but are fully applicable to a system with a smaller number of dimensions.[16]

In the first review, published in 1991,[17] two of the three known methods of preparation of polymeric LBF were examined: (1) the formation of monolayers from monomers on the surface of a liquid (water), their polymerisation in the monolayer, and their transfer to a solid support and (2) the formation of monolayers from monomers, their transfer to a solid support, and the polymerisation in the LBF of each layer or the multilayer film as a whole. A third method envisages the formation of monolayers on the surface of water from complete polymers with subsequent transfer to a solid support. The principal difference between these procedures (responsible for the differences between the approaches to the study of the corresponding systems) consists in the fact that in the first two cases the initial monolayers are formed from low-molecular-mass compounds (monomers), while in the last procedure they are formed from high-molecular-mass compounds. Although many of the problems associated with the transfer of polymer monolayers to solid supports are similar for the first and third procedures, this by no means applies to all of them. Thus the monomers forming the monolayer must be diphilic, insoluble in water, and involatile, but these requirements are not obligatory for monolayers of macromolecules. For example, poly(methyl methacrylate), which does not exhibit distinct diphilic properties, and cellulose derivatives or poly(vinyl alcohol), which are soluble in water, nevertheless form monolayers on the surface of water. These features of high-molecular-mass compounds, on the one hand, expand the number of objects of study and the possibility of using organised planar structures, and, on the other hand, create specific problems in the formation of LBF.

The study of the properties of macromolecules on the surface of water (a liquid) and their influence on the formation of multilayer structures on a solid support is essential for the preparation of high-quality LBF with a minimum number of defects and a homogeneous orientation, thickness, and surface density from polymer monolayers.

It is essential to note that the optimistic prediction in the first review[17] of an increase in the intensity of research into polymer monolayers and LBF expected in the immediate future has unfortunately not so far come true. Systematic studies on polymer monolayers, similar, for example, to the studies carried out on diacetylene monolayers and LBF, are not being prosecuted at the present time. Furthermore, the results of earlier investigations, many of which have not lost their current value, are inadequately taken into account in present day research.

The history of the research into macromolecules in monolayers began with the studies by Devaux in 1903.[18] Since then and up to the Second World War, mainly natural[19–21] and synthetic[22–24] polymers were investigated. However, most of these studies and systematic treatment of data on polymer monolayers date back to the 1940s–1950s.[25–27] In subsequent years, such investigations were performed quite vigorously and were marked by sudden surges due to the appearance of some new polymeric object or the discovery of interesting properties in an existing material. This refers, for example, to studies on polyorganosiloxanes (1960–1970) or to the current interest in conducting polymers (polythiophenes, polypyrroles), as well as fullerenes and their derivatives.[28,29]

Overall, two stages can be distinguished in the chronology of studies on thin polymer films. The early and longest stage involves mainly the investigation of monolayers of macromolecules on the surface of water. In the subsequent 15 years more attention was devoted to LBF in connection with the development of research into molecular architecture. Since LBF are formed by transferring monolayers from the surface of a liquid and reproduce to some extent the structure of these monolayers, the equivalence of both stages or aspects of the research into problems of molecular design becomes evident.

These considerations have determined the structure of the present review, in which the conditions governing the formation, equilibria, stability, and phase states of polymer monolayers and the influence on the latter by the molecular mass of the polymer, the length of the side chain, the composition and pH of the support, temperature, and other factors are analysed. Questions concerning the correspondence between the structural-morphological characteristics of monolayers of high-molecular-mass compounds on the surface of a liquid and in LBF also occupy an important place. The behaviour of monolayers in the collapse region as well as the specific features of the use of thin films of polymers for the formation of LBF are examined.

II. The genuine existence of polymer monolayers on the surface of a liquid

The short but rich in content review by Gaines in 1991[30] takes us back one hundred years to the period where the question of the genuine existence of monolayers of large molecules arose as a result of studies by Pokels.[31] Gaines believes that the 'either polymer or monolayer' dilemma still remains the order of the day, i.e. the question of the genuine existence of polymer monolayers remains of current interest. The genuineness of the monolayer or of the spreading process, i.e. of the existence of a state of the polymer layer in which each monomer unit is in contact with the surface of the subphase, has been tested in accordance with Crisp's recommendations.[26] According to the latter, genuine spreading occurs in the case where reproducible surface pressure (π)–area (A) relations are obtained when the concentration of the solution from which the monolayer is formed or the initial spreading area are altered, and also when the monolayer is deposited from different solvents. When the monolayer is formed by helical (polydimethylsiloxane on a low-energy liquid support[32]) or coiled (polystyrene[33]) macromolecules, it cannot formally be regarded as genuine. However, if its constituent molecules have several stable conformations and structural transformations (for example helix–coil) are possible on the surface of the liquid, then also the study of nongenuine monolayers of this kind may prove useful.

In the review mentioned above,[30] the author addresses the question whether it is possible that the macromolecular coils produced as a result of coiling up in the bulk of the solution could become uncoiled on reaching the surface of the liquid with formation of a true monolayer. There are apparently no fundamental objections to a positive answer to this question. Furthermore, an important argument in support of such an answer arises from the repeatedly established agreement

between the experimental limiting areas of the close-packed monolayer (A_0 at $\pi \to 0$) and the analogous parameters obtained from models.

Less unambiguous results were obtained in tests of the genuineness of the monolayers carried out in accordance with Crisp's criteria. In his studies on poly(vinyl acetate), poly(methyl methacrylate), and poly(methyl acrylate) monolayers, Crisp found that variation of the conditions in the preparation of the monolayers does not alter the compression isotherm. In these experiments, the concentration of the solutions was varied from 0.005% to 0.2% and the solvents were the 1 : 1 water–propyl alcohol mixture, acetone, and benzene for poly(vinyl acetate) and acetone, benzene, and toluene for the remaining two polymers.[25] However, in contrast to this, a dependence of the position of the compression isotherms on the concentration of the solution deposited on the surface of water has been observed in another study[27] for poly(methyl methacrylate) monolayers. Thus, when the concentration was varied from 0.018% to 0.2%, the limiting area per molecule (A_0) changed from 21 to 18 Å^2 (A_0 = 14.5 Å^2 according to Crisp). An even more marked influence of the concentration of the solution on A_0 has been observed[33] for polystyrene: an increase in the concentration of the solution from 0.033% to 0.2% lowered the area by a factor of 2.

The importance of these studies is evident, just as it is evident that they must be based on the ideas of the classical theory of polymer solutions and the modern views arising from the scaling method.

The deposition of monolayers from solutions in good, poor, and θ-solvents, where the macromolecular coils have different sizes and the nature of their interaction with the solvent and with one another is likewise different, can lead to the formation of various surface structures in the monolayers. The concentration of the polymer solution is also a fundamental parameter, which determines, for example, the degree of overlap of the coils. The transfer of the macromolecules from the bulk to the surface, occurring when the polymer solution spreads on the surface of a liquid, is accompanied by complex processes. The ratio of the rates of spreading and evaporation of the solvent, the replacement of the solvent by the liquid constituting the subphase (water), the influence of the field of surface forces, and the limitations as regards the possibility of a rearrangement in the conformation of the macromolecules imposed by the wall (surface) are factors which still have to be analysed.

The form of the macromolecules in the three- and two-dimensional states can be conveniently correlated by resorting to the scaling concept. We shall assume that the polymer is deposited from an effective solvent, the quality of which does not change on passing to the two-dimensional system, i.e. from the bulk-phase solution to the monolayer. In this case, the size of the macromolecules (R) is determined by a critical parameter in the form of a power exponent for different numbers of effective segments in the macromolecule (N) which are different for the three- and two-dimensional systems.[34,35]

Three-dimensional space: $R \sim N^{3/5}$
Two-dimensional space: $R \sim N^{3/4}$

This implies an increase in the size of the flattened macromolecular 'coils' when the molecules pass from the bulk of the solution to the surface and hence the existence of a threshold concentration

$$\frac{1}{A^*} = \frac{N}{S}$$

(where S is the area of the effective segment), for which there is a transition from a dilute two-dimensional solution to a semidilute solution where the flat coils begin to overlap on the surface of the solution. The possibility of a limited interpenetration of the planar coils in a two-dimensional system probably accounts for the stability of the polymer monolayers and the reversibility of the $\pi - A$ isotherms in compression–expansion cycles.

III. The stability of polymer monolayers

It is necessary to distinguish two approaches to the problem of the stability of monolayers. The first, commonest, reduces to the observation of the decrease in the area of the monolayer at a constant surface pressure and of the surface pressure when the mobile barrier is stopped (A = const) in the course of a definite arbitrarily selected time interval. As a rule, the purpose of such experiments is to establish the possibility of maintaining the necessary density of the monolayer in the course of the formation of the LBF.[36,37] Within the framework of this approach, the stability of the monolayers can be increased by altering the temperature and by introducing stabilising additives into the monolayer or the subphase and, in the case of ionogenic compounds, also by altering the pH of the support, by employing electrolyte solutions as the subphase, etc.

The second, more rigorous approach is associated with the establishment of thermodynamic equilibrium in the monolayers. It is based on a number of conditions, the main ones of which are the possibility of applying the techniques of thermodynamics and statistical physics to the calculation of the characteristics of the system, the determination of the phase state of the monolayers and of the transitions between them, and comparison of the results obtained by different workers. Within the framework of this approach, one has to solve the problem of the selection of a standard state of the system,[38] for which at least three versions have been proposed.

1. The state with an equilibrium spreading pressure,[39,40] i.e. with a surface pressure, established in the monolayer, which is in equilibrium with the volume of the substance.[41–44]

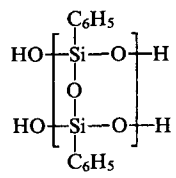
2. The state with a surface pressure corresponding to the phase transition between liquid-expanded and liquid-condensed states of the monolayer.[45,46]

3. The state with a surface pressure corresponding to the transition of the gaseous monolayer to a liquid one.[45,47]

Evidently the choice of the standard state is dictated by the behaviour of the monolayer. The rare data on the gaseous state of monolayers and the controversy concerning the phase transition between two liquid states do not engender optimism as regards the selection of the last two parameters as the standard ones even for the thoroughly investigated low-molecular-mass compounds. The only disadvantage of the equilibrium spreading pressure as a criterion of the thermodynamic stability of the monolayer is perhaps the fact that many compounds do not spread from the bulk phase under the usual experimental conditions (room temperature). The solution of this problem, i.e. the determination of the equilibrium spreading pressure (π_e) for such compounds, is seen by some workers[48] as a procedure involving the deposition on the surface of water of a concentrated solution of the test substance (for example, dipalmitoylphosphatidylcholine) until the maximum surface pressure is attained. This quantity is identified with π_e. It is believed[48] that this procedure is rapid, reliable, and reproducible and yields values of π_e which agree with the equilibrium spreading pressure determined by the traditional method involving spreading from the bulk phase. Another method for the determination of π_e has been proposed by Albrecht.[49] The pressure corresponding to the collapsed monolayer (palmitic acid), which is compressed under controlled conditions, is adopted as the equilibrium spreading pressure. Albrecht[49] notes the importance of this procedure for the determination of isotherms for polymers with long relaxation times. In principle, both procedures considered can be useful. However, one must understand that in either case the monolayer is in equilibrium not with its bulk phase (crystals) but with a hydrated form of the latter, which has an equilibrium spreading

pressure $\pi_e' > \pi_e$. For low-molecular-mass compounds, these questions have been examined in detail by Trapeznikov and coworkers.[50,51] For polymer monolayers, such studies have not yet been carried out.

Analysis of the temperature variations of the equilibrium spreading pressure has been carried out[52] in relation to ladder oligophenylsilsesquioxanes (M = 1 200) and polyphenylsilsesquioxanes (M = 60 000) on the surface of water.



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As can be seen from Fig. 3, neither the oligomer nor the polymer spreads spontaneously from the bulk phase at 20 °C. The curve for the oligomer consists of the linear sections AB and BC with different slopes and of a high-temperature section parallel to the abscissa axis. The initial section (AB) has the highest slope; at T = 30 °C, the curve exhibits a break, the surface pressure at this point corresponding to the collapse pressure of the oligomer monolayer. This point may be associated with the onset of the formation of a new hydrated bulk phase of the oligomer, the properties of which differ from those of the bulk phase initially placed on the surface of water. The $\pi_e - T$ relation for the polymer is of a different type: as the temperature is raised from 20 to 35 °C, π_e changes insignificantly, after which its more rapid increase is observed. At T > 55 °C, the pressures π_e for the oligomer and polymer become similar and change only slightly on further increase in temperature. The appearance at the point C of yet another hydrated form of the oligomer is indicated by the following observations. At T = 60 °C, the white oligomer powder on the surface of water begins to undergo surface fusion and becomes transparent, assuming the form of lenses, which again become white at T = 70 °C. We may note that the melting points of the oligomer and the polymer are 150 and 400 °C respectively. Consequently, during spreading from the bulk phase on the surface of water, high-molecular-mass compounds can yield several hydrated forms, each of which has its own equilibrium spreading pressure π_e'. The existence of such forms with high values of $\pi_e' > \pi_e$ accounts for the possibility of obtaining reproducible and reversible monolayer compression isotherms for both low-molecular-mass compounds and for polymers. In this case, the metastable state of the monolayer of the initial (bulk phase) material proper becomes stable (corresponds to equilibrium) for hydrated derivatives of the latter. Therefore measurement of the temperature variations of the equilibrium spreading pressure or the determination of π_e' from data for the spreading of concentrated solutions may be recommended as procedures for the estimation of the degree of equilibrium in true monolayers.

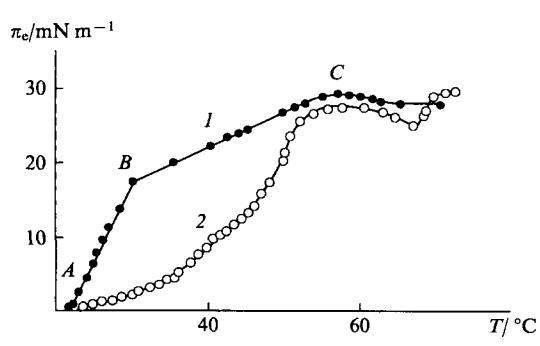


Figure 3. Temperature dependence of the equilibrium spreading pressure (π_e) for oligophenylsilsesquioxane (curve *1*) and polyphenylsilsesquioxane (curve *2*) on the surface of water.[52]

An important procedure for the determination of the stability of monolayers involves the analysis of their relaxation properties.[53–55] The critical parameters of the compression isotherms, obtained for surface pressures exceeding π_e or π_e', are determined by the relation between the relaxation times of the molecular processes occurring on compression of the monolayer and the time of the measurement, which is inversely proportional to the rate of deformation (but not compression) of the monolayer. It has been shown[56] for an arachidic acid monolayer that, with increase in the observation time from 600 to 3 × 10^5 s (the rate of deformation diminished correspondingly from 10% to 0.02% min^{-1}), the monolayer collapse pressure decreases from 60 to 20 mN m^{-1}. Unfortunately, such experiments are so far extremely rare for polymers having distinct viscoelastic properties and a large set of relaxation times.[57]

IV. The influence of the molecular mass of the polymer on the properties of the monolayers

The question of the influence of the molecular mass (or degree of polymerisation), a fundamental characteristic of macromolecules, on the behaviour of monolayers was actively discussed several decades ago. The outcome of these discussions is contained in the reviews already mentioned.[25,26,43,52] Here we present only a brief analysis of these problems, having supplemented it with the results of studies carried out in this field during the last twenty years. The commonest point of view is one according to which the $\pi - A$ isotherms are independent of the molecular mass in the range of surface pressures usually measured (π > 0.5 mN m^{-1}). This was first demonstrated[19] for cellulose derivatives. A similar result has been obtained[58] for hydroxypropyl- and hydroxyethyl-cellulose monolayers. A weak dependence of the compression isotherms on the degree of polymerisation has been established for poly(vinyl acetate),[25] poly(ethyl succinate),[23] and polyorganosiloxanes.[59–61] However, an increase in the limiting area per monomer residue from 18.7 to 26.8 Å^2 with increase in the molecular mass of the polymer from 2.5 × 10^4 to 10^6 has been observed[62] for poly(methyl methacrylate) monolayers. The ratio of the areas depends on the rate of compression of the monolayer, the monolayer of the high-molecular-mass specimen showing a more marked dependence. The dependence of A_0 on the molecular mass, found[63] for monolayers of oligoesters on the surface of water, vanishes when a 40% aluminium sulfate solution, which improves the spreading of the oligomers, is used as the subphase.

The differences in the behaviour of monolayers of polymers with low and high degrees of polymerisation are in many respects associated with the influence of the end groups of the molecules, which alter their polarity and the ability to spread or dissolve in the subphase. Naturally such influence is more significant in the case of short chains.

Whereas the question of the influence of molecular mass on surface pressure and surface potential remains controversial, the dependence of the mechanical properties of monolayers on the dimensions of macromolecules is not open to doubt. Despite this and also the large amount of information obtained from data on the viscoelastic properties of monolayers about the characteristics of the behaviour of macromolecules in a two-dimensional state (ranging from a dilute solution to the condensed phase), such studies are rarely carried out at the present time.

The final aim of the majority of studies designed to establish the dependence of the compression isotherms on the size of the macromolecules is the determination of the molecular masses of the polymers. Since this parameter is calculated on the basis of the two-dimensional analogue of the van't Hoff equation and its

modifications, the monolayer must be in the gaseous (vapour) state, although this state can be by no means always achieved for large molecules. Guastalla, who measured the surface pressure with a sensitivity to within 0.001 mN m^{-1}, may be regarded as the pioneer in this field of study.[64] Subsequently many attempts were undertaken to calculate the molecular masses of polymers in the region of isotherms with low surface pressures.[26,43,65] In particular, the molecular mass of a polymer obtained in the polymerisation of a double-stranded silane lipid in a monolayer has been determined recently.[66]

Numerous studies have been devoted to the determination of the molecular masses of polymers in the range of comparatively high surface pressures and hence high surface concentrations of the test substance. On the basis of such data, which have been reviewed,[52] one cannot reach a conclusion either about the possibility of using this region of compression isotherms to estimate the molecular mass of the polymer or whether the molecular mass found refers to the entire molecule or its segment.

V. The phase states of polymer monolayers

Much attention has been devoted in the past to the phase states of monolayers of low-molecular-mass compounds. There exist several classifications of these states,[67–69] which have been proposed by Adam,[42] Dervichian,[70] Harkins,[41] Stenhagen,[71] Lundquist,[72] and Lin.[73] Furthermore, the refinement of the structures of monolayers in different states is still being continued and communications are being published concerning the observation of new states of monolayers comprising small molecules.[67]

The phase states of monolayers of high-molecular-mass compounds have remained less investigated (and are being less investigated). Since Crisp's time, little attention has been paid to this question and the subdivision which he proposed for polymer monolayers into expanded and condensed can hardly be regarded as a classification of states. The causes of the situation which has arisen can be scarcely attributed to the poor 'distinctiveness', according to Gaines,[43] of the $\pi - A$ relations for polymer monolayers. It appears that, at the level attained in the study of polymer monolayers at the present time, it has not been possible to formulate an adequately rigorous classification of their phase states for a number of other reasons. Firstly, there have been virtually no systematic studies nowadays on the structure of polymer monolayers by modern methods, which are frequently employed for monolayers of low-molecular-mass compounds. The second reason is the complexity of polymeric objects and the consequent need to develop definite principles of study, which are applicable within the framework of a particular group of compounds. The latter consideration requires explanation. The classical objects for the study of the states of monolayers of low-molecular-mass substances are aliphatic acids and alcohols. By altering the length of the aliphatic chain in these compounds, it is possible to attain all the states of the monolayer ranging from gaseous to solid-condensed. From this it follows that the length of the hydrocarbon chain or its increment are fundamental characteristics, which determine the properties of the aliphatic alcohol and acid monolayers. In the previous section, it was shown that a fundamental characteristic of polymers—the molecular mass—hardly influences the state of the polymer monolayers and, if such influence does exist, it arises solely from the change in the fraction of the end groups on the surface. Therefore, comparison of the properties of monolayers of high-molecular-mass compounds is valid only within the framework of specially selected groups of polymers. Modern polymer chemistry provides interesting possibilities for the construction of homologous series of different types of large molecules. We shall attempt to designate such series.

1. Polymers without distinct diphilic properties, i.e. without side chains. Typical representatives are polyethers with different lengths of the polymethylene chain between the oxygen atoms. By increasing the complexity of the polar unit (ester, carbamate, and other groups) separating the polymethylene chains, it is possible to obtain other types of such systems. Copolymers and block copolymers of this series, with a variable ratio of the fragments in the main chain, are also interesting objects with controllable variation of the characteristics of the monolayers.

2. Polymers with weak diphilic properties, i.e. polymers having short side chains. In this case, the behaviour of the monolayer depends on the structure of not only the main chain but also of that of the side chain.

3. Polymers with long side chains. In the presence of long spacers in the main chain, the side chains behave to some extent independently of one another. The spacer can be inserted also between the main and side chains. The compatibility in the monolayer of incompatible monomers carrying specific functional groups can be achieved as a result of the spreading of the copolymer made up of the corresponding monomers.

4. Macrocyclic, ladder, and other polymers with a more complex chemical structure and behaviour.

The second possible method of combining different polymers may be based on a chemical principle where the variation of the properties of monolayers and LBF is considered within the framework of a single class of compounds, for example polyacrylates. This approach makes it possible to reduce to a minimum the differences in the chemical nature of the polymers and to trace in a fairly pure form the influence of the structure of the chains on the characteristics of the two-dimensional systems formed from them.

The latest reviews on polymer monolayers refer to the 1960s; during the period which has elapsed since then, many new studies, devoted to traditional and new polymers, including those specially synthesised for the formation of surface films, have been published. Bearing in mind the special interest in LBF, attention has been concentrated in these studies on functionalised monolayers.

It appears that analysis of the development of the field of surface chemistry should include a discussion of those properties of polymer monolayers which determine the possibility of the formation of high-quality LBF, functionalised films, and surfaces.

An essential condition for the preparation of LBF with a specified thickness and orientation is the formation of a genuine monolayer not containing nonspreading material. The question arises what should be the structure of the polymer chain and the ratio of the lengths and the compositions of the side chains and spacer groups. Should one in such cases graft the group with the required function to the polymer chain or should one produce a mixed monolayer with the matrix polymer? The use of binary mixtures (for the composition of side chains or copolymers) removes the problem of synthesis but the problem of compatibility then arises, especially if one is dealing with components having side chains of different lengths. Furthermore, it is essential to take into account the possibility of interlayer and intralayer diffusion in the LBF made up of mixed monolayers which disturbs the organisation of the monolayers established on the surface of the liquid. The immobilisation of the low-molecular-mass component can be achieved in at least four ways: (1) by the formation of a mixed monolayer from the chemically noninteracting polymer and an additive which are insoluble in the subphase; (2) by the introduction of a water-soluble polymer into the subphase under the monolayer of the second low-molecular-mass component; (3) by the introduction into the subphase of a functional additive under the polymer monolayer; (4) by the formation of a mixed monolayer of the polymer (oligomer, monomer) with an additive and subsequent immobilisation of the additive by cross-linking with a specified density.

The choice of the method for the formation of functionalised monolayers and LBF depends on the purpose of the two-dimensional system being formed. Modern macromolecular chemistry and molecular design have given rise to virtually unlimited possibilities for the construction of stable heteromolecular structures based on polymers.

Following the chosen chemical principle for the arrangement of polymers in groups, it is useful to begin the discussion with the traditional thoroughly investigated polymers of the acrylic and methacrylic series.

VI. Polyacrylates and polymethacrylates

1. Monolayers and Langmuir – Blodgett films based on homopolymers

The widely investigated acrylic and methacrylic polymers make it possible to follow the influence of the structure and composition of the main and side chains of the macromolecules on the properties of their monolayers. The base polymer is undoubtedly poly(methyl methacrylate) (PMMA). The increased interest in this polymer during recent years is due to its use as a positive electron-beam resist in the traditional technology for the deposition of a polymer solution onto a support.[74] The increase in the sensitivity and resolution of elements consisting of PMMA and its copolymers can be achieved by their deposition onto a solid support by the Langmuir – Blodgett method.[75]

The compression isotherms of monolayers of PMMA stereoisomers[76] are illustrated in Fig. 4, while Table 1 presents the molecular masses and limiting areas of the PMMA monolayers obtained by different workers. Evidently, in the formation of a true equilibrium monolayer, the differences between the polymer solution concentrations employed, the solvents, and the rates of compression should not have influenced quite so much the values of A_0. For monolayers of low-molecular-mass compounds (for example, aliphatic acids), it is difficult to imagine the existence of such discrepancies in the measurements of the limiting area. However, for small molecules the problems of stereoregularity, which are extremely important (as can be seen from Fig. 4) for the position of the compression isotherm, are manifested in a different way. Furthermore, the steric hindrance due to the chain structure of the polymers apparently precludes the complete assumption by the PMMA elementary units of the *cis*-conformation of the methoxycarbonyl groups most favourable for the formation of the monolayer (Fig. 5). It follows from the study of Labbauf and Zack[80] that the *cis*-form of the PMMA elementary unit gives rise to larger limiting areas than the *trans*-form. The experimental facts indicating the incomplete spreading of PMMA in a monolayer on the surface of water can apparently be explained[31]

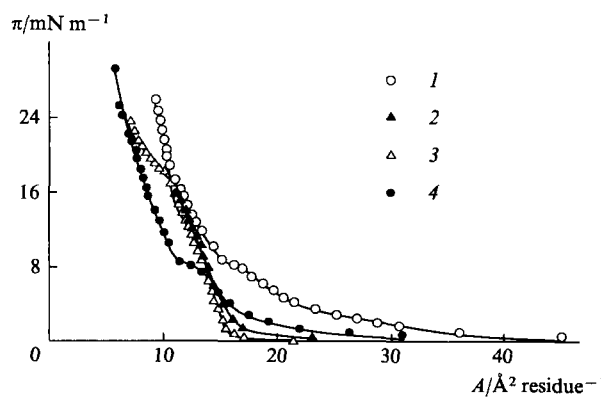


Figure 4. Surface pressure – area isotherms for monolayers of stereoisomers of poly(methyl methacrylate):[76] (*1*) isotactic; (*2*) atactic; (*3*) syndiotactic; (*4*) stereoblock (isotactic + syndiotactic).

Table 1. The limiting areas (A_0) of poly(methyl methacrylate) monolayers for different molecular masses of the polymer.

Molecular mass	A_0/Å² residue⁻¹	Ref.
–	14.5	25
25000	16.1	62
110000	16.1	62
640000	18.2	62
> 1000000	18.1	62
153000	17.6	77
90000	17.0	78
480000	16.4	79
76000	14.5[a]	33
32600	13.8[a]	33
30500	15.2[a]	33
200000	18.0	27
188000	15.6	75
139000	18.4	80
340000	15.8	81
71000	17.0	82
500000	17.0	82
265000	19.4	82
490000	17.7	83
56000	18.7	84
155000	18.7	84
–	16.0	30
–	20.0	85

[a] Calculated with the aid of $\pi - A$ relations quoted by Parker and Shereshefsky.[33]



Figure 5. Isomers of the ester groups of poly(methyl methacrylate): (*a*) *trans*-; (*b*) *cis*-.[80]

by the high cohesion between the main chains of the polymer. Naturally in this case it is extremely difficult to seek a relation between the molecular mass of the polymer and the limiting area of the monolayer. Such behaviour of the PMMA monolayers is not general: for other polymers forming true monolayers, there is good agreement between the experimental compression isotherms obtained by different workers.

The replacement of the methyl group in the main chain by a hydrogen atom, i.e. the transition from methacrylic to acrylic polymers, increases sharply the ability of the polymer to form a true monolayer.

More extensive possibilities for controlling the structure of the monolayer and for introducing into the latter functionally significant fragments are associated with the alteration of the side groups of the polymers under consideration. The simplest example is provided by the increase in the length of the chain of the ester alkyl group in poly(alkyl methacrylates). As can be seen from Fig. 6, the replacement of the methyl group by the ethyl group in the side chain of the polymer greatly diminishes the cohesion between the main chains of macromolecules and leads to the expansion of the monolayer. Further increase in chain length and temperature[86] steadily increases the limiting areas and intensifies

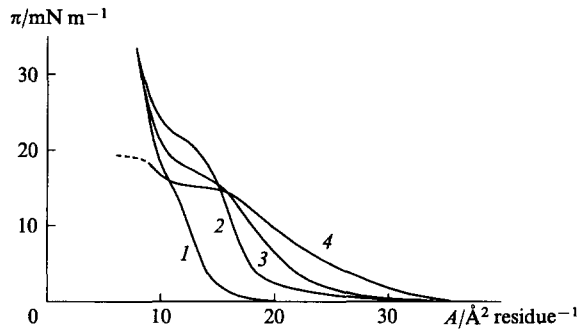


Figure 6. Surface pressure–area isotherms for monolayers of poly(alkyl methacrylates).[25] Alkyl: (*1*) methyl; (*2*) ethyl; (*3*) n-propyl; (*4*) n-butyl.

the tendency to form a plateau on the compression isotherms. Small side chains are incapable of interacting with adequate intensity and their role reduces to separating the main chains and lowering their cohesion. On the other hand, long hydrocarbon chains (C_{18}) impart a high rigidity to the condensed monolayer.[25]

The great interest in the study of poly(octadecyl acrylate) (PODA) and poly(octadecyl methacrylate) (PODMA) in monolayers[25,85–99] is caused, on the one hand, by the polymeric nature of these compounds and, on the other, by the presence of long hydrocarbon chains, which makes it possible to regard each elementary unit of the polymer as a classical diphilic surface-active low-molecular-mass substance. The discrepancies between the compression isotherms obtained by different workers for these polymers have been analysed.[90] It was postulated that these differences are caused by the type of solvent from which the monolayers were formed, the purity of the polymer, its molecular mass and/or its polydispersity, and the method used to obtain the compression isotherms. It has been shown that the discrepancies between the data of different workers are due mainly to methodological causes, i.e. the conditions under which the $\pi-A$ isotherms were obtained. It must be emphasised that the differences may be induced also by the crystallisation of the side chains of the polymer, which apparently begins from the hexadecyl members of this series.[86] An increase in temperature to 12 °C for poly(hexadecyl methacrylate) and to 29 °C for PODMA converts the solid polymer monolayers into liquid ones.[86]

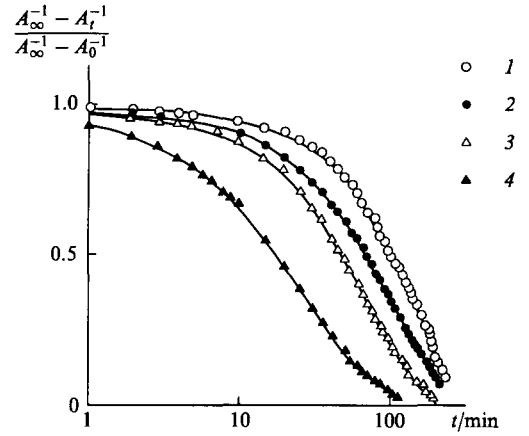
The crystallisation of PODMA in the monolayer at different temperatures and surface pressures has been investigated.[98] It has been shown that the crystallisation kinetics may be described with the aid of the Avrami equation:[100]

$$-\ln\frac{A_\infty^{-1}-A_t^{-1}}{A_\infty^{-1}-A_0^{-1}}=kt^n,$$

where A_0, A_t and A_∞ are the areas per monomer unit at times 0, t, and ∞, n is a constant characterising the mechanism of the formation of the nuclei and the type of the growing structures, and k is the rate constant of the process.

Using these constants as adjustable parameters, a good agreement was obtained between theory and experiment. Fig. 7 shows that the crystallisation process proceeds at low surface pressures and is completed in the course of 2 h. Crystallisation disturbs the equilibrium nature of the monolayer, which is manifested by the hysteresis of the compression isotherms.

The possibility of crystallisation must be taken into account in the study of the kinetics of two-dimensional polymerisation accompanied by the shrinking of the monolayer. This question has been examined[92] in the analysis of the polymerisation of octadecyl methacrylate (ODMA). The same communication contains interesting data concerning the compatibility of ODMA and PODMA monolayers. Fig. 8 presents the dependence of the



Symbols	π/mN m⁻¹	n	ln k (min⁻¹)
1	1.3	1.30	−6.40
2	1.9	1.20	−5.27
3	2.5	1.15	−5.01
4	3.2	1.00	−3.27

Figure 7. Dependence of $(A_\infty^{-1}-A_t^{-1})/(A_\infty^{-1}-A_0^{-1})$ on t for a PODMA monolayer at 30 °C.[98] Curves — theory; symbols — experiment.

average area of a mixed monomer and polymer monolayer on composition for different surface pressures. The shaded regions correspond to the crystallisation of the side chains, the upper contour of these regions corresponding to the area of the monolayer before crystallisation and the lower contour corresponding to the area after the completion of crystallisation. Crystallisation must be taken into account at low surface pressures and for degrees of conversion of the monomer exceeding 50%.

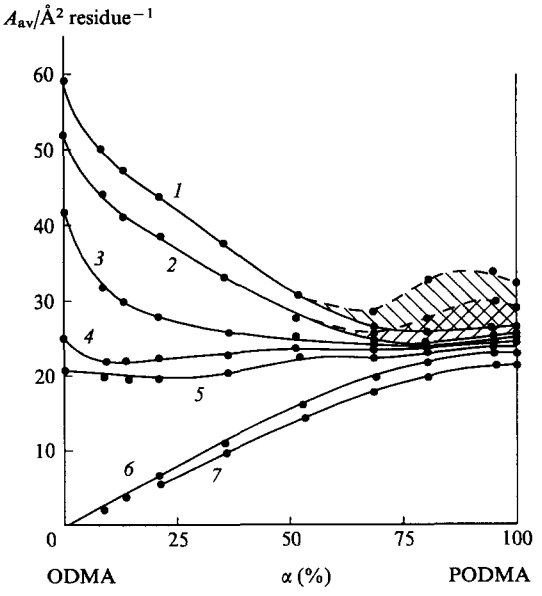


Figure 8. Dependence of the average area (A_{av}) per monomer residue on the polymer content (α = degree of conversion) in a mixed ODMA/PODMA monolayer at T = 27 °C and different surface pressures (mN m⁻¹): (*1*) 0.5; (*2*) 2.0; (*3*) 4.0; (*4*) 7.0; (*5*) 13.0; (*6*) 30.0; (*7*) 40.0. The cross-hatched regions correspond to the crystallisation of the side chains.[92]

Despite the major role of secondary cohesion, manifested for long-chain poly(alkyl methacrylate) in the crystallisation of side chains, the influence of the structure of the main chain of the polymer also persists. As can be seen from Fig. 9, the PODA monolayer is more condensed than the monolayer of its methacrylic analogue, i.e. the absence of methyl groups attached to the main chain in the first polymer diminishes the steric hindrance to its conformational rotation.[87]

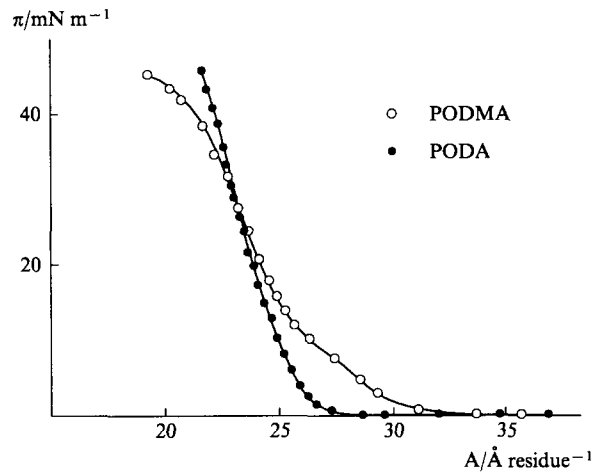


Figure 9. Surface pressure – area isotherms for PODA (M_w = 23 300, M_n = 13 000) and PODMA (M_w = 321 000, and M_n = 97 200) monolayers.[87]

These data agree with the results of the measurement of the resistance to the evaporation of water (r) through PODMA and PODA monolayers:[90] the values of r for the PODA monolayer are several times higher than for PODMA but are an order of magnitude lower than for octadecanol. Evidently, the high rigidity of the polymer chain prevents the close packing of the hydrocarbon chains in the monolayer. The introduction of a small amount of octadecanol into the polymer monolayer makes it possible to attain the level of r values characteristic of a pure octadecanol monolayer.[90]

The orientation of the side chains in LBF based on PODA and PODMA has been investigated[87,88] by polarisation IR spectroscopy in the transmission and glancing incidence versions. It has been shown[87] that an orientation of the hydro-carbon side chains almost perpendicular to the surface of the support occurs in mono- and multi-layer LBF of the Z type for both monomers. It has also been noted that their orientation depends on the type of the main polymer chain and the surface pressure at which the monolayers have been transferred. However, it has been found[88] that the orientation of the PODMA side chains in the monolayer LBF differs significantly from the perpendicular orientation of these groups in the multilayer LBF.

The introduction of aromatic substituents into the side chain of a methacrylic polymer [poly(phenyl methacrylate) and poly(benzyl methacrylate)],[101,102] leads to the formation of a condensed monolayer with small limiting areas. Although the authors themselves[101,102] have assigned the monolayers of these homopolymers to the expanded type, nevertheless the low values of A_0 and the temperature dependence of the surface pressure characteristic of a collapsed monolayer indicate the absence of true spreading.

Thus, among the investigated methacrylic homopolymers substituted most simply in the side chains, the most stable monolayers are formed by homopolymers which contain moderately and very long aliphatic side chains. We shall consider in greater detail the properties of one of them — poly(isobutyl methacrylate) (PIBMA), which forms true monolayers and high-quality LBF. It has been shown[103] that the compression isotherm for this polymer has a point of inflection at A = 19 Å^2 per monomer residue (the calculated A_0 is 20–21 Å^2 per residue), after which the monolayer collapses according to X-ray diffraction data. The linearity of the $\pi - A$ relation for $\pi < 0.5$ mN m^{-1} made it possible to determine the molecular mass of the polymer, which was found to be close to the value determined viscometrically for the PIBMA bulk-phase solution (1.7×10^5 and 2.3×10^5 respectively). There are interesting data, obtained by Naito,[103] concerning the influence of the hydrophobic properties of the surface of the solid support on the degree of transfer of the monolayer (ρ) onto the latter (the vertical method). Fig. 10 presents the dependence of ρ on the wetting angle (θ) for water on the surface of silicon. The degree of wetting was changed by varying the time of the preliminary treatment of the surface of silicon in hexamethyldisilazane. Fig. 10 shows that $\rho = 1$ for $0° < \theta < 90°$ as the support moves upwards from the aqueous subphase, while for the opposite direction of motion we have $\rho = 1$ for $\theta > 73°$. This angle corresponds to θ for water on both types of surfaces of the transferred polymer LBF. Fig. 11 illustrates the dependence of the degree of transfer on the number of LBF pairs for two silicon supports with $\theta = 65°$ and 100°. The first layer was deposited by immersing the support in the subphase. It is seen that ρ is close to 1 for a support with $\theta = 100°$. Supports with $\theta = 65°$ exhibit a considerable scatter in the values of ρ, i.e. the first monolayer exerts a significant influence on the formation of the subsequent layers. We may note two features of LBF made up PIBMA:[103] the absence of defects in the LBF (scanning electron microscopy, magnification 5×10^4) and the suppression of cadmium stearate recrystallisation processes in alternating LBF containing ten internal monolayers of the above low-molecular-mass surfactant and three outer PIBMA monolayers.

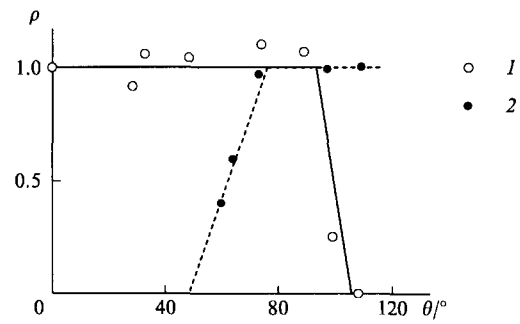


Figure 10. Dependence of the degree of transfer of the PIBMA monolayer on the wettability of the silicon surface which has been rendered hydrophobic.[103] Surface pressure in the transfer process 12.5 mN m^{-1}. Direction of motion of the support: (*1*) upwards; (*2*) downwards.

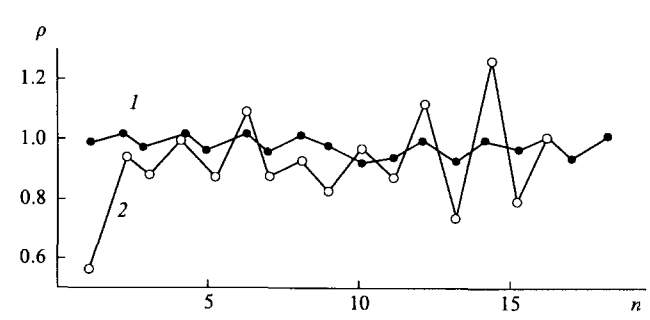


Figure 11. Dependence of the degree of transfer of the PIBMA monolayer onto silicon supports rendered hydrophobic to different extents on the number of layers.[103] Wetting angle for water: (*1*) 100°; (*2*) 65°.

Multilayer PIBMA LBF with a thickness up to 200 Å have also been investigated [104] and the extent of their defectiveness was analysed by the method involving electrolytic decoration with copper. In full agreement with Naito's data, [103] Matsuda et al. [104] showed that the LBF made up of four monolayers (42 Å) is homogeneous and has a lower density of defects (pin holes) than the analogous cadmium arachidate LBF.

More complex heterostructures containing PIBMA have been obtained: [105] (1) LBF made up of alternating PIBMA and heptacosa-10,12-diynoic or arachidic acid monolayers (altogether 20 heterolayers); (2) LBF made up of alternating units comprising one acid layer and three PIBMA layers (altogether 20 heterolayers); (3) LBF consisting of alternating PIBMA and acid bilayers (altogether 10 heterolayers). LBF of the Z type (relative to the acids) were formed in the first two cases, whilst in the third Y type LBF were produced. It was shown that, in the LBF of the first type, one polymer layer does not prevent its rearrangement and penetration by acid molecules. The diffusion of acid molecules is suppressed with increase in the number of PIBMA layers (the second type of the LBF structure). Nevertheless the authors [105] concluded that, in order to obtain more perfect heterostructures with a higher stability as a function of time, it is necessary to employ a polymer which is more rigid than PIBMA.

2. Monolayers and Langmuir – Blodgett films based on copolymers

The presence of substituents in each monomer unit of acrylic and methacrylic homopolymers creates definite difficulties in the formation of highly organised monolayers and LBF. [89] One of the ways of solving this problem involves the introduction of a hydrophilic spacer, which separates the side and main chains. It has been shown [106, 107] in relation to double-stranded methacrylic lipids that the introduction of a spacer leads to the formation of stable monolayers, the collapse pressure and the limiting area of which are close to the corresponding parameters for the monomeric lipid.

Another procedure, leading to an increase in the stability of polymer monolayers, involves the inclusion of a hydrophilic spacer in the main chain. A procedure such as hydrolysis of poly(n-butyl acrylate) to different extents has been used for this purpose. [108] Table 2 shows that, with increase in the degree of hydrolysis, the limiting area of the monolayer diminishes owing to the displacement of polar acid groups from the surface to the subphase. However, the presence of polar groups makes it possible to regulate the structure of the monolayer by varying the pH and by introducing an electrolyte into the subphase. According to the data in Table 2, an increase in the sodium chloride concentration in the aqueous subphase leads to the return of the acid groups to the surface and hence to an increase in the limiting areas, the theoretical and experimental values of A_0 being virtually identical for a 15% NaCl concentration.

Table 2. The limiting areas of poly(n-butyl acrylate) (PBA) monolayers for different degrees of hydrolysis of the polymer and different sodium chloride concentrations in the subphase. [108]

Degree of hydrolysis (%)	A_0/Å^2 residue^{-1}				
	Water	5% NaCl	10% NaCl	15% NaCl	Theoretical value
0	29.5	–	–	–	29.3
28	19.5	23.8	26.4	27.3	27.2
36	17.5	22.5	25.7	26.8	26.7
45	16.5	20.8	24.2	25.7	25.9
53	16.0	20.4	23.9	25.3	25.4

Studies of copolymer monolayers have just as long a history as those of homopolymer monolayers. As in the case of traditional investigations of copolymers in bulk and in solution, the main problem remains the elucidation of the influence of the ratio of the monomer residues constituting the copolymer on the characteristics of the systems considered — in the given instance two-dimensional systems. The properties of monolayers comprising copolymers and mixtures of the corresponding homopolymers have been compared in a number of studies. Attention was concentrated in these investigations (most of which were carried out during the period preceding the active study of LBF) on the phase behaviour of the systems. Recently much attention began to be devoted to the possibility of obtaining LBF from monolayers of copolymers (including block copolymers) and mixed monolayers. Mixed polymer monolayers and especially copolymer monolayers with low-molecular-mass surfactants are of great practical importance, since, compared with monolayers and LBF made up of copolymers and mixed polymer monolayers, they facilitate the introduction of functional additives and the regulation of the properties of the two-dimensional systems.

Hitherto these problems have been most fully investigated for methacrylic and acrylic copolymer monolayers containing side chains with different numbers of carbon atoms. Copolymers of methyl and hexadecyl acrylates, [109] butyl and dodecyl methacrylates, [110] octadecyl and dodecyl methacrylates, [111, 112] butyl and octadecyl methacrylates, [91] and methacrylic acid and methyl acrylate, [113] as well as diblock copolymers of PMMA and polyvinyl(4-pyridinium) bromide [114] have been investigated. Vigorous studies on monolayers have been carried out for copolymers containing double-stranded elementary units or spacers of different composition in the main chain. [106, 107, 115–117]

The properties of monolayers comprising copolymers and mixtures of the homopolymers of octadecyl methacrylate (PODMA) and butyl methacrylate (PBMA) examined above have been investigated. [91] Figs 12 and 13 illustrate the dependence of the surface pressure, corresponding to three characteristic points on the compression isotherms for the copolymers and mixtures, and of the limiting area of the monolayer on its composition. The PBMA monolayer of the liquid-condensed type has two singular points corresponding to a phase transition (14.3 mN m^{-1}) and collapse (16.7 mN m^{-1}), while the PODMA monolayer of the solid-condensed type has a single singular point at 52.6 mN m^{-1} corresponding to collapse. All three singular points are present on the isotherms for the mixed monolayers containing between 30 and 70 mol.% of PODMA. On the basis of Crisp's phase rule for mixed mono-layers (the two components are compatible in the monolayer if π at the singular point varies with composition and conversely), it was concluded [91] that, for a 70% PODMA content, the homopolymers are incompatible. The compression isotherms for copolymer monolayers have a single singular point (collapse) and, for PODMA contents in the copolymer molecule up to 60%, the monolayer remains in the liquid-condensed state. The transition of the copolymer monolayer from the liquid to the solid state can be detected also on the dependence of the limiting area of the monolayer on composition (Fig. 13), which exhibits a sharp jump towards lower values of A_0 for a 70% content of PODMA. It follows from Fig. 13 that three compatibility regions are characteristic of the mixed monolayers: for low contents of PODMA (low surface pressure) and PBMA (high surface pressure), the components are compatible, whereas in the middle range of compositions the polymers are incompatible in the monolayer.

The properties of monolayers of dodecyl methacrylate–octadecyl methacrylate copolymers and the corresponding mixed homopolymer monolayers have been compared. [111–113] As for other combinations of the monomers, (C_4 and C_{18}) [91] and (C_{14} and C_{16}), [109] an increase in the content of the long-chain fragment (C_{18}) in the copolymer leads to the formation of a more condensed monolayer: the collapse pressure increases, the singular points vanish, and the compressibility diminishes.

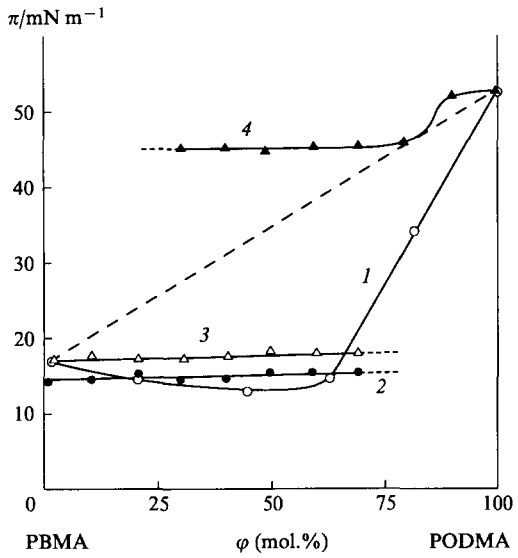


Figure 12. Dependence of the surface pressure at the characteristic points on the compression isotherms on the ratio of PODMA and PBMA in the copolymers (curve *1*) and the mixtures (curves *2*–*4*).[91]

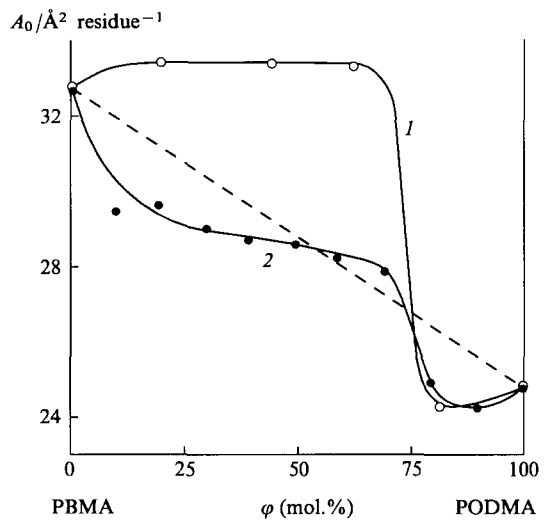


Figure 13. Dependence of the limiting areas (A_0) of the monolayers comprising the copolymers (curve *1*) and mixtures of the PODMA and PBMA homopolymers (curve *2*) on their ratio in the mixture.[91]

Consequently, by increasing the fraction of the long-chain fragment in the copolymer, it is possible to achieve a transition from the liquid to the solid state of the monolayer. The reverse transition, leading admittedly to disequilibrium in the monolayer, is achieved by increasing the temperature. For methacrylic copolymers containing C_{12} and C_{18} hydrocarbon groups in the side chain, such transitions occur in the temperature range 20–39 °C. Table 3 presents the conditions for the formation of liquid-condensed monolayers of poly(alkyl methacrylates) (homopolymers, copolymers, and mixtures). It is of interest to note that, on formation of the liquid state, the average length of the hydrocarbon side chain in the copolymer (copolymers *d*, $C \leqslant 14.2$) at 20 °C is the same as the number of carbon atoms in the side chain of the homopolymer (homopolymer *a*) at the same temperature. For a mixture of homopolymers, the transition to the liquid state occurs for a smaller average length of the side chain (mixture *f*, $C \leqslant 12.6$). Mixtures form

Table 3. Conditions in the formation of liquid-condensed monolayers of poly(n-alkyl methacrylates).[112]

Monolayer	Average number of carbon atoms in alkyl group	Transition temperature/°C
Homopolymer		
a	⩽14	20
b	⩽16	35
c	⩽18	39
Copolymer (C_{12} + C_{18})		
d	⩽14.2 (⩽36% ODMA)	20
e	–[a]	35
Mixture of C_{12} and C_{18}		
f	⩽12.6 (⩽10% ODMA)	20
g	⩽13.2 (⩽20% ODMA)	35
h	–[a]	39

[a] Almost all the polymers form liquid-condensed monolayers.

more stable monolayers than the individual phases of the homopolymers, each of which may contain a small amount of another phase.[112]

The influence of the composition of the subphase on the properties of the monolayers and LBF of the 1 : 1 methacrylic acid – methyl acrylate copolymer has been investigated.[113] On the surface of pure water, this copolymer does not form a stable monolayer. The introduction of Cd^{2+} ions into the support improves its stability. The solid monolayer of the copolymer on the surface of an aqueous solution containing La^{3+} ions at pH 6.89 has the highest stability. When the copolymer monolayers are transferred to the hydrophilic surface of glass from the Langmuir trough by the usual vertical method, the dependence of the degree of transfer (ρ) on the number of cycles has the form illustrated in Fig. 14*a*. Evidently a Z type transfer takes place, the degree of transfer increasing with increase in the number of layers. In order to obtain higher-quality LBF from the copolymer, the authors[113] used a Langmuir trough with moving walls. This made

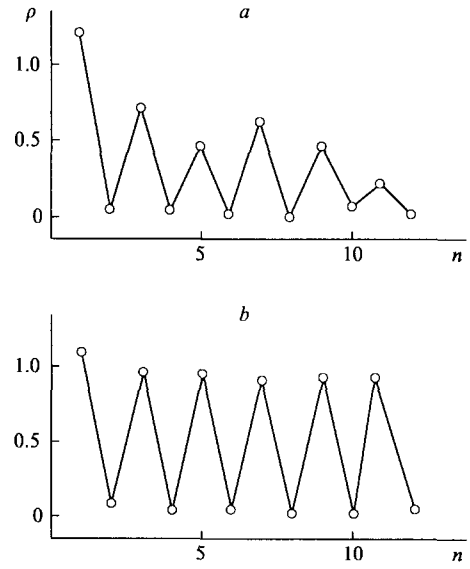


Figure 14. Dependence of the degree of transfer (ρ) on the number of cycles for the methacrylic acid – methyl acrylate copolymer LBF:[113] (*a*) usual Langmuir trough; (*b*) Langmuir trough with moving walls.

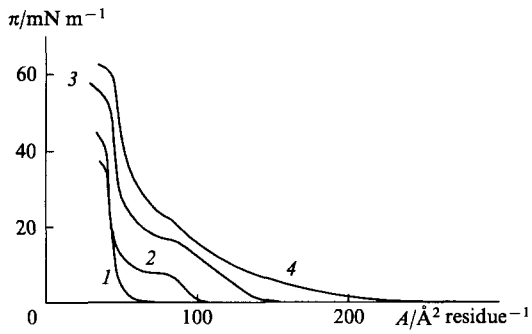
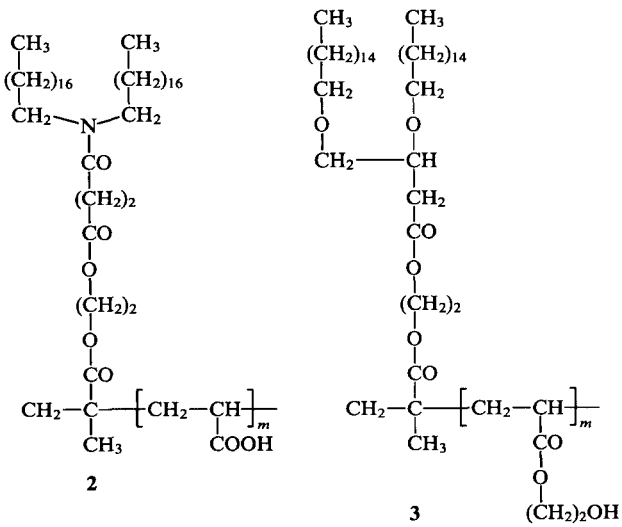


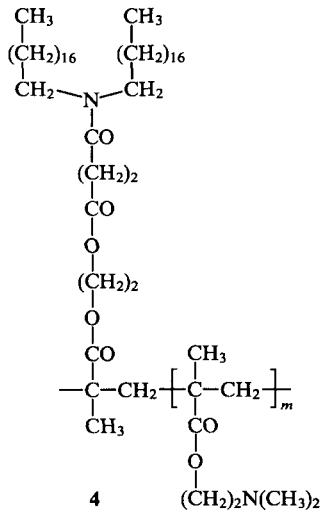
Figure 15. Surface pressure–area isotherms for the homopolymer (curve *1*, $m = 0$) and the copolymers **2** with different spacer: substituted residue ratios (m): (*2*) 1; (*3*) 5; (*4*) 10.[115]

it possible to improve significantly the quality of the LBF whilst retaining the Z type of transfer (Fig. 14*b*). This conclusion is confirmed by the measurements of the wetting angles (θ) for water after each passage of the support through the monolayer: θ for water does not change for two opposed directions of motion of the support. The values of $\cos\theta$ for LBF were lower than for coatings obtained from a solution on a rotating support. This indicates a definite preferred orientation of the elementary units of the copolymer in the LBF. It was shown by IR Fourier spectroscopy and X-ray diffraction that the La^{3+} ion-stabilised LBF comprising the copolymer, which does not possess long-chain side chains, has a layered structure with a monolayer thickness of 8.4 Å. The formation of LBF from cross-linked two-dimensional networks gives rise to hope for an improvement of their thermal and mechanical stabilities.

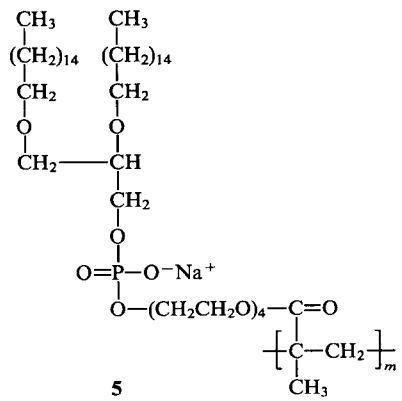
The influence of the hydrophilic spacer on the behaviour of monolayers of copolymers of double-stranded lipids with acrylic acid (**2**) and with hydroxyethyl acrylate (**3**) has been investigated.[106,107,115–117] Fig. 15 presents the $\pi-A$ relations for the 2-(3-dioctadecylcarbamoylpropionyloxy)ethyl methacrylate–acrylic acid copolymer **2** with different contents of a hydrophilic spacer in the main chain (m is the number of elementary units of the spacer per substituted monomer residue). Evidently, with increase in m, the monolayers expand and the pressure corresponding to the phase transition from the liquid to the solid state of the monolayer increases. With increase in the content of unsubstituted acrylic acid residues in the copolymer, the phase transition temperature falls. X-Ray diffraction analysis of 30-layer LBF made up of copolymer **2** showed[115] that the intensity of the diffraction peaks increases with increase in m, whilst their width diminishes. The repeat period increases from 40.8 Å for the homopolymer to 59.5 Å for the copolymer with $m = 5$ and then decreases to 55.9 Å for the copolymer with $m = 10$. When the fraction of acrylic acid in the copolymer is too high, it becomes impossible to obtain LBF. The thermal stability of LBF rises with increase in m: the multilayer structure of copolymer **2** breaks down at 40 °C for $m = 1$, at 70 °C for $m = 5$, and at temperatures exceeding 120 °C for $m = 10$. The acrylic acid residues in the copolymer play a dual role. Functioning as hydrophilic spacers, they increase the mobility and the degree of order in the long-chain components of the copolymer. At the same time, the thermal stability increases by virtue of the formation of hydrogen bonds. Evidently these characteristics may be controlled by introducing electrolytes into the support or by changing its pH. Similar results have been obtained[107] for copolymer **3**.



The possibility of the practical employment of LBF based on copolymer **4**, containing a double-stranded spacer and a double-stranded monomer in proportions of 5:1, as a selective gas membrane has been examined.[118–120] The LBF of this copolymer with a thickness up to 60 monolayers were formed on a porous polymer support and its permeability to CH_4, N_2, CO_2, and H_2S was investigated at different temperatures. It was established that the membrane is selective with respect to H_2S and CO_2 relative to N_2 and CH_4, the selectivity increasing on heating above 35 °C. The rise in selectivity with temperature was explained by the disordering of the hydrocarbon side chains of the copolymer, which was detected by reflection-adsorption IR spectroscopy. The possibility of the chemical interaction of gaseous H_2S and CO_2 with the copolymer constituting the LBF plays an important role in the variation of the selectivity of such membranes.

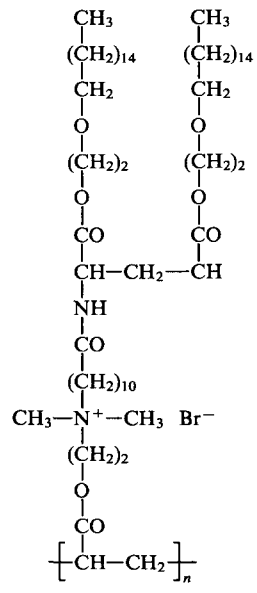


Asymmetric membranes have been formed[121] on the surfaces of porous polytetrafluoroethylene supports in the form of LBF of copolymer **2** ($m = 5$) and homopolymer **5**. The influence of heat treatment on the structure and properties of the membranes was investigated by IR Fourier spectroscopy, both in transmission and in reflection at glancing incidence, and also by high-resolution scanning electron microscopy. It was established that heat treatment of the LBF (20 and 30 monolayers) below the melting points of the block copolymers leads merely to an insignificant disordering of the alkyl chains ($2C_{18}$ and $2C_{16}$) and to the disappearance of a large number of macroscopic defects. The dependence of the permeability of the heat-treated membranes on the size of the penetrant molecules led Stroeve et al.[122] to the conclusion that microdefects are retained in the LBF after heat treatment. Heating of the LBF above the melting point of the block copolymers disturbs the order in the layers and leads to the appearance of cavities and to the flow of the polymer within the pores.



5

LBF based on double-stranded ammonium derivatives of the polyacrylic acid **6** have found an interesting application [123] in studies on surface forces, which had been carried out earlier [124–126] mainly using LBF made up of low-molecular-mass surfactants.



6

The monolayer of compound **6** was transferred onto a solid hydrophilic support (mica) the latter moving from the air into the aqueous phase. The relations between the reduced attractive force (F/R; R is the radius of curvature of the surface of mica) and the distance (D) between the two surfaces of mica coated by a monolayer of compound **6** are presented in Fig. 16 for three liquid media. It is seen from the figure that the attractive force between the surfaces and pure water extends over a distance up to 3000 Å and that the surfaces merge for $D \simeq 760$ Å. Their separation requires an adhesive (breaking away) force of 280 mN m^{-1}, which is characteristic of hydrophobic surfaces. [127] It has been noted [123] that these forces differ from the long-range electrostatic repulsive forces and van der Waals attractive forces ($D \leqslant 30$ Å; force required to break adhesion 55 mN m^{-1}), which arise between unmodified negatively charged mica surfaces. [128] The formation of a stable monolayer on the surface of mica, achieved by an unusual transfer procedure (downwards onto a hydrophilic support), is due to the electrostatic interaction between the cationic polymer and the negatively charged mica surface. The upward movement of the support through the air/water interface leads to the formation of a less stable monolayer.

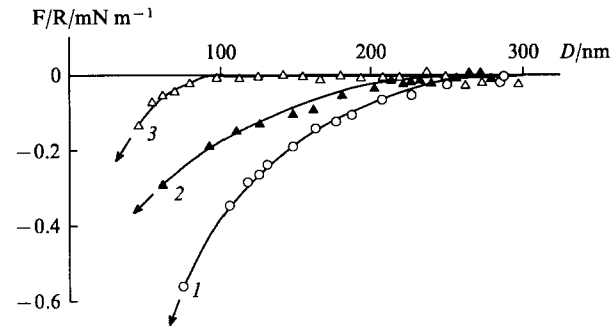


Figure 16. Dependence of the reduced attractive force on the distance between the surfaces of mica with monolayer LBF comprising polymer **6**. [123] Medium: (*1*) pure water; (*2*) 0.01 M NaBr solution; (*3*) 0.1 M NaBr solution.

Fig. 17 illustrates the influence of pH on the compression isotherms and on the $F/R-D$ relations for a monolayer of a derivative of the methacrylic acid oligomer **7**. The monolayer was deposited onto a mica surface which had been rendered hydrophobic. In a neutral aqueous medium, long-range repulsive forces are manifested ($D \sim 3000$ Å), increasing markedly with increase in pH (Fig. 17*b*). At low pH, repulsion occurs only over short distances $D \simeq 600$ Å, which is due to the influence of the degree of ionisation of the acid groups on the conformation of the macromolecules (at a high degree of ionisation, the extended conformation of macromolecules obtains). It is of interest to note that, when the mica surfaces coated by a monolayer of compound **7** approach one another, the repulsion increases gradually and not sharply, in contrast to pure mica. This has been explained by a change in the conformation of the chains and the recombination of charges. [128]

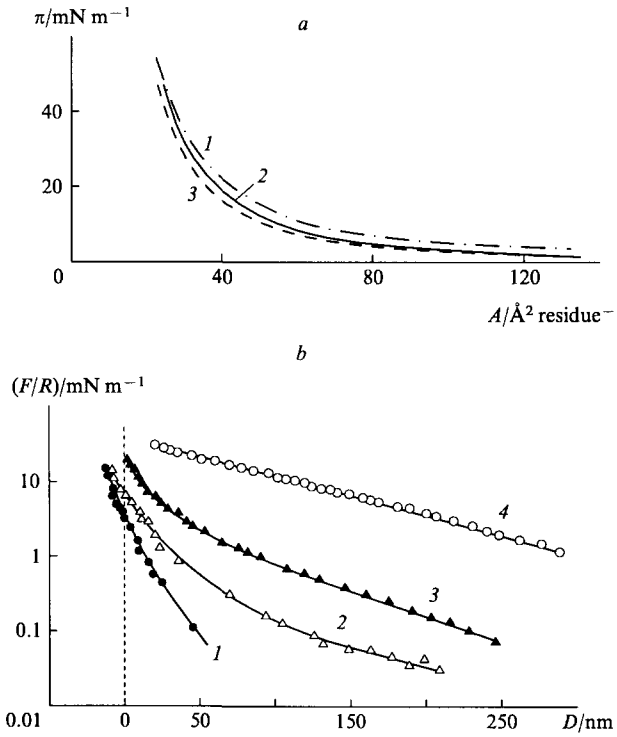
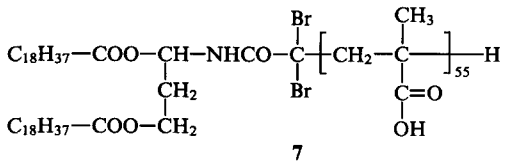


Figure 17. The influence of pH on the compression isotherms (*a*) and on the $F/R-D$ relations (*b*) for a monolayer comprising the oligomethacrylic acid derivative **7**: [123] (*a*) pH 3.1 (curve *1*), 5.6 (curve *2*), and 8.1 (curve *3*); (*b*) pH 3.5 (curve *1*), 4.6 (curve *2*), 5.6 (curve *3*), and 8.2 (curve *4*).



7

Thus the study of the surface forces acting between solid surfaces on which LBF have been deposited makes it possible to determine the quality of the LBF, the orientation of the molecule, and the interaction between them, i.e. to characterise quite fully the functionalised organic surfaces.

Gaines[30] formed homogeneous LBF from a homopolymer—syndiotactic PMMA—on the hydrophobic silicon surface. The dependence of the thickness of the LBF, measured ellipsometrically, on the number of transfer cycles is illustrated in Fig. 18. Evidently there is a linear relation between these parameters. The specific surface of a single monolayer, found ellipsometrically and on the basis of compression isotherms, was respectively 9.1 and 10.9 Å. Y type LBF have also been formed from PMMA on the surface of hydrophilic chromium films.[75] The thickness of 17-layer LBF, measured ellipsometrically, was 143 Å, i.e. 8.5 Å per monolayer. A test of this LBF as a positive electron-beam resist showed that the surface density of pin holes in the PMMA LBF was three orders of magnitude lower than in the film of the same thickness obtained from a solution of the polymer on a rotating support.

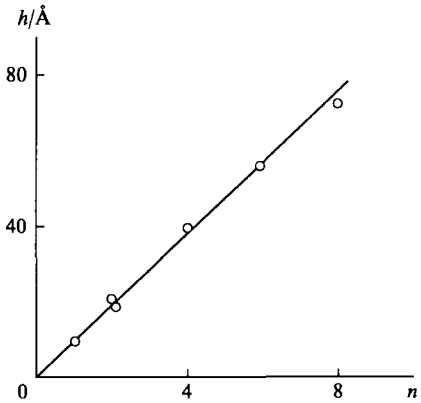


Figure 18. Dependence of the thickness of a syndiotactic PMMA film, deposited on a hydrophobic silicon surface at a surface pressure of 10 mN m^{-1}, on the number of transfer cycles.[30]

Acrylic and methacrylic polymers, into the side chains of which functional-group substituents have been introduced, have come to be widely used recently in the study of nonlinear optical (NLO) effects. A strategy for the creation of new NLO systems has been described.[129] It reduces, firstly, to the exclusive employment of monomeric objects and, secondly, to the introduction of perfluorocarbon groups, which ensure more marked hydrophobic properties for a shorter chain compared with hydrocarbon analogues. The influence of the number of bilayers formed by polymers **8** and **9** on the generation of the second optical harmonic was investigated.[129] Fig. 19 illustrates the dependence of the amplitude of the second harmonic (proportional to the square root of the intensity) on the number of bilayers (N) in the LBF comprising derivatives of acrylic (**8**) and oxazoline (**9**) polymers. Evidently the linearity of the relation is retained up to $N = 40$. The comparative decrease in the signal at $N > 40$ indicates the disturbance of the polar structure with increase in the number of layers. This effect may be associated with the fact that the LBF were obtained using two procedures: initially the first 40 layers and then, after several hours, the remaining layers.

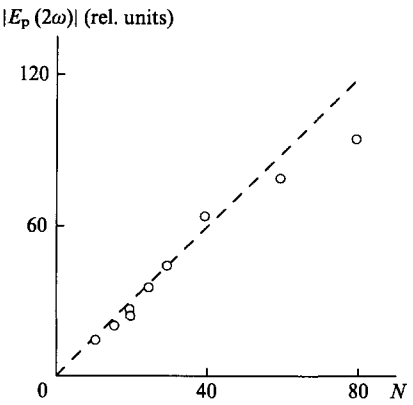
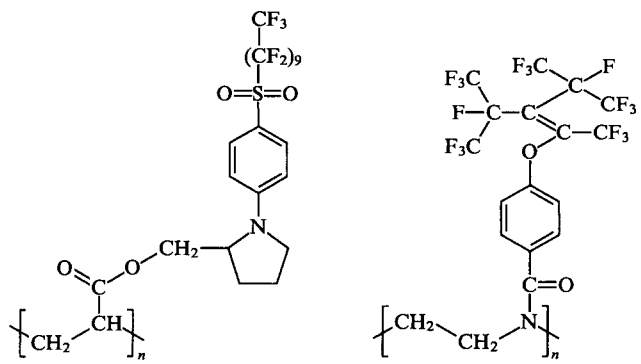


Figure 19. Dependence of the amplitude of the second harmonic on the number of LBF bilayers.[129] The dashed line represents the linear fit to the relaiton for $N \leqslant 40$.



8 9

Fig. 20 illustrates the high stability of the polymer LBF, confirming the usefulness of the strategy selected by the authors.

The synthesis of polymethacrylates containing NLO-active fragments in the side chains has been described[130] and the results of studies on second harmonic generation with the LBF of a polymethacrylate derivative have been presented.[131] It has been shown that the formation of LBF from mixed monolayers of polymer **10** and stearic acid hardly alters the orientation of the side chains: according to polarisation UV spectroscopic data, the angle of inclination of the side chains relative to the support in the LBF of polymer **10** is 30° and in that made up of a mixture of polymer **10** and the aliphatic acid is 25°.

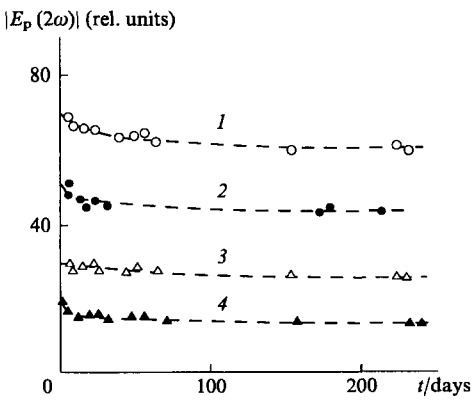
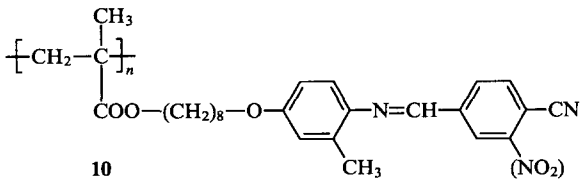
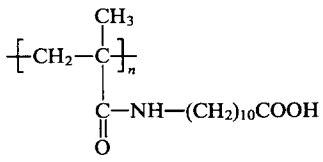


Figure 20. Dependence of the amplitude of the second harmonic on the LBF ageing time for specimens consisting of different numbers of bilayers:[129] (*1*) 40; (*2*) 30; (*3*) 20; (*4*) 10.



10

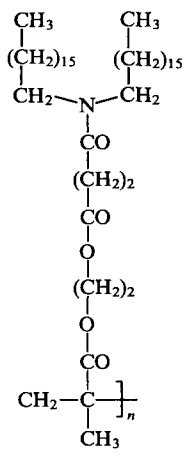
A similarity of the angles of chain inclination (36°) has been found [132] for the methacrylate derivatives **11** photopolymerised in the LBF. The authors note that this procedure is promising for the formation of LBF for NLO studies and applications.



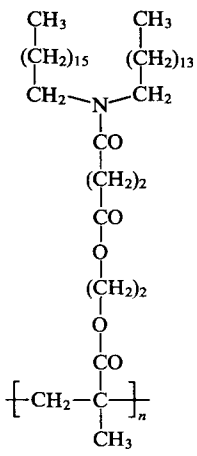
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The employment of methacrylic polymers **12**–**15** with different configurations and compositions of the side chains for optical waveguides has been described. [133]

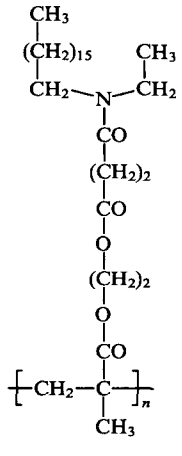
In the series of polymers presented above, the capacity for the formation of liquid monolayers increases from compound **12** to compound **15**. 500-Layer LBF (thickness 0.8 μm) have been obtained from polymer **14**. It was observed that the waveguides based on them suffer very low losses (2 dB cm^{-1} for wavelengths of 633 and 785 nm) by virtue of the low degree of order in the side chains, preventing the formation of light scattering domains.



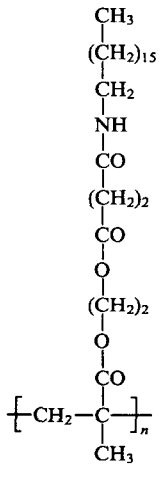
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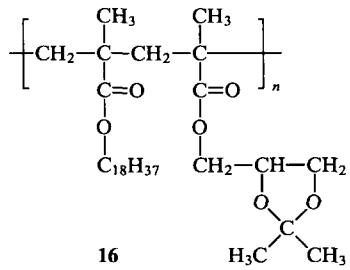
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15

The low stability of LBF of low-molecular-mass compounds at elevated temperatures and *in vacuo*, the mutual diffusion of molecules belonging to different layers of the LBF, [134–137] and finally the possibility of the loss of the low-molecular-mass component from the monolayers (constituting the LBF) mixed with the polymer are all factors which have stimulated studies on high-molecular-mass multilayer, including alternating, structures.

The insulating properties and stability of LBF of stearic acid and the methacrylic copolymer **16**, deposited on the surface of silver, have been investigated [138] by the time-of-flight mass spectrometry of secondary ions.



16

Fig. 21 shows that the LBF of copolymer **16**, with a thickness equivalent to five monolayers, fully prevents the emission of secondary Ag^+ ions through the film. On the other hand, nine layers of stearic acid by no means fully suppress the diffusion of these ions.

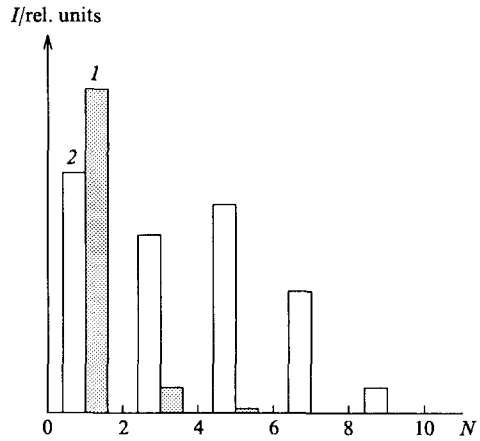
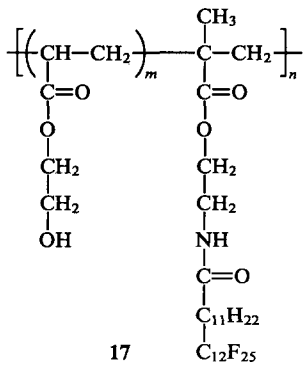


Figure 21. Dependence of the intensity of the signal due to secondary silver ions (normalised with respect to the $C_3H_5^+$ peak) on the number of layers: (*1*) for the methacrylic copolymer **16** LBF; (*2*) for the stearic acid LBF. [138]

In order to investigate the diffusion of the low-molecular-mass product from mixed monolayers involving the methacrylic polymer **16**, mixed 1 : 1 LBF with a fluorescent probe (a diphilic cyanine dye) were formed. Two mixed monolayers were deposited on the surface of silver on which a monolayer of copolymer **16** had already been deposited. Up to eight further monolayers of methacrylic copolymers were formed on the surface of the LBF obtained in this way. Fig. 22 illustrates the influence of the number of layers of copolymer **16** on the intensity of the mass spectrometric signal of the dye cation. Evidently two monolayers of the copolymer are sufficient to decrease significantly the signal intensity, but even eight layers do not fully suppress the diffusion of the dye ions through the copolymer LBF. The high stability of the LBF investigated is expressed by the retention of its properties on exposure to air at 10 °C for nine months and after boiling in water for 15 min. [138] Similar studies have been carried out [139] for copolymer **17**.



17

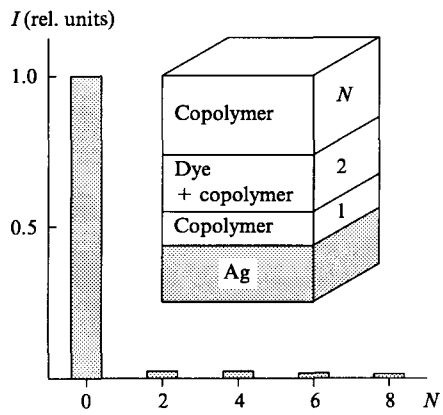


Figure 22. Dependence of the intensity of the signal due to secondary dye ions (normalised with respect to the $C_3H_5^+$ peak) on the number of outer layers of the methacrylic copolymer **16** for a mixed LBF.[138]

3. Mixed monolayers

In the analysis of the behaviour of monolayers of certain copolymers, the two-dimensional compatibility of mixtures of the corresponding homopolymers was examined. In this section we shall discuss in greater detail the behaviour of binary mixtures of polymers on the surface of a liquid. The principal questions which will be considered concern the compatibility of homopolymers in the two-dimensional state, the influence of the main and side chains on the compatibility of the polymers, including the case of markedly different lengths of the side chains in the components of the monolayer, and the determination of the thermodynamic parameters of the mixed monolayers.

The compatibility of the first and second members of the series of poly(alkyl acrylates)—PMMA and poly(ethyl methacrylate) (PEMA)—has been analysed.[81,140,141] On the basis of the compression isotherms for individual and mixed monolayers, calculations were made of the parameters characterising the excess free energy of mixing (ΔG_m) as described by Goodrich,[142] the coordination number of the two-dimensional quasi-lattice (Z') as described by Singer,[143] the partial immersion factor (f_m) as described by Frisch and Simha,[144] and the interaction energy (η^2/Z) between rigid segments lying on the surface†.[145] The dependence of ΔG_m on the mole fraction (φ) of PEMA in the PEMA–PMMA mixture is presented in Fig. 23. It is seen that the minimum negative value of ΔG_m corresponds to φ = 50%. The closeness of Z' to 2 for both the homopolymers themselves and for their mixtures (according to Davies and Rideal,[146] the flexibility is ~1%) indicates the rigidity of the acrylic macromolecules in the monolayers on the surface of water. The parameter f_m also does not change markedly for different component ratios, which indicates a similar degree of immersion of parts of the macromolecules in the aqueous subphase. The minima in the parameters η^2/Z and ΔG_m and also in the area of the monolayer at φ = 50% indicate the maximum cohesion between the segments of the macromolecules in this range of component ratios. As noted previously for other objects,[43,79,147] the maximum cohesion for the equimolar component content in the monolayer can be explained by the fact that the most rigorous alternation of the units of both polymers on the subphase can be attained for this component ratio. It has also been noted[81,140] that at 20–30 °C both components are compatible in the monolayer whatever the ratio.

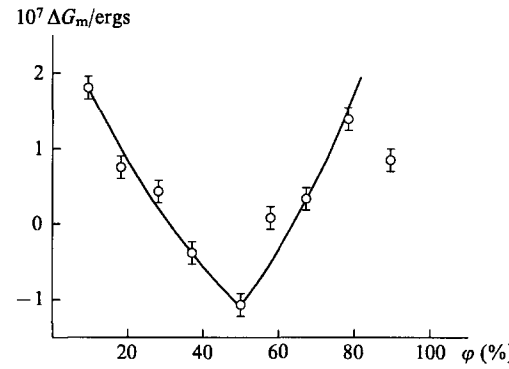


Figure 23. Dependence of the free energy of mixing on the composition of a monolayer comprising a PEMA–PMMA mixture.[140]

The compatibility with PMMA of the next member of the series—poly(propyl methacrylate) (PPMA)—has been investigated[148] for monolayers at the air/water and hexane/water interfaces. Using the parameters of the two-dimensional Huggins equation of state[149] and the ellipsometric method for the determination of the thickness of the monolayers, it has been shown that two-dimensional PMMA–PPMA mixtures are compatible on the surface of water and are thermodynamically more stable than monolayers of the pure polymers. The compatibility is due to the identical horizontal orientation of the side chains of both polymers on the surface of water, which is also promoted by the identical thickness (14 Å) of the PMMA and PPMA monolayers.[148,150]

The next member of the series—poly(n-butyl methacrylate) (PBMA)—is also compatible with PMMA in a monolayer on the surface of water.[79] The negative deviations of the surface area of the mixed monolayer from additivity and the minimum in the excess free energy for the equimolar component ratio (as for the mixed monolayers of PMMA and the lower homologues) indicate an increased stability of such a binary monolayer and the predominance of attractive forces between the molecules. The horizontal orientation of the side chains of the PBMA molecules for a low content of PMMA in the mixed monolayer changes to the vertical orientation and a strong interaction between the main chains of the polymers in the equimolar mixture.

Similar results, obtained for these binary mixtures, have been reported in another study.[140] The author analysed mixed monolayers of PEMA with PBMA. It is of interest that the behaviour of this system differs significantly from that of the mixed monolayers of PMMA with PEMA and PPMA: the monolayers of the individual components are thermodynamically more stable than the mixed PEMA–PBMA monolayers. It was shown that the maximum energy of mixing ΔG_m and the maximum parameter η^2/Z correspond to the 1:2 component ratio in the mixed monolayer. In this region, the positive deviations of the area of

† It is noteworthy that the thermodynamics, statistical physics, and molecular dynamics of monolayers of low-molecular-mass compounds and polymers are developing quite vigorously. However, analysis of the existing theories is outside the scope of the present review.

the monolayer from additivity reach maximum values. The results can be explained by the higher degree of hydration of the segments of the macromolecules in the mixture and the higher energies of repulsion between them for the component ratio indicated.

The vertical orientation of the long side chains of PODMA and the horizontal orientation of the short side chains of PMMA in their mixed monolayers on the surface of water prevent the formation of compatible monolayers.[148] This conclusion is based on data obtained with the aid of compression isotherms, according to which the area of the monolayer changes additively as its composition varies and the collapse pressure is independent of composition.

As mentioned above, mixed monolayers of PODMA and PBMA are compatible only in the range of compositions corresponding to a low content of the second component.[91] In mixed monolayers of poly(dodecyl methacrylate) and poly(octadecyl methacrylate), the inclined orientation of the dodecyl side chains and the vertical orientation of the octadecyl ones preclude the formation of a two-dimensional system with fully compatible components over the entire range of compositions,[112] although the mixtures can produce more stable films than the separate phases of the individual polymers.

A similar approach, based on the analysis of the dependence of the limiting areas and collapse pressures, for poly(phenyl methacrylate)–poly(hexyl methacrylate) systems permitted the conclusion[102] that the mixed binary monolayers are incompatible on the surface of water in all the two-dimensional phase states of the monolayer. These data can also be accounted for by the different orientations of the side groups. In the mixed monolayers of poly(phenyl methacrylate) and poly(benzyl methacrylate), the identical orientation of the aromatic groups leads to the formation of fully compatible two-dimensional systems whatever the component ratio.[102]

The study of the compatibility of high-molecular-mass and low-molecular-mass compounds in monolayers is important for the preparation of functionalised LBF. An increase in the compatibility of molecules belonging to different classes of compounds can be achieved by employing molecules with ionisable groups. This problem has been investigated in relation to binary mixtures of PMMA with stearic, arachidic, myristic, and oleic acids and with stearylamine, the degree of ionisation of which can be regulated by varying the pH of the aqueous subphase.[151–153] The compatibility of such components is determined by two factors: the orientation of the side groups and the intensity of the intermolecular interactions, which become more intense on ionisation of polar groups. Nonionisable saturated acids and PMMA are incompatible in the monolayer. The unsaturated oleic acid, the orientation of the chains of which is close to that of the ester groups of PMMA, is compatible with this polymer whatever the component ratio. The negative influence of the differences in the orientation of the side groups of the polymer and the chains of low-molecular-mass surfactants on the compatibility in the monolayers can be neutralised by intensifying the interactions between polar groups of the polymer and the ionised groups of the acid or the amine. Thermodynamic analysis of the PMMA–stearic acid and PMMA–stearylamine binary systems[151] demonstrated that the mixed layers are more stable than the monolayers of the individual compounds. With increase in temperature, the stability of the monolayers falls. The compatibility of the components in such monolayers is determined by the enthalpy term in the free energy and depends on the degree of ionisation of the molecules. Evidently, an improvement in compatibility can be achieved also for ionisable macromolecular systems.

* * *

The properties of the monolayers and LBF of acrylic and methacrylic homopolymers, their mixtures, and copolymers embrace virtually all the principal approaches to the analysis of the behaviour of macromolecules in monolayers and a considerable proportion of the existing ideas concerning the preparation and properties of polymeric LBF.

The properties of monolayers of nonionisable homopolymers can be regulated by altering the length of the ester side chains, by introducing a hydrophilic spacer uncoupling the main and side chains, or by the partial hydrolysis of the side chains, which leads to the formation of a copolymer incorporating ionisable groups. An increase in the length of the ester groups leads initially to the expansion of the monolayer and then to its condensation as a result of the secondary cohesion between the long side chains. Crystallisation of these chains explains, on the one hand, the discrepancies between the data of different workers who investigated poly(octadecyl methacrylate) monolayers under different experimental conditions and, on the other, can lead to the formation of poor quality LBF owing to the oscillations of the meniscus along the three-phase contact line. Crystallisation processes in the LBF itself can be suppressed by forming on the latter several monolayers of an amorphous polymer with a specified rigidity. The introduction of a hydrophilic spacer, separating the main and side chains of a double-stranded lipid, leads to the formation of stable monolayers, the collapse pressure and limiting area of which are close to the corresponding parameters of the low-molecular-mass lipid. The generation of ionisable acid groups on hydrolysis of an acrylic homopolymer extends the possibilities for the variation of the conformation and packing density of the units of the macromolecules on the surface of water by varying the concentration of the electrolyte in the aqueous support or its pH.

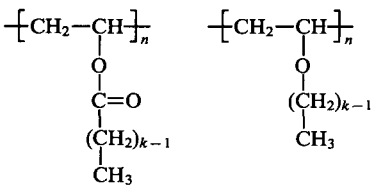
By varying the composition of the copolymer or the mixed monolayer, it is possible to achieve its transition from one state to another and to alter the phase composition and the structural organisation of the phases. These transformations are carried out by varying the length of the side chains of the comonomers, by the specific alteration of the length of the hydrophilic spacer in the main chain, and also by the copolymerisation of nonionogenic and ionogenic monomers.

Mixed monolayers of polymers and especially polymers and low-molecular-mass surfactants are of practical value, since, compared with monolayers and LBF based on copolymers, they facilitate the introduction of functional additives and the regulation of the properties of two-dimensional systems. Regulation of the states of these monolayers and phase separation processes makes it possible to create monolayers with definite molecular and phase compositions. This opens, in its turn, a path to the formation of, for example, skeletised LBF with a controllable size and disposition of cavities and to the formation of functionalised LBF with a specified structure and surface density of integrated special groups. The structures and properties of mixed monolayers have been scarcely analysed from these standpoints and the possibilities for the construction of a particular phase structure of the monolayers have still not been utilised.

Despite the rigidity of the PMMA monolayer, in many instances it is possible to create from this polymer fairly uniform LBF characterised by a low density of defects and to use them as a positive electron-beam resist. The formation of more ordered LBF is to be expected when acrylic and methacrylic polymers with moderate and considerable lengths of the hydrocarbon chains and their copolymers or mixed monolayers are employed. These polymers and their derivatives are already being used to create non-linear optical systems, thick (500 layers) wave guides with low losses, selective membranes, and insulating layers.

VII. Poly(vinyl ethers) and poly(vinyl esters)

Among the representatives of polymers of this type, the parent polymer of which is poly(vinyl alcohol), the poly(vinyl esters) **18** have been most thoroughly investigated in monolayers. The poly(vinyl ethers) **19** have not been attracting the attention of investigators recently.



18 **19**

The interest in poly(vinyl alcohol) (PVA) is associated with the possibility of obtaining monolayers of this water-soluble polymer on the surface of water. The stability of PVA monolayers on the surface of water is determined to a large extent by the acetate groups remaining after the hydrolysis of poly(vinyl acetate),[25] which is used to obtain PVA. PVA monolayers belong to the liquid-expanded type; their compressibility is high and they are disrupted at low surface pressures. The absence of appreciable dissolution of PVA in the support is indicated by the rapid restoration of the film following the expansion of a compressed monolayer, which could not have occurred for a simple equilibrium between the solution and the surface layer.

The characteristics of the variation of the compression isotherms for monolayers with increase in the length of the side (ester or ether) chain in poly(vinyl ethers)[154] and poly(vinyl esters)[155] are similar to those which were noted for acrylic and methacrylic polymers.

Poly(vinyl ester), especially poly(vinyl acetate) (PVAC) and poly(vinyl stearate) (PVST), monolayers have been investigated to a much lesser extent than poly(vinyl ether) monolayers.

The active study of PVAC monolayers on the surface of a liquid[25,26,77,79,85,155–172] has been undertaken in view of their highly equilibrium nature: there is no hysteresis on the compression–expansion isotherms obtained at high speed. The thermodynamic properties of PVAC monolayers have been investigated[156,158] and it has been shown that the macromolecules are arranged on the surface of water in the form of two-dimensional deformed coils. They are moderately flexible and the interaction (attractive) forces between them are weak. These properties of PVAC have led to prospects for the preparation of monolayers using nonspreading polymers, such as the ethylene–propene copolymer, by grafting vinyl acetate groups onto them.[145]

Interesting data concerning the inversion of the quality of solvents for PVAC on passing from three-dimensional to two-dimensional solutions have been published.[170] The surface θ temperatures have been calculated from the dependences of the second virial coefficient on the reciprocal of temperature, obtained from the compression isotherms, and it was shown that methanol (a poor solvent for the bulk phase solution) becomes a good solvent for PVAC in the monolayer. This result, confirmed by Huggins's theory and experimental data for supports containing NaCl or methanol, is associated with the competition of two processes in the formation of the monolayer: the spreading of the polymer and the solubilisation of the solvent by the subphase.

Poly(vinyl stearate) monolayers have been investigated in connection with the problem of their nonuniformity with respect to the area of the Langmuir trough.[173] A linear decrease in the surface pressure with increase in the distance from the mobile barrier has been established. Fig. 24 shows that the pressure gradient depends on the area of the monolayer and that the change in π may reach a considerable magnitude (> 10 mN m^{-1}). In the case of the monomer (vinyl stearate), a homogenous monolayer is formed. The effects due to the inhomogeneity of polymer monolayers must be taken into account in the study of LBF.[173,174] The inhomogeneity of polymer monolayers, associated with the low rate of relaxation, can be eliminated by introducing into the latter diphilic low-molecular-mass plasticisers. Problems concerning the compatibility of high- and low-molecular-mass components in monolayers become important under these conditions.

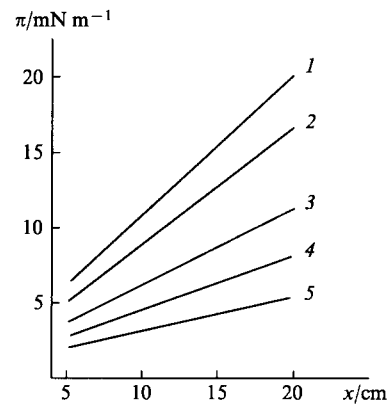


Figure 24. Dependence of the surface pressure in the poly(vinyl stearate) monolayer on the distance between the Wilhelmy plate and the fixed edge of the trough for different average areas (Å^2 per residue):[173] (*1*) 21.2; (*2*) 21.5; (*3*) 22.0; (*4*) 22.5; (*5*) 23.0.

The study of mixed monolayers of vinyl stearate and PVST showed[174] that the surface pressure, measured on collapse, depends in a complex manner on the composition of the surface film. These data permit the conclusion that the components are incompatible at least in this region of the compression isotherms. The surface potential of the monolayer and the absorption at 950 cm^{-1} (out-of-plane scissors vibrations of the hydrogen atoms of the vinyl group) of an 80-layer LBF comprising mixed monolayers deposited on a germanium plate varies linearly with composition under these conditions. These integral characteristics, which are insensitive (in the given version) to the phase composition, have been used[174] to analyse the kinetics of the two-dimensional polymerisation of vinyl stearate. The PVST monolayer, obtained by the polymerisation of the monomer on the surface of water, was transferred much less effectively onto the surface of the germanium film ($\rho = 0.1$) than the monolayer prepared from PVST polymerised in the bulk phase.

In the study of the properties of mixed PVAC monolayers with low-molecular-mass compounds, two interesting facts were noted:[157] the reversibility of the compression isotherms with a rigorous additivity of the areas for mixtures of equal weight and high collapse pressures of the mixed monolayers, exceeding in most cases the π_c for the individual compounds (Table 4).

Table 4. The monolayer collapse pressures (mN m^{-1}) for individual compounds and their equilibrium binary mixtures with PVAC.[157]

Component	Individual monolayer	Mixed monolayer
Poly(vinyl acetate)	23	23
Stearic acid	42	55
n-Hexacosanoic acid	58	68
n-Hexatriacontanoic acid	58	70
2-Hydroxyethylstearic acid	57	69
Methyl stearate	36	41
1-Octadecanol	42	39
Cholesterol	42	38

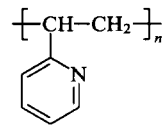
These results can be explained by the more intense interaction of the acetate groups with the carboxy-groups than their interaction with the hydroxy-groups or ester groups. Nevertheless, in view of the similarity of the collapse pressures for the monolayers of the pure polymer and its mixture, one can conclude, in conformity with Crisp's rule, that the compounds investigated are incompatible.

The identical orientation of the long hydrocarbon chains of PVST and stearic acid promotes their compatibility in mixed monolayers.[175] On the other hand, oleic acid, the hydrocarbon chain of which has the same length but is oriented horizontally along the surface of water owing to the presence of the double bond,[176] is incompatible with PVST in the monolayer but is compatible with PVAC.[177]

The decisive role of the orientation of the side chain is manifested also in the compatibility of polymer–polymer systems. Thus the similarity of the chemical structures of the PVAC and PMMA molecules promotes the complete compatibility of these polymers on the surface of water and the formation of ideal mixtures.[79,171] It must be emphasised that the dependences of the surface pressure on composition are monotonic for the uncollapsed and collapsed phases of this system and indicate the formation of true surface and bulk-phase solutions of the above polymer. A complete compatibility is also attained in mixed monolayers of PVAC and poly(ethyl acrylate) by virtue of the similar orientation of the units on the surface of water.[172] On the other hand, mixtures of PVAC with poly(vinyl butyrate) are compatible only in the region of equimolar ratios of the components. Such behaviour, similar to that examined above for PMMA–PBMA mixtures, can be explained in this instance not by the differences between the chain orientations but by the differences between the interactions of the units of these polymers with the molecules of the subphase.[171] All three isomeric poly(butyl methacrylates) (n-, *iso*-, and *tert*-butyl) are incompatible with PVAC in the monolayer.[79]

The PVST and PODMA polymers are compatible in mixed monolayers, which are more stable than the monolayers of the individual components. The incompatibility of PVAC and PVST in the monolayer is due to the different orientations of the ester side groups of these macromolecules on the surface of water.[148] Apparently a more homogeneous distribution of the monomer residues on the surface of water can be attained by forming the monolayers from copolymers of vinyl acetate and vinyl stearate.[155,178]

One of the few examples of compatibility in the monolayer of a polymer not containing a long hydrocarbon chain and classical surfactants is provided by binary mixtures of poly-2-vinylpyridine **20** with stearic acid, methyl stearate, or stearylamine.[179] In contrast to monolayers of the corresponding low-molecular-mass compound, neither temperature (15–35 °C) nor pH (6.2, 9.4) influence the compression isotherm. Thermodynamic analysis of the properties of monolayers of binary systems permitted the conclusion that the components are compatible in all three cases. For monolayers of compound **20** in a mixture with methyl stearate or stearylamine, the compatibility is determined by the enthalpy factor and is achieved through interactions between the polar groups of the components of the monolayer. The compatibility in the polymer **20**–stearic acid system is determined by the entropy factor and is apparently achieved by the immersion of the pyridylethylene units in the subphase. Owing to the high solubility of poly-2-vinylpyridine in the subphase, it has not been possible to obtain[30] a stable monolayer of poly-4-vinylpyridine with a reproducible surface pressure. Even the statistical copolymer of 4-vinylpyridine with 48 mol.% of acrylonitrile gives rise to monolayers which are stable only at a surface pressure $\leqslant 5$ mN m^{-1}.[30]

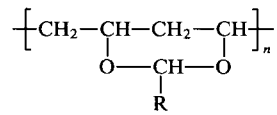


20

Thus the properties of the monolayers of poly(vinyl esters) have been investigated in fair detail. A distinctive feature of the first representative of this series—poly(vinyl acetate)—is the high stability of the monomers formed and high collapse pressures for mixed monolayers with low-molecular-mass compounds. These properties give rise to the hope for a wider employment of this polymer (and of its long-chain analogues) for the formation of stable monolayers and LBF. The ionisable polyvinyl derivatives of the type of polyvinylpyridine, which can be compatible with long-chain low-molecular-mass surfactants, merit a more vigorous investigation in monolayers. In the immediate future, one may expect an increase in the interest of investigators in the study of the structures and properties of LBF of these polymers and their mixtures with functionalised molecules.

VIII. Poly(vinyl acetals)

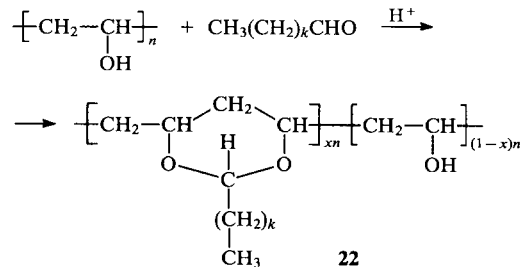
The polyalkylals **21** belong to the class of traditional polymers which have been used for a long time in practice. They are interesting objects for study in monolayers and LBF in view of the simplicity of their synthesis, which makes it possible to obtain macromolecules with different lengths of the side chains and with different degrees of acetal formation and also in view of the possibility of the cross-linking of the macromolecules.



21

Polymers containing electron-donating and electron-accepting groups have also been obtained recently, which has made it possible to investigate energy transfer processes in alternating LBF.

Polyacetals are obtained by the acetal formation reaction of poly(vinyl alcohol) in an acid medium. The degree of acetal formation x can vary within wide limits and can reach 80%.



22

Fig. 25 presents $\pi - A$ relations for five poly(vinyl acetals) with different lengths of the side chain ($k = 0-12$).[180] It can be seen that the collapse pressure of the monolayer increases and the compressibility diminishes with increase in k. The discrepancies between the limiting areas of the monolayers of poly(vinyl acetals) obtained by different workers[25,180,181] can be seen in Fig. 26. Evidently, the weak dependence of A_0 on n for long-chain homologues is due to the presence of the six-membered ring, which eliminates the influence of the hydrocarbon chain. The degree of polymerisation, which varies, for example for polyvinyloctal, from 300 to 2 600 ($x = 0.75-0.79$), also does not affect the limiting areas.[181] With decrease in x, the limiting areas diminish, which is associated with the hydrophilic nature of the

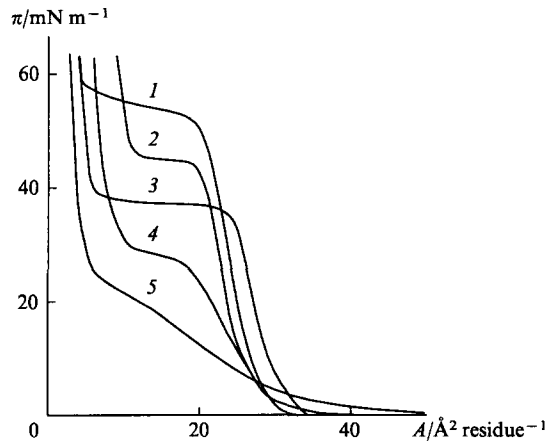


Figure 25. Compression isotherms for poly(vinyl acetals) **22** with different values of k: [180] (*1*) 12; (*2*) 10; (*3*) 6; (*4*) 2; (*5*) 0.

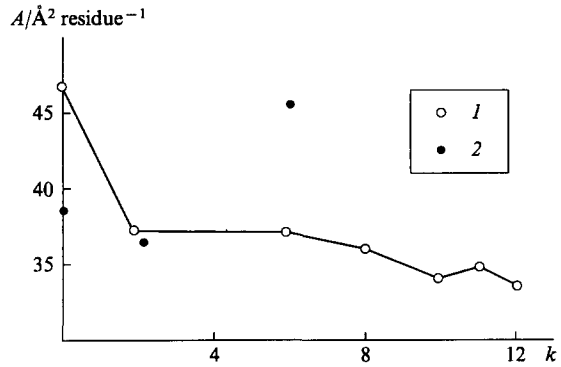


Figure 26. The influence of the length of the side chain (k) of poly(vinyl acetals) on the limiting areas of the monolayers according to the data of Oguchi et al. [180] (*1*) and Crisp [25] (*2*).

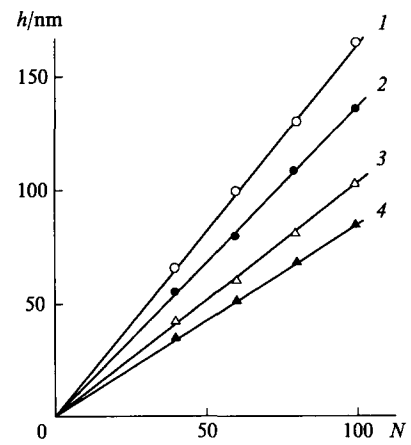


Figure 27. Dependence of the LBF thickness on the number of layers for four homologues of compound **22** with different values of k: [181] (*1*) 12; (*2*) 10; (*3*) 6; (*4*) 2.

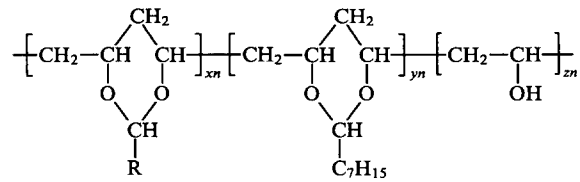
alcohol groups immersed in the subphase even at low surface pressures. The hysteresis of the isotherms for the polyvinyloctal monolayers compressed to $\pi \simeq 50$ mN m^{-1} [180,182] can be ruled out when the monolayers are obtained from mixed solutions of the polymer and iodine in chloroform. [182] The iodine atoms plasticise the monolayer and diminish its rigidity and the packing density of the side chains compared with the pure polyvinyloctal.

The fairly high homogeneity and stability of the poly(vinyl acetal) monolayers make it possible to obtain thick (up to 100 layers) Y type LBF. [180] Fig. 27 presents the dependence of the ellipsometrically determined thickness of the LBF on the number of layers for four homologues of compound **22** with k = 2, 6, 10, and 12. The linearity of the relations and their monotonic course in conformity with the size of the hydrocarbon chain as well as their slope, which yields the length of the hydrocarbon chain ($\sim$14 Å for k = 10 and 12), indicate the high quality of the LBF. [180,181]

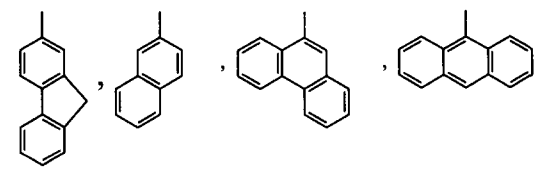
These LBF can be used as negative electron-beam resists. The sensitivity of such a resist depends on the chain length of the acetal groups through which cross-linking takes place. [183] Although the sensitivity of the resists was lower on deposition by the LBF method than in the case where they were prepared by the traditional centrifugal procedure, the resolution for the former is appreciably higher and is determined by the diameter of the electron beam.

It is of interest to carry out similar studies with Z type LBF, which can be obtained from monolayers of iodine-containing polyvinyloctal. The introduction of chromophoric electron-donating and electron-accepting groups into the molecules of poly(vinyl acetals) makes it possible to investigate the photophysical properties of polymeric LBF.

Chromophoric fluorene, naphthalene, phenanthrene, and anthracene groups have been introduced into polyvinyloctal **23** as a result of the reaction of PVA with the corresponding aldehydes. [184,185] The fraction of chromophoric groups in the chain (x) did not exceed 0.12.



23

R = 

Analysis of the fluorescence spectra of two-layer LBF of chromophoric polyvinyloctals showed that aggregation (formation of excimers) does not occur and that the chromophores are distributed in the amorphous film as isolated species.

The influence of the thickness of the inert spacer layer in polyvinyloctal on the effectiveness of the energy transfer from the donor (fluorenyl) to the acceptor (anthryl) is illustrated in Fig. 28. The alternating LBF consisted of two layers of fluorene and anthracene derivatives of polyvinyloctals, between which N layers of chromophore-free polyvinyloctal were distributed. It is seen from the fluorescence spectra that the effectiveness of the energy transfer is controlled by the number of layers N: for a system without a spacer layer (N = 0), the emission of fluorenyl (300–330 nm) is quenched by the acceptor and amounts to only 25% of the intensity for systems with N = 8 or 10. Under these conditions, the sensitised emission of anthryl is observed in the range 390–460 nm in the spectrum of the system with N = 0. [184]

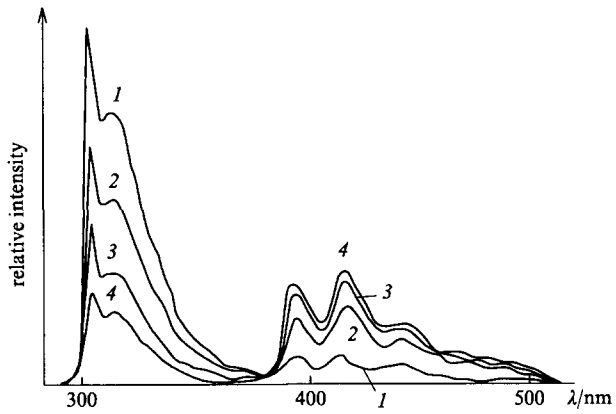


Figure 28. Fluorescence spectra of LBF containing layers of fluorenyl and anthryl derivatives of compound **23** separated by different numbers (N) of polyvinyloctal layers.[184] N = 10 (curve *1*), 8 (curve *1*), 4 (curve *2*), 2 (curve *3*), and 0 (curve *4*).

The effectiveness of the energy transfer can serve as a criterion for the determination of the thermal stability of LBF containing layers of chromophoric polyvinyloctals alternating with inert layers.[185] Fig. 29 presents the temperature variation of the ratio of the emission intensities of the acceptor at 438 nm (I_A) and the donor at 350 nm (I_P) for the 'phenanthryl/6/anthryl' system. Heating of this system (curve *1*) increases appreciably the ratio I_A/I_P starting from 40 °C. This is associated with the mutual approach of the chromophoric groups on heating. A further increase in temperature leads to the irreversible disordering of the system, which persists on its subsequent cooling (curve *1'*).

The thermal stability of poly(vinyl acetals) can be appreciably increased by cross-linking of the macromolecules with formaldehyde via the free alcohol groups.[185] The effectiveness of the cross-linking was determined from the change in the intensity of the fluorescence of the chromophoric poly(vinyl acetal) after it had been maintained in dichloromethane. As can be seen from Fig. 29, heating (curve *2*) and cooling (curve *2'*) of the cross-linked LBF have only a weak influence on the intensity ratio I_A/I_P, which indicates the constancy of the structure of the corresponding LBF.

Thus poly(vinyl acetals) provide a series of possibilities for the introduction of various functional groups into them. Based on them, it is possible to obtain cross-linked LBF with a high thermal stability. Evidently, these polymers will be investigated more vigorously in the immediate future.

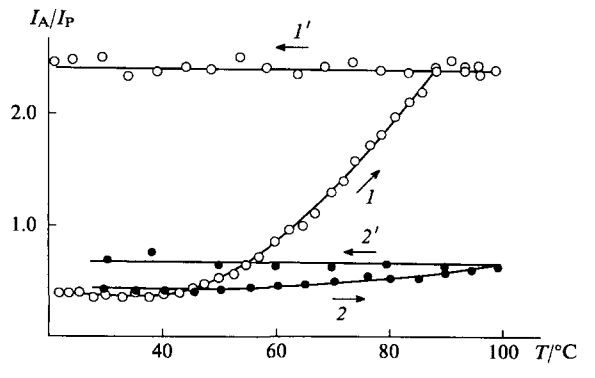


Figure 29. The influence of heating on the effectiveness of energy transfer (I_A/I_P) for noncross-linked (curves *1* and *1'*) and cross-linked (curves *2* and *2'*) 'phenanthryl/6/anthryl' systems.[185]

IX. Polymers based on maleic and fumaric acid derivatives

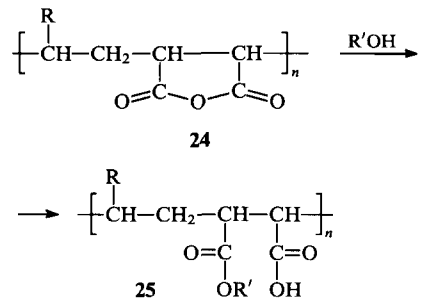
Two types of monomers and polymers derived from the isomeric maleic and fumaric acids and investigated in monolayers and LBF are known.

The first type includes the octadecyl monoesters of fumaric (ODF) and maleic (ODM) acids and the polymers based on them. The monolayer expands on photopolymerisation of ODF on the surface of water and contracts on photopolymerisation of ODM.[186,187] A 1:3 mixture of monomers polymerises without change in the area of the monolayer and can be used to form LBF with a low content of defects (cracks), the appearance of which is usually caused by the contraction of the monolayer on polymerisation.

The elastic properties of LBF of saturated ODF as well as the monomeric and polymerised ODF, 1:3 ODF–ODM mixtures, and ω-octadecenyl fumarate have been investigated by Brillouin spectroscopy.[188] The elastic constants of 30-layer LBF have been determined and it has been shown that they are low, decreasing still further on polymerisation for the majority of systems investigated owing to the formation of microcracks in the ODF on photopolymerisation. The polymerisation of mixed LBF comprising ODF and ODM leads to a slight increase in the elastic constants, which agrees with data obtained, showing the absence of contraction in this system on polymerisation.

Evidently the possibilities of these monomers for the creation of functionalised organic surfaces and organised films are far from having been exhausted.

Copolymers of vinylmaleic anhydride **24** belong to the second more widely investigated type. The reaction of compound **24** with water leads to the formation of poly(dicarboxylic acids) and that with alcohols affords the polyesters **25**.



24

25

Fig. 30 (see over) illustrates the influence of the ester side chain on the compression isotherms of the copolymers obtained by the esterification of poly(octadec-1-enyl-maleic anhydride). As can be seen from the figure, in contrast to the polymers examined previously in this instance the limiting areas of the monolayers increase linearly with increase in the length of the ester group, while the shape of the curves is retained. Hence it follows that the ester chains do not assume a vertical position on compression of the monolayer.[190]

Since the copolymers **25** contain unsubstituted carboxy-groups, the structure of their monolayer may be regulated by varying the pH of the subphase. For the copolymer with R' = CH_3, an increase in the pH of the subphase from 4.0 to 10.0 leads to an increase in the limiting area of the monolayer from 53 to 68 Å^2 per residue and to an increase in the collapse pressure from 22 to 40 mN m^{-1}.[189] Such behaviour can be explained by the ionisation of the carboxy-groups, which intensifies the repulsion between the molecules and the monolayer.

Recently these results were revised.[191] It was shown that at π = 30 mN m^{-1} the pH does not affect the area of the monolayer and that the collapse pressure does not increase with pH but either diminishes or passes through a minimum. The authors[191] note that the expansion of the monolayer as a result of the ionisation

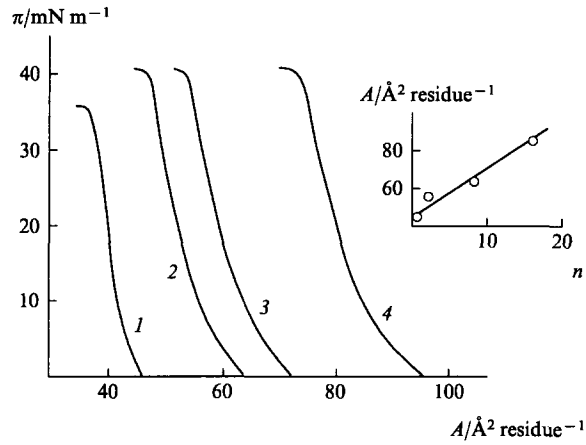


Figure 30. Compression isotherms for monolayers of copolymers of type **25** with R = $(CH_2)_{15}CH_3$ and different R′:[189] (*1*) H; (*2*) CH_3; (*3*) $(CH_2)_7CH_3$; (*4*) $(CH_2)_{15}CH_3$. The inset illustrates the dependence of the limiting area on the length of the group R′.

of the carboxy-groups can be compensated by the attraction due to the ion–dipole interactions or hydrogen bonding between the ionised carboxylate groups and the neutral acid residues.

High-quality Y type LBF have been obtained from compound **25** at pH 4.0–7.0 and 30 °C.[190,192,193] The introduction of Na^+ ions into the subphase significantly impairs the quality of the LBF, while in the presence of Cd^{2+} ions the LBF obtained are almost insoluble 'in all the solvents'.[189]

The influence of pH on the degree of transfer of copolymer monomers is illustrated in Fig. 31. The sharp decrease in ρ at pH > 8 can be explained by the development of repulsive forces between the surface of silicon and the ionised monolayer. The sharp increase in the viscosity of the monolayer at pH > 8.5 can also affect the quality of the LBF formed.[194] The degree of ionisation of the monolayers transferred onto a silicon prism has been determined[191] by distorted total internal reflection IR spectroscopy. The pK_a corresponding to the pH at which 50% ionisation takes place was found by monitoring the absorption bands of the unionised carboxy-groups. For the non-esterified and monoester derivatives of compound **25**, the pK_a were found to be in the range 8.0–8.5. This confirms the observed relation between the degree of transfer of the monolayer and the degree of ionisation of its constituent polymer.

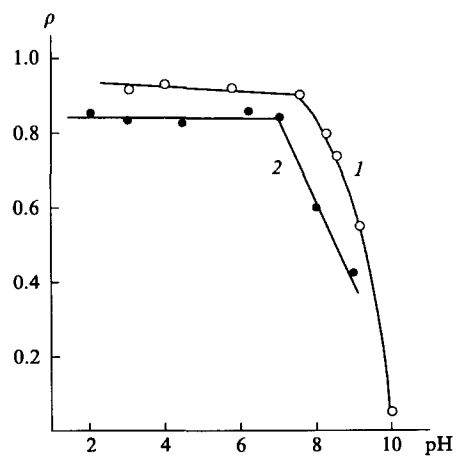


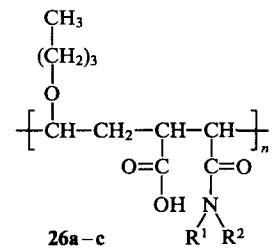
Figure 31. Dependence of the degree of transfer for the first ten LBF layers on pH for copolymer **25** with R = $(CH_2)_{15}CH_3$ and R′ = CH_3 (curve *1*) and H (curve *2*).[191]

The influence of pH, ionic strength, and the concentration of Ca^{2+} ions in the subphase on the properties of monolayers of the hexadecyl vinyl ether–maleic acid copolymer, which constitute models of biological membranes, has been investigated[195] in a study of processes involving the binding of Ca^{2+} ions by membranes during muscle and nerve activity, in membrane transport, in enzymic reactions, etc.

The height of the Schottky barrier in metal–dielectric–semiconductor heterostructures may be regulated with the aid of LBF of poly(octadec-1-enylmaleic anhydride).[193] A change in the degree of hydrolysis of the anhydride groups in the Au–LBF–GaP system alters the height of the Schottky barrier as a result of the accumulation of electrons (increase in the charge) on the oxygen atom of the anhydride group.

The copolymers obtained as a result of the modification by the corresponding amine of the butyl vinyl ether–maleic anhydride copolymer **25** have interesting properties.[196]

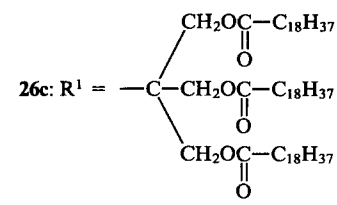
Y type LBF of compounds containing single-stranded (**26a**), double-stranded (**26b**), and triple-stranded (**26c**) side chains were formed in the above study on the surface of porous (0.2 μm) polycarbonate films (Nuclepore) and the influence of the structure of the monolayer and of the number of layers in the LBF on the permeability of such a membrane to the electrolyte (KCl) was analysed.



26a–c

26a: $R^1 = C_{18}H_{37}$, R^2 = H.

26b: $R^1 = R^2 = C_{18}H_{37}$.



R^2 = H.

In order to determine the KCl flux (0.5 M solution), the conductivity of the aqueous phase was measured, assuming that there is a linear relation between the conductivity and the KCl concentration. Fig. 32 presents the dependence of the KCl flux on the number of layers of compound **26b** in the LBF at 22 °C. It is seen from the figure that the electrolyte flux diminishes sharply on deposition of 6–8 monolayers and subsequently remains unchanged. The influence of the number of side chains in the elementary unit of the copolymer molecule on the electrolyte flux is illustrated in Fig. 33. The electrolyte flux is not arrested by the LBF of the single-stranded derivative **26a** and is weakly inhibited by the LBF of the triple-stranded derivative **26c**. The double-stranded copolymer **26b**, which gives rise to the closest packing in

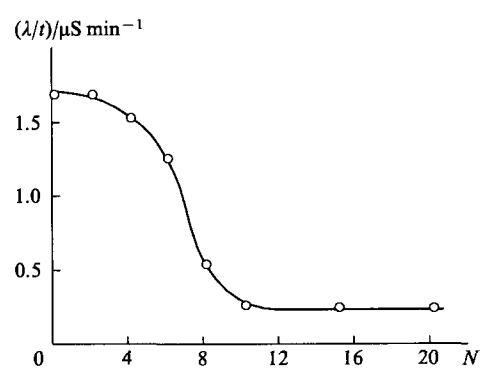


Figure 32. The influence of the number of layers of polymer **26b** (*N*) on the flux of KCl (λ/T) through a membrane at 22 °C.[196]

the monolayer (the limiting area of the **26b** monolayer is smaller than for the other two analogues), offers the greatest resistance to the electrolyte flux in the LBF. For membranes cast on a nuclear ultrafilter from solutions of compounds **26a–c**, the dependence of the flux on the number of side chains was not observed.[196] The stability of the LBF in aqueous solutions and the reproducibility of the results of the measurements of their permeability suggest the possibility of the practical employment of these selective membranes.

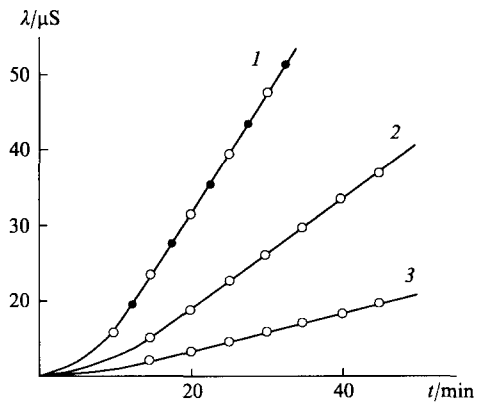


Figure 33. The permeability to KCl of LBF (20 layers) comprising polymers **26a** (curve *1*), **26c** (curve *2*), and **26b** (curve *3*) at 22 °C. Filled circles — data for the initial porous membrane (without LBF).[196]

X. Synthetic polypeptides and polyorganosiloxanes. Monolayers consisting of helical molecules and thin films

It was noted above that an essential condition for the preparation of LBF with a calibrated thickness and a definite orientation of molecules is the formation of a true equilibrium monolayer in which each monomer residue is in contact with the surface of the aqueous subphase. In contrast to monolayers of low-molecular-mass compounds, for which collapse with formation of the bulk phase almost always occurs for $A < A_0$, for polymeric objects with extensive conformational possibilities a decrease in the area can lead to the formation of monolayers made up of more complex molecular structures: helices and coils. We shall examine the properties of such monolayers in relation to synthetic polypeptides and polyorganosiloxanes. For the latter, we shall also analyse the possibility of the formation of stable thin polymer films on the surface of a liquid. Both these aspects are associated with the behaviour of the monolayers in the collapse region.

1. The behaviour of polymer monolayers on collapse

Many investigators[25,41–43,197–201] have been interested in the problem of the collapse of monolayers of low-molecular-mass compounds; polymer monolayers have been investigated to a much lesser extent in this respect. A brief analysis of this question can be usefully begun with the methods for the determination of the area of a close-packed polymer monolayer. Whereas the determination of the limiting areas of monolayers of low-molecular-mass substances by extrapolation to zero surface pressure is not open to disagreement, for polymer monolayers this parameter is determined in different ways. Two methods are normally employed for the determination of A_0: by extrapolation or from the beginning of the plateau on the compression isotherm. In this connection, it is essential to note that it is frequently difficult to determine the linear section for monolayers of the expanded type while for monolayers of the condensed type A_0 is frequently smaller than the area calculated on the basis of the model owing to the high interchain cohesion. Evidently, the uncertainty in the determination of the limiting area hinders the comparison and interpretation not only of experimental but also of theoretical results, since all the equations of state of monolayers include A_0 as a parameter.

There are differences in the behaviour of films of the liquid-expanded and condensed types compressed to small areas ($A < A_0$). The presence of a plateau over a wide range of areas is characteristic of the former, whereas for the latter the plateau is either absent or is weakly expressed. The first explanations, relating the existence of a plateau to the reorientation of the side chains, were criticised.[25] The concept of the 'upper film', based on the fact that the surface pressure increases on compression of the monolayer to a thickness equal approximately to $A_0/2$,[25] is poorly justified since the second rise in surface pressure (as will be seen from the data presented in the present section) depends on many factors. Nevertheless, data concerning the formation of two-layer or three-layer organic acid films have been presented for low-molecular-mass compounds.[202,203] However, there is no reliable evidence for the existence of such films.

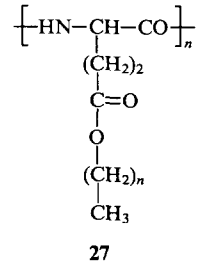
One of the ways of retaining the two-dimensional organisation after the collapse of the true monolayer involves the formation of single-layer films of helical molecules.

2. Polypeptides

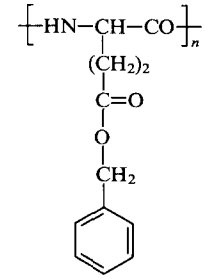
The properties of monolayers of natural proteins have been investigated very intensely and have been described in a series of monographs and review articles.[204–208]

Monolayers of synthetic polypeptides have been investigated in fair detail as models of biological membranes.[203,209–211] Since the biological aspects of the behaviour of monolayers of protein molecules are not the subject of the present review, we shall analyse the properties of synthetic polypeptide monolayers within the framework of the traditional approaches to polymeric objects. On this basis, we shall turn attention to the conformational transformations in the monolayers, the formation of multilayers on the surface of a liquid, the change in the structural homogeneity and rheological properties of monolayers on compression, and certain other questions.

Among synthetic polypeptides, poly-γ-alkyl-L-glutamates **27** and poly-γ-benzyl-L-glutamate **28** have been most thoroughly investigated. By altering the composition of the aqueous subphase and the type of solvent from which the monolayer is formed, it is possible to regulate the structure of the macromolecule on the surface of the liquid. The limiting area of the poly-γ-methyl-L-glutamate monolayer on the surface of a dilute solution of formic acid is greater by a factor of 1.5 than A_0 for the same monolayer on a pure aqueous subphase.[209] The authors' view[209] that a helical conformation of the macromolecules corresponds to the smaller areas has been frequently justly criticised.[212,213]



27



28

Fig. 34 presents the isotherms for poly-γ-methyl-L-glutamate monolayers deposited on the surface of water from a mixture of solvents.[212] It can be seen that the isotherms for the monolayers obtained from solution in pyridine with an admixture of chloroform have low values of A_0 and a high compressibility. On the other hand, the monolayer formed from solution in

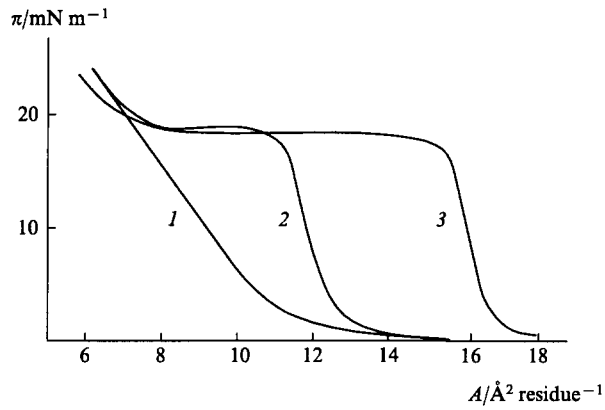


Figure 34. Compression isotherms for poly-γ-methyl-L-glutamate monolayers obtained on the surface of water from a mixed chloroform–pyridine solvent:[212] (*1*) 93% pyridine; (*2*) 77% pyridine; (*3*) 100% chloroform.

chloroform has a low compressibility, high limiting areas, and an extended plateau. Analysis of the IR spectra of monolayers of the polypeptides deposited at different surface pressures showed that the monolayers obtained from chloroform (higher A_0) consist of macromolecules in the form of α-helices, while in the monolayers formed from pyridine the macromolecules are in the extended β-conformations. It is of interest to note that, on compression of both types of monolayers, there is no transition from one type to another.[212]

Although doubts have been cast[211] on the possibility of the formation of β-structures in the monolayer, rheological studies[214] indicate significant differences in the behaviour of poly-γ-methyl-L-glutamate monolayers obtained from solutions in pyridine (β-structures) and in chloroform (α-helix). In contrast to the monolayer containing β-conformers, the surface viscosity (η_s) of which diminishes with increase in temperature, the η_s of the monolayer made up of α-helices increases. The $\eta_s - T$ relation for the poly-γ-methyl-L-glutamate monolayer, the molecules of which are in the form of α-helices, is illustrated in Fig. 35, which shows that an increase in temperature leads to irreversible changes in the monolayer: on subsequent decrease in temperature to 17 °C, the surface viscosity does not diminish. Such behaviour has been explained by the partial denaturation of the α-helices and the formation of hydrogen bonds between the molecules. The irreversibility of the temperature variation of the surface potential of the monolayer confirms this conclusion.[214]

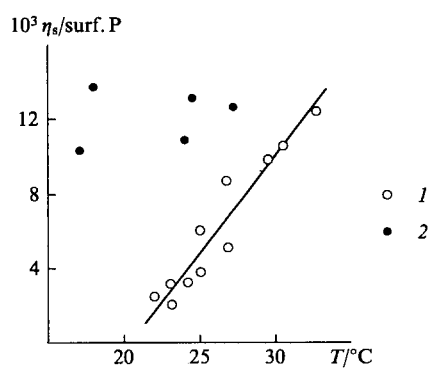


Figure 35. Temperature dependence of the surface viscosity (η_s) for a poly-γ-methyl-L-glutamate monolayer (initial structure—α-helices):[214] (*1*) data obtained with increase in temperature; (*2*) data obtained on subsequent reduction of temperature; A = 28.1 Å² per residue.

The novel results of Malcolm's studies[215,216] make it possible to examine the behaviour of polypeptide monolayers in the light of the important problem of the inhomogeneity of monolayers of viscoelastic systems, of which these polymers are typical representatives.

The form of the compression isotherms for poly-γ-ethyl-L-glutamate monolayers is influenced by the method of measurement of the surface pressure (Fig. 36).[216] For A > 12.5 Å² per residue, the isotherms obtained by the Wilhelmy and Langmuir (surface balance) methods are identical. However, the length of the plateau depends on the method of measurement, the position of the sensor (plate or strip) relative to the mobile barrier or the edge of the trough, and the orientation of the plate.

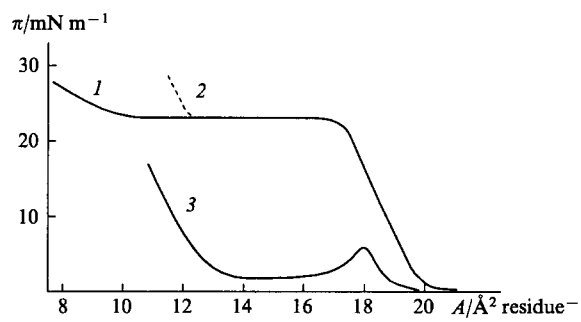


Figure 36. Compression isotherms for poly-γ-ethyl-L-glutamate monolayers:[216] (*1*) Langmuir balance with the sensor on the edge of the trough; (*2*) Wilhelmy method with the plate located 10 cm from the edge of the trough parallel to the barrier; (*3*) horizontal pressure applied to a glass plate 3 cm wide located in the same position as the Wilhelmy plate.

Thus in the measurement of the surface pressure by the Wilhelmy method, where the sensor is placed at a distance of 10 cm from the edge of the trough parallel to the mobile barrier, another increase in π (end of the plateau) is observed at A = 12.5 Å² per residue, while in the measurement by the Langmuir method, which is based on the measurement of the surface pressure at the edge of the trough, a new increase was observed at A = 9.5 Å² per residue. By placing the plate at different distances from the edge of the trough, Malcolm[216] showed that the length of the plateau decreases linearly with increase in this distance (Fig. 37).

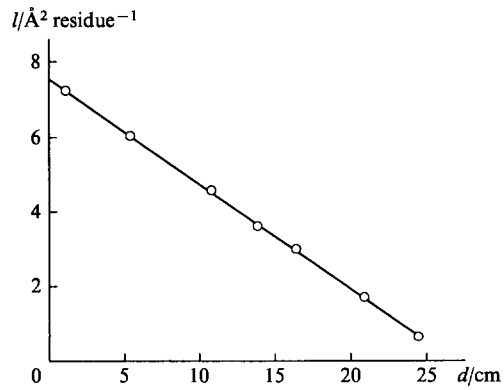


Figure 37. Dependence of the length of the plateau (*l*) on the compression isotherms for poly-γ-ethyl-L-glutamate monolayers on the distance (*d*) of the Wilhelmy plate from the edge of the trough.[216]

The deviation of the Wilhelmy plate from the vertical is characteristic of the measurement of π for viscoelastic polymer monolayers. Fig. 36 presents the dependence (curve *3*) of the horizontal force acting on the plate on the area of the monolayer.

Evidently the force increases in parallel with increase in the surface pressure before the beginning and at the end of the plateau. Together with this force, which is apparently thermodynamic in nature (the Marangoni effect), mechanical forces make a significant contribution to the displacement of the plate.

The effects described above are associated with the inhomogeneity of the poly-γ-ethyl-L-glutamate monolayers arising on compression. With the aid of thin strips of sulfur powder deposited through a template on the surface of the monolayer parallel to the barrier, the distribution of the inhomogeneities in the monolayer was visualised.[216] The displacement of the sulfur powder strips in the central part of the trough on compression of the monolayer is illustrated in Fig. 38.

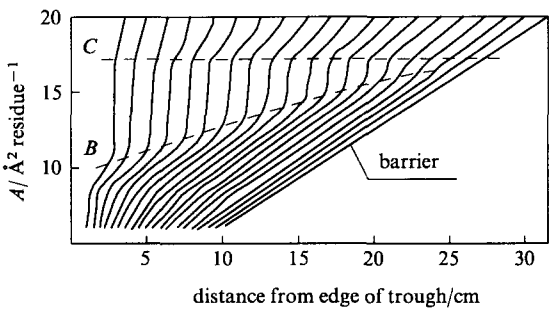


Figure 38. Displacement of sulfur powder strips along the central line of the trough from its edge on compression of a poly-γ-ethyl-L-glutamate monolayer.[216] Line *C* corresponds to the area for which the plateau begins; line *B* corresponds to transition to the bilayer film.

Up to the line *C*, corresponding to the onset of the increase in surface pressure and the formation of a bilayer film, the compression of the monolayer proceeds fairly uniformly. The region between the straight lines *C* and *B*, corresponding to the conversion of the monolayer film into a bilayer film, contains lines with slight displacements, and its size agrees well with the length of the plateau and the compression isotherms obtained by the Wilhelmy method. Finally, for $A < 9.5$ Å^2 per residue, the bilayer film collapses. The structure of the film is distorted most in the vicinity of the Wilhelmy plate and at the edges of the trough. The complex flow line distribution patterns arising on compression of the monolayers must be taken into account in the treatment of the results. In particular, viscometric data for polypeptide monolayers, which are interpreted in terms of denaturation processes,[214] can also be accounted for by experimental causes.[216] Similar problems arise in the analysis of the compatibility of the monolayers[217,218] and the kinetics of their collapse.[219]

In order to diminish or exclude the effects associated with the poor homogeneity of highly viscous monolayers, it is recommended[216] that symmetrical compression (the Wilhelmy method) or the surface balance method be employed. Naturally, these recommendations refer both to measurements of the surface potential and to viscometric studies on monolayers as well as the formation of homogeneous LBF. Different procedures for the compression of monolayers have been discussed[220,221] and the important role of rheological characteristics in the formation of homogeneous monolayers has been demonstrated[222] in relation to stearic acid and cadmium and aluminium stearates. By measuring the distribution of the surface pressure on the surface of the monolayer, it was shown[222] that the surface pressure is uniformly distributed over the entire surface for the acid and cadmium salt monolayers, the viscosity of which is low. In the case of the highly viscous aluminium stearate monolayer, the differences in π ($\Delta\pi$) can exceed 20 mN m^{-1}. Such behaviour has been explained from the standpoint of the dynamics of a liquid, which establishes direct proportionality between $\Delta\pi$ and η_s.

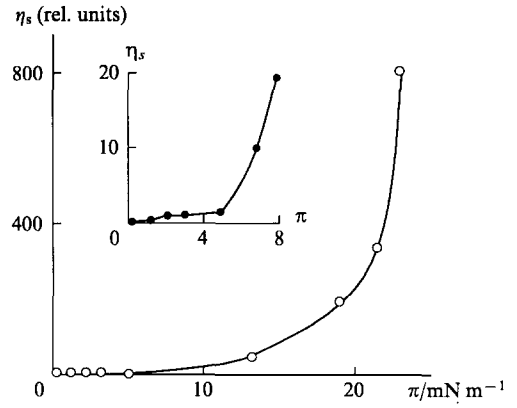


Figure 39. Dependence of the surface viscosity (η_s) on the surface pressure (π) for a poly-γ-methyl-L-glutamate monolayer at 17 °C.[218]

Fig. 39 presents the $\eta_s - \pi$ relation for a monolayer of poly-γ-methyl-L-glutamate α-helices.[218] Evidently the differences in the values of π on nonuniform compression of the monolayer can lead to abrupt changes in surface viscosity by factors of tens and hundreds.

In connection with the problem of the relationship between structure and the physicochemical properties of cell membranes, much attention has been devoted in the study of polypeptide films to their compatibility with lipids.[218,223–228] The compatibility was analysed for two conformations of the polymer molecules and also for monolayer and multilayer films.

The enantiomeric forms of poly-γ-methyl-L-glutamate are fully compatible in monolayers, like binary mixtures of other polypeptides.[211] The compatibility between polypeptides and lipids depends on the state of the monolayer of the latter (expanded or condensed).[223] The polypeptide in the β-form is incompatible with arachidic acid on the surface of 0.01 M HCl solution.[224] In the form of α-helices, poly-γ-benzyl-L-glutamate is compatible with palmitic and stearic acids in the monolayer for a polymer mole fraction in excess of 0.9.[227] In a multilayer film, these components are incompatible. On the other hand, poly-γ-methyl-L-glutamate is compatible with these acids both in the monolayer and in a multilayer film. The differences in the behaviour of the binary systems considered are determined by the different levels of aggregation of the polypeptide molecules in the films, by the different modes of interaction between the acids and polypeptides, and by the phase state of the acid monolayers. The properties of mixed monolayers of polypeptides and phospholipids can also be explained in the light of these ideas.[226] Analysis of the rheological properties of mixed monolayers of polypeptides with phospholipids and with cholesterol made it possible to establish a correlation between the surface viscosity of the monolayers and the stability of bilayer lipid membranes.[218]

Together with the use of polypeptide monolayers for the modelling of biological systems, multilayer (more than 500 monolayers) LBF of methyl glutamate–alkyl glutamate copolymers have attracted the attention of investigators recently as promising materials for optical wave guides with low losses[229,230] and also as photoresists and electron-beam resists.[231]

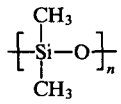
Thus the unusual feature of polypeptides consists in the fact that they form quasi-true monolayers of α-helices, the compression of which results in the formation of two- and three-layer films.[232–234] The breakdown of this conformation can be achieved by altering the temperature of the system and the composition of the support and of the solvent from which the monolayer is formed. The length of the plateau on the compression isotherms is determined by the method of measurement of the surface pressure and by the position of the sensor relative to the barrier and the walls of the trough. The inhomogeneity arising on compression of highly viscous monolayers, with long relaxation

times, leads to appreciable differences between the surface pressures for different sections of the trough. These effects can be reduced or eliminated in symmetrical compression or with the aid of special designs of the Langmuir trough. An increase in the homogeneity of polypeptide monolayers is essential for the construction of adequate models of biological membranes and also for the formation of high-quality LBF, which may find application in fibre optics.

3. Polyorganosiloxanes

a. Polydimethylsiloxane monolayers

Polyorganosiloxanes belong to the class of polymers which have been investigated in detail in monolayers. Most of the studies have been carried out on polydimethylsiloxane **29**.[235–245] The interest in this polymer is caused not only by its practical use as a surfactant in aqueous and nonaqueous media[246,247] but also by the possibility of forming stable monolayers from helical molecules.



29

Combined studies which have been carried out on polydimethylsiloxane (PDMS) monolayers and thin films made it possible to supplement the existing ideas concerning the structural transformations of this polymer on the surface of a liquid and also to consider the possibility of converting the monolayers into thin stable films.[52,239,240,245]

Fig. 40 presents the dependence of the surface pressure (determined by the Wilhelmy and Langmuir methods), the surface viscosity (determined using a rotating viscometer), and the surface potential (ΔV, determined by use of an ionising ^{210}Po electrode) on the area of the PDMS monolayer (M_η = 1.25 × 10^6). The sensitivity of the sensors (~0.01 mN m^{-1}) did not permit the measurement of surface pressures for areas in excess of 37 Å^2 per monomer residue. For A = 35–60 Å^2 per residue, the surface potential oscillates during scanning parallel to the surface, which indicates the inhomogeneity of the monolayer. In this range of areas, the macromolecules and their associated species lie on the surface of water in the form of discs—two-dimensional analogues of statistical coils; the siloxane dipoles adjoin the water molecules, while the methyl groups are directed towards the air phase. As a result, the *trans*-configuration of the PDMS molecules, which obtains in the bulk phase, is converted into the *cis*-configuration in the surface layer. In the range of areas from 37 to 20 Å^2 per residue, the isolated regions comprising the polymer approach one another and water is displaced from the gaps between them.[52,242] This process does not require much energy expenditure and π therefore increases only slightly. Starting from A = 20 Å^2 per residue, π increases sharply up to 7.6 mN m^{-1}; for A = 14 Å^2 per residue and in the range from 14 to 7.5 Å^2 per residue, π remains unchanged. The change in the hydration state of the monolayer when it is compressed has been examined in detail in a number of studies.[242–244] The constancy of the surface pressure for A < 14 Å^2 per residue indicates the formation of a helical conformation of the macromolecules: the energy expenditure in the displacement of the Si–O dipoles from the surface of the subphase is made good by the energy gain due to the internal compensation of the siloxane dipoles.

The exact determination of the region where macromolecules are converted into the helical form is of fundamental importance from the understanding of the processes involving the collapse of the true monolayer and the formation of transient films. Taking into account the ΔV–A relation as well as the temperature dependence of π (Fig. 40), one may conclude that the formation of helices in the monolayer begins for areas in the

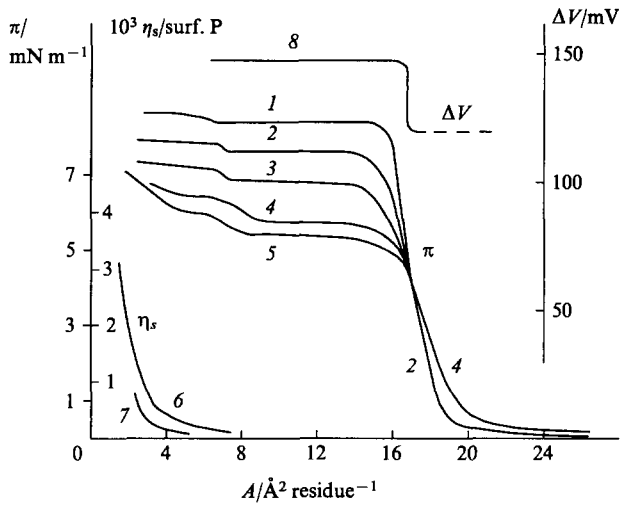


Figure 40. Dependence of the surface pressure (π), surface viscosity (η_s), and surface potential (ΔV) on the area of a PDMS monolayer on the surface of water at different temperatures (°C):[239] (*1*) 10; (*2*) 20; (*3*) 30; (*4*) 40; (*5*) 50; (*6*) 20; (*7*) 40; (*8*) 20.

range 16–17 Å^2 per residue, i.e. in the region of constant π. If a model comprising horizontally coaxial rings lying one on top of the other is used as an approximation to the helix, then in the case of PDMS containing 3, 6, and 8 monomer units corresponding to one turn of the helix, the following occupied areas are obtained: 10, 7.8, and 6.2 Å^2 per residue.[248] Thus the jump in surface pressure at A = 7.6 Å^2 per residue most probably corresponds to the formation of a close-packed monolayer of PDMS helices each containing six siloxane bonds per turn. The axes of the helices are arranged parallel to the surface of water.

In order to refine the mechanism of the conformational transformations in the PDMS monolayer, the temperature dependences of π and η_s were determined. Comparison of the dependences of the surface pressure on the area at different temperatures show that, for large values of A, the temperature coefficient of π is positive and small. With decrease in the area, the temperature coefficient changes sign and increases in absolute magnitude. The characteristic points for curves corresponding to different temperatures correspond to different areas. This permits the conclusion that the processes occurring in the monolayer at different temperatures during the compression process are identical.

In the region of the true monolayer, the surface viscosity is low (< 10^{-5} surf. P) (Fig. 40). An appreciable rise in η_s begins on formation of a close-packed monolayer made up of helices, the viscosity of the monolayer diminishing with increase in temperature.

The entropy (s_s) and enthalpy (h_s) of spreading were calculated with the aid of the temperature variations of the surface pressure.[41]

$$s_s = \left(\frac{\partial \pi}{\partial T}\right)_{A,a},$$

$$h_s = -\left[\frac{\partial(\pi/T)}{\partial(1/T)}\right]_{A,a} = T\left(\frac{\partial \pi}{\partial T}\right)_{A,a} - \pi,$$

where a is the overall area of the monolayer and of the free surface of water and T is the absolute temperature.

The calculation of the thermodynamic functions of spreading was preceded by the determination of the degree of equilibrium of the monolayer. By varying the concentration of the solutions, the number of drops, and the area provided for spreading and also by measuring the reversibility of the isotherms, it has been

shown that they are reproducible and hence the monolayer is in equilibrium.

The $s_s - A$ and $h_s - A$ relations for two temperatures are presented in Fig. 41. The thermodynamic functions and their relation with the structural transformations in the monolayer have been subjected to a detailed analysis.[52,239] Here we shall note that the change in the sign of the thermodynamic functions on compression of the monolayer in the region of $A \simeq 17$ Å^2 per residue indicates a transition of the system to a more ordered state. This transition may be associated with the formation of a monolayer of helical PDMS molecules, which is accompanied by the self-compensation of the Si–O dipoles.[236] The signs of s_s and h_s change for the same value of A as the one at which a jump ΔV was observed.

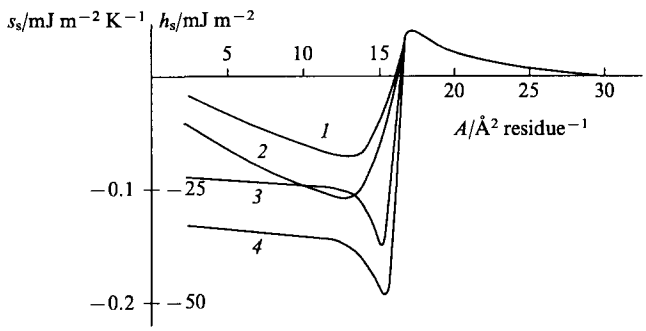


Figure 41. Dependence of the entropy (curves *1* and *3*) and enthalpy (curves *2* and *4*) of spreading on the area of a PDMS monolayer on the surface of water at 45 °C (curves *1* and *2*) and 15 °C (curves *3* and *4*).[239]

The experimental results obtained in the study of PDMS monolayers on the surface of water were subjected to a theoretical treatment using the familiar Singer,[143] Davies,[146] Motomura and Matuura,[249] and Frisch and Simha[144] equations of state for polymer monolayers. These equations and the parameters of the monolayers of high-molecular-mass compounds calculated with their aid have been subjected to a detailed analysis.[52] The calculations showed that the flexibility of the PDMS chains on the surface of water is extremely low despite the fact that in the bulk phase the polymer is extremely flexible. Evidently, the loss of one degree of freedom and also the retardation or complete absence of rotation, which are a consequence of the spreading of the polymer, render the chain conformationally rigid.

In order to refine the conclusions reached in the study of PDMS monolayers on the surface of water and also in order to elucidate the influence of the surface energy of the subphase on the properties of monolayers of this monomer, a study has been made of the behaviour of PDMS monolayers on the surface of aqueous 1,4-dioxane solutions at different concentrations.[52,250]

Dioxane concentration in solution (vol. %)	0	1	5	15	50	100
Surface tension of the solutions/nM m^{-1}	72.5	68.7	58.8	54.2	37.4	32.5

Fig. 42 presents the surface pressure (surface viscosity)–area isotherms at 20 °C for some of these subphases. The figure shows that, as the subphase becomes more hydrophobic, the shape of the $\pi - A$ isotherm changes: the surface pressure diminishes, the horizontal section vanishes, and the slope of the initial section decreases.

Evidently, replacement of the polar water molecules in the surface layer by the nonpolar dioxane molecules weakens the interaction of the subphase with the polar siloxane groups of the polymer. The change in the thermodynamic functions of spreading for polydimethylsiloxane monolayers on the surface

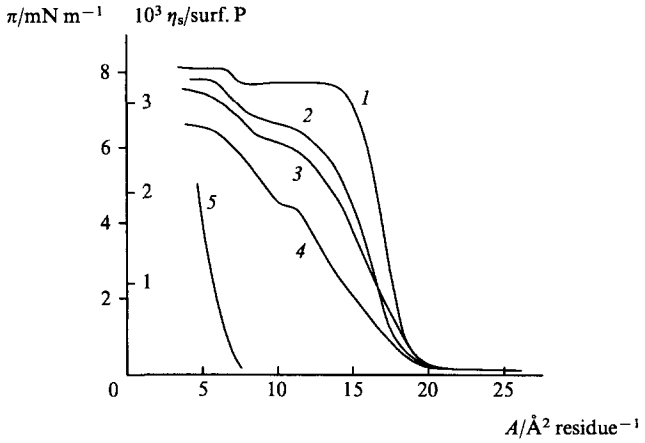


Figure 42. Dependence of the surface pressure (curves *1*–*4*) and surface viscosity (curve *5*) on the area of a PDMS monolayer on the surface of water (curve *1*) and solutions of dioxane in water (curves 2–5) at 20 °C.[250] Dioxane concentration (vol.%): (*2*) 5; (*3*) 15; (*4*) and (*5*) 50.

of a 50% aqueous solution of dioxane is illustrated in Fig. 43. Evidently, the entropy and enthalpy of spreading vary in the negative region for all the areas of the monolayer. The change in the sign of the thermodynamic functions on compression of the polymer monolayer on the surface of water (Fig. 41) was associated with the formation of the helical conformation of the macromolecules. On the other hand, in the case of the low-energy organic support, only the helical conformation is produced. The viscosity of this monolayer, like that of the monolayer on the surface of water, becomes appreciable only on formation of a close-packed film of helical molecules and when they are subsequently squeezed out from the surface of the support (Fig. 42).

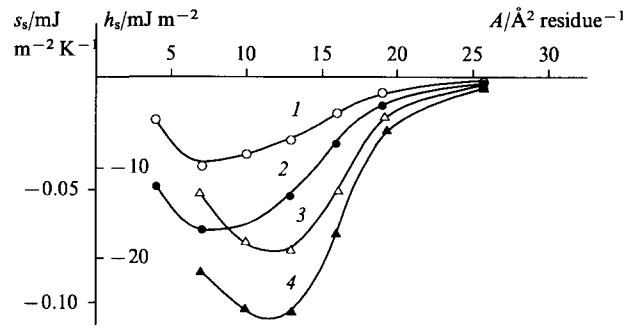


Figure 43. Dependence of the entropy (curves *1* and *3*) and enthalpy (curves *2* and *4*) of spreading on the area of a PDMS monolayer on the surface of a 50% solution of dioxane in water at 45 °C (curves *1* and *2*) and 15 °C (curves *3* and *4*).

In contrast to the PDMS monolayer on the surface of water, the compression of which up to the formation of a dense helical monolayer entails a change in ΔV by 150 mV which then remains constant, for the monolayer on the surface of 50% aqueous solution of dioxane $\Delta V = 0$ for all areas.

Important information about the influence of the surface energy of the subphase on the conformational transformations in the PDMS monolayer was obtained in a study of the spontaneous spreading of the polymer from the bulk phase on the surface of water, dioxane, and 5% and 50% solutions of dioxane in water. Fig. 44 presents the dependence of π and ΔV on the spreading time (t) of PDMS. Evidently the films are formed spontaneously on these supports. However, ΔV is nonzero only on

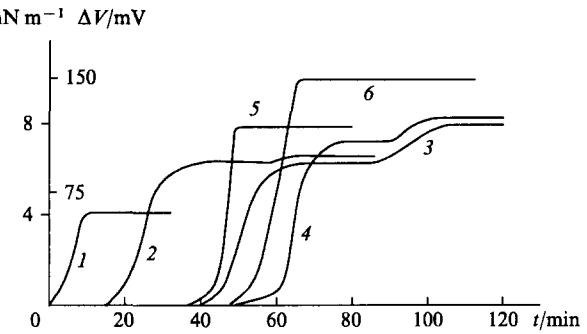


Figure 44. Kinetics of the spreading of PDMS on the surface of dioxane (curve *1*), solutions of dioxane in water [50% (curve *2*) and 5% (curves *3* and *5*)], and water (curves *4* and *6*): [250] (*2*) – (*4*) π; (*5*) and (*6*) ΔV.

dioxane solutions at concentrations ⩽5%. This result shows that the dipoles of the elementary units of PDMS are self-compensated in the helical macromolecule, while the zero dipole moment of the dioxane molecules ensures the constancy of ΔV whatever their orientation.

With increase in the concentration of dioxane in water, the rate of formation of the film from the bulk phase also increases and reaches a maximum on pure dioxane, despite the fact that PDMS hardly dissolves in dioxane and the surface tension of the latter is lower by a factor of 2 than that of water (Fig. 44). The macromolecules probably pass from the bulk phase to the film in the same helical conformation as that obtaining in the statistical coils of the bulk phase. The additional energy expenditure on the compression of two-dimensional discs and the new formation of helices on spontaneous compression of the monolayer, of the kind occurring at the air – water interface, is then ruled out.

Thus PDMS on a liquid hydrophobic surface forms a monolayer of helical molecules regardless of whether the polymer is deposited from solution or from the bulk phase.

b. Thin polydimethylsiloxane films on the surface of a liquid

The two-dimensional coil – helix conformational transition in the PDMS monolayer during its compression or spreading from the bulk phase must be regarded as a transition between a true monolayer and a thin polymer film. This film corresponds to equilibrium on the surface of the liquid. In this connection, a series of questions arise. What is the thickness which the films thus formed can have? Will they be stable? How will the stability be related to the surface energy of the subphase?

Hitherto the possibility of the formation of stable films thicker than single-layer films of both low-molecular-mass and high-molecular-mass substances on the surface of a liquid has been questioned. Whereas for low-molecular-mass compounds these ideas were based on numerous experimental studies,[41] such studies had not been made for high-molecular-mass compounds and in particular polymers.

In the studies of synthetic polypeptide monolayers on the surface of water examined above and in a recently published investigation [251] of monolayers of alkyl-trimethylammonium salts on the surface of mercury, the conclusion that multilayer films are formed was based on the presence of bends in the compression isotherms and on the analysis of the corresponding areas The stability of the films obtained in the above investigations is not discussed.

The possibility of the formation of a film as a result of the spreading of the substance from the bulk phase is regulated by the Young – Dupré relation

$$\sigma_A > \sigma_B + \sigma_{AB},$$

where σ_A, σ_B, and σ_{AB} are the interfacial tensions at the air – water, air – polymer, and polymer – water interfaces respectively.

The question of the thermodynamic stability of the film can be elucidated by comparing the free surface energies of the film and the close-packed monolayer. [52,240,245]

The specific free surface energy (F_s) for the phase state of the substance on a liquid surface is defined as $F_s = F_s^0 = \sigma_B + \sigma_{AB}$. With decrease in the film thickness (h), F_s becomes a function of h.

If the film is stable for all thicknesses up to and including the phase state, the following condition should hold:

$$\frac{dF_s}{dh} \leqslant 0.$$

The change in F_s can be calculated from the change in the surface pressure as a function of h. Fig. 45 (curve *2*) illustrates for cholanic acids [252] a typical $F_s - h$ relation for films of low-molecular-mass crystalline compounds on the surface of water. Other traditional surfactants, for example cetyl alcohol and stearic acid, give rise to curves of similar shape. It is seen from Fig. 45 that, for a cholanic acid film, the stability condition holds only up to h = 20 Å. With further increase in thickness, the film collapses with formation of the bulk phase of the test substance in equilibrium with the monolayer. The difference between F_s corresponding to the plateau and the minimum value of F_s yields the energy expenditure in the transfer of the substance from the two-dimensional state (monolayer) to the three-dimensional state.

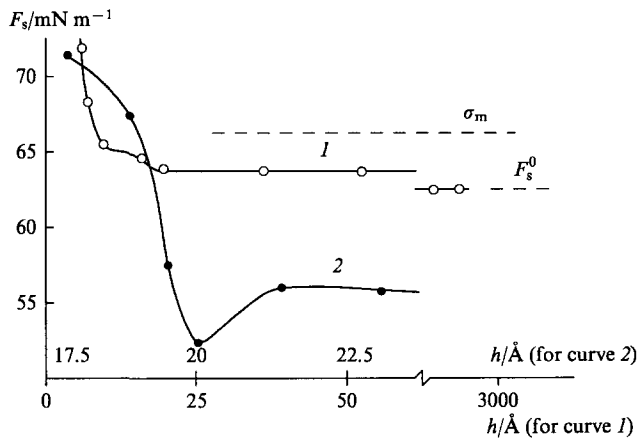


Figure 45. Dependence of the free surface energy (F_s) on the thickness (h) of PDMS (curve *1*) and cholanic acid (curve *2*) films on the surface of water. [240]

For a PDMS film on the surface of water (Fig. 45, curve *1*) we have for all values of h

$$\frac{dF_s}{dh} \leqslant 0.$$

However, if the $F_s - h$ relation is plotted for liquid low-molecular-mass surfactants of the type of oleic acid, then the stability condition will also hold for them over a wide range of thicknesses but not for all thicknesses. When a layer of substance constituting a phase is formed on the surface of the support, i.e. $h \to \infty$, then

$$\frac{dF_s}{dh} > 0.$$

For such systems, it is convenient to consider the relation between the free surface energy of the film and the surface tension of the subphase coated by a close-packed monolayer (σ_m).

If the difference

$$\sigma_m - F_s^0 = S_f^0 ,$$

called by Harkins the finite spreading coefficient, is less than zero, then films thicker than the monomolecular film are unstable. In the opposite case ($\sigma_m - F_s^0 > 0$), the formation of a multimolecular film is energetically more favourable.

Evidently, the formulation

$$\sigma_m - F_s = S_f$$

is more general. In this case, the finite spreading coefficient is the limiting value of S_f, i.e. at $h \to \infty$, we have:

$$\lim_{F_s \to F_s^0} S_f = S_f^0$$

All the systems considered by Harkins[41] had $S_f^0 < 0$. In particular, $S_f^0 = -6$ mN m^{-1} for oleic acid on the surface of water. The results obtained for low-molecular-mass surfactants, the behaviour of which in monolayers differs from that of macromolecules, did not provide grounds for their formal transfer to surface layers of high-molecular-mass compounds.

We may also note that, according to the data of Joany and De Gennes,[253] the 'equilibrium thickness of the film deposited on a large area exceeds the monolayer thickness if the spreading coefficient (the initial spreading coefficient is considered) is sufficiently small'. This can be explained by the competition between the long-range forces, which endeavour to keep the film thicker, and spreading. A fairly low spreading coefficient is too weak a source of energy to transfer the molecules to the monolayer. Although these ideas of the above authors[253] refer to the initial spreading coefficient and not to the final one, the essence of the considerations which they express and which were described above does not change.

We now return to Fig. 45. The dashed line corresponds to the value of σ_m for a close-packed PDMS monolayer on the surface of water. The fact that the values of F_s for large thicknesses of the PDMS film (curve *1*) lie below the dashed line (the values of σ_m) indicates the stability of the film for all values of h. Fig. 45 also indicates the value of F_s^0 for PDMS on the surface of water.

We shall now consider the relation between the ability of PDMS to form thin stable films and the surface tension of the subphase.[240] Solutions of dioxane in water were used as the subphase. The values of σ_{AB} were calculated from the wetting angles (θ) for drops of these solutions on the surface of the polymer by the formula

$$\sigma_{AB} = \sigma_A - \sigma_B \cos\theta .$$

The results of the calculations (in mN m^{-1}) are compiled in Table 5, from which it is seen that the film stability condition ($S_f^0 > 0$) holds until the surface tension of the subphase is greater than 58.8 mN m^{-1} (5% solution of dioxane in water). The extremely interesting correlation between the stability of PDMS films and the two-dimensional discs – helices conformational transition is noteworthy: the PDMS films on the liquid surface are stable until there remains a possibility of the retention of the planar conformation, which occurs on subphases with $\sigma_A > 58.8$ mN m^{-1}.

In connection with the stable existence of PDMS films of different thickness on the surface of a liquid, the properties of the transitional region between the monolayer and the bulk state of the polymer were investigated. Fig. 46 illustrates the dependence of the surface pressure, the surface viscosity, and the resistance to the evaporation of water on the thickness of the PDMS film. Despite the high molecular mass of the polymer (1.25×10^6), the viscosity of its film for small thicknesses is low and varies only slightly with increase in thickness. The low values of η_s in the region of low h reflect the structure of the film, which consists of helical molecules, the cohesive interactions between which are weak, while the length of the sections of the chains displaced from

Table 5. The influence of the surface tension of the subphase on the finite spreading coefficient of PDMS.

Dioxane concentration in water (vol.%)	σ_A	σ_{AB}	F_s^0	σ_m	S_f^0
0	72.5	42.5	62.5	66.5	4.0
1	68.7	42.2	62.2	63.7	1.5
2	66.4	41.3	61.3	62.4	1.1
4	64.5	40.3	60.3	61.0	0.7
5	58.8	35.3	55.3	55.0	−0.3
10	55.5	33.0	53.0	52.0	−1.0

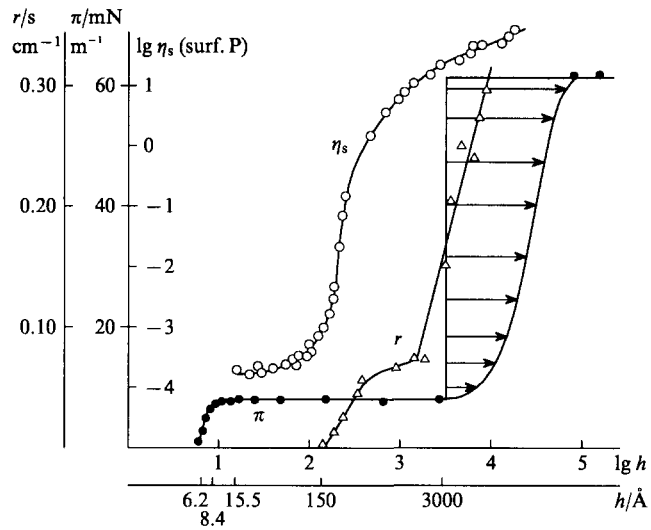


Figure 46. Dependence of the surface pressure (π), surface viscosity (η_s), and the resistance to the evaporation of water (r) on the thickness (h) of PDMS films on the surface of water.[240]

the surface is insufficient for intertwining. The absence of a measureable resistance of the film to the evaporation of water for small film thicknesses confirms this view. For $h = 130 - 150$ Å, the surface viscosity increases sharply and an appreciable increase in the protecting effect of the film against the evaporation of water is observed. This characteristic range of PDMS film thicknesses can be related to the formation of a monolayer from statistic coils. Calculation shows that the diameter of a dense statistical coil for a molecular mass of the polymer of the order of one million is 140 Å. The nature of the variation of lg η_s in the region where $h > 150$ Å shows that the increase in viscosity is caused by the intertwining of the chains of the macromolecules rather than by the increase in the number of layers in the film (in this case, the viscosity would have varied in proportion to the thickness). In the region where $h = 3000$ Å, the film viscosity becomes equal to the bulk viscosity: $\eta_0 = \eta_s/h$. The existence of a critical thickness of the transitional region in thin PDMS films has been confirmed in a study of the flow of the polymer into the pores of nuclear Lavsan ultrafilters.[254]

Starting with $h = 3000$ Å, the surface pressure rises sharply and π begins to depend on the rate of compression. If a load is applied instantaneously to the film perimeter, then π changes abruptly to 62 mN m^{-1} (the Langmuir method), remaining constant on further increase in thickness.[240] The increase in surface pressure in this region cannot be described by the equation

$$\pi = \sigma_A - (\sigma_B + \sigma_{AB}) .$$

Calculation of the correction term for this equation shows that its value (54 mN m^{-1}) is close to that of the thermodynamic work of adhesion of PDMS to water (52 mN m^{-1}). The equation presented above must be rewritten, adding to its right-hand side a correction term equal to the work of adhesion.

Thus there is a transitional region in stable films, the properties of which differ from those of the polymer in bulk, between the monolayer and the PDMS bulk phase on the surface of the liquid. These films, transferred by the Langmuir–Blodgett method onto the surface of mica, have a homogeneous structure according to data obtained by transmission electron microscopy.[52]

On the other hand, recent studies on PDMS monolayers by Brewster angle microscopy have shown[255] that the monolayers on the surface of water have a domain structure also for areas corresponding to the expanded state and to the collapsed film. The relaxation times for the deformation of the domains, agreeing with the extremely low linear tensions of the domain boundaries ($\sim 10^{-13}$ N), have been determined[255] and it has been noted that the relaxation times depend only slightly on the molecular mass of the polymer. This means that the polymer chains are not intertwined on the surface of water and that the interactions between them, determining the viscosity of the monolayer, take place via monomer units. The observed domain structure of the monolayer for large areas does not conflict with the ideas described above. However, the mechanism of the behaviour of the film after the collapse of the monolayer requires further refinement.

The possibility of the formation of stable thin films of polyphenylmethylsiloxane has been discussed[256] in connection with the unusual temperature variation of the surface pressure of its oligomers (Fig. 47). For the monolayer of a polymer with a molecular mass of 2240, π diminishes with increase in temperature and at 37 °C becomes zero. A similar trend has been observed for a polymer with a lower molecular mass and also for the temperature variation of the equilibrium spreading pressure. In the latter case, $\pi = 0$ at 55 °C. Such behaviour of the systems can be accounted for by the decrease in the initial spreading coefficient with increase in temperature, leading to the formation of stable thin films on the surface of a liquid.

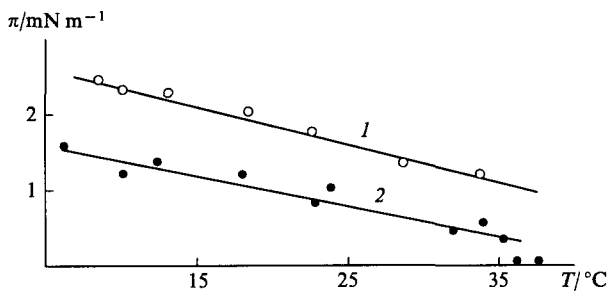


Figure 47. Temperature variation of the surface pressure of oligophenylmethylsiloxanes for a monolayer area of 11 Å^2 per residue.[256] Molecular mass: (*1*) 1470; (*2*) 2240.

c. Monolayers of certain other polyorganosiloxanes

The replacement of the methyl groups in PDMS by ethyl or phenyl groups weakens appreciably the ability of these polymers to form stable monolayers on the surface of water.[52] On the other hand, ladder polymers—polyphenylsilsesquioxane and polyethylsilsesquioxane—form stable viscous monolayers with high collapse pressures. For example, the collapse pressure for polyethylsilsesquioxane is higher by a factor of four than for PDMS.

The acid groups $(CH_2)_{10}COOH$ introduced into the side chains of polydimethylsiloxane and polyhydromethylsiloxane promote an increase in the surface activity of the polymers and in the collapse pressure (>30 mN m^{-1}). The monolayers are transferred quantitatively onto solid supports by the Langmuir–Blodgett method. Analysis of the electrical properties of alternating LBF of these polymers and eicosylamine showed that they are promising for use in pyroelectric devices.[257]

Monolayers of rod-shaped siloxane polymers—phthalocyaninatosiloxanes **30**—have been investigated.[258–261]

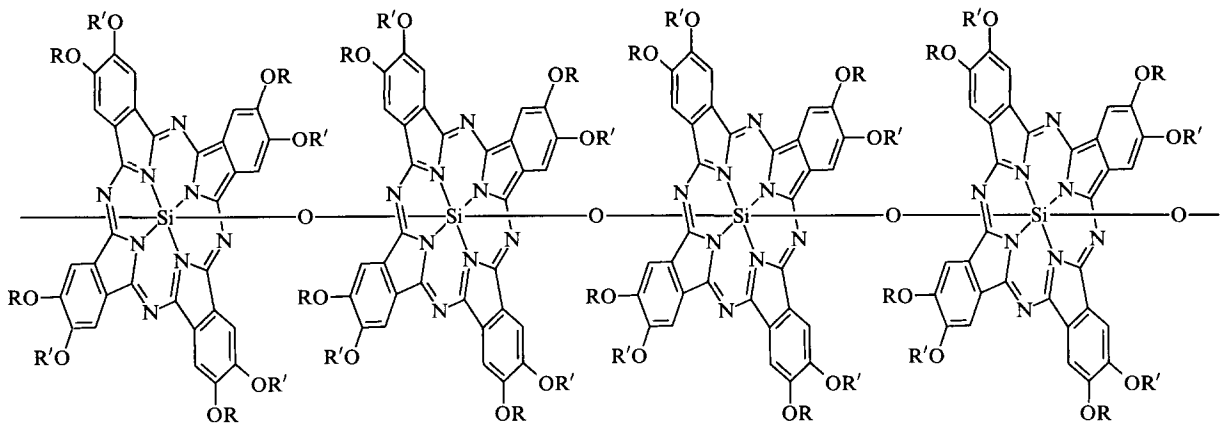
On compression of monolayers of polymer **30** with R = CH_3 and R′ = $(CH_2)_7CH_3$, the cylindrical molecules undergo a reorientation from the horizontal to the vertical position. The interactions between the polymer molecules and the aqueous subphase, which are responsible for the high stability of the monolayers, have been discussed resorting to ideas concerning the polarisation of the central aromatic nucleus, the proton exchange between the subphase and the monolayer, and the oxidation-reduction activity of the phthalocyanine group.[259] The way in which the molecules of compound **30**, containing unsaturated bonds in the peripheral chains, undergo reorientation changes on compression of the monolayer. In this case, the molecules creep onto one another, retaining the orientation parallel to the subphase. The process involving the aggregation of the molecules to microcrystallites has been investigated by transmission electron microscopy for monolayers having different areas transferred onto a carbon support by the Langmuir–Schaefer method.[261]

The diblock copolymers of dimethylsiloxane with methyl methacrylate and bisphenol A carbonate have been investigated in monolayers on the surface of water.[262,263] In both cases, blocks of the second type exert a condensing effect on the PDMS monolayers. It is of interest that the compression isotherms for the block copolymer and the mixed monolayer of the homopolymers (PDMS and PMMA) do not differ greatly from one another but do differ significantly in shape from the additive curve and deviate from the latter.[30] Analysis of the behaviour of binary mixed monolayers of PDMS and polymethylphenylsiloxane with oleic acid showed that the reconstruction of the surfactant monolayer in the presence of the polymer increases the collapse pressure.[264] For mixed monolayers of PDMS with palmitic acid and cetyl alcohol, this effect is manifested to a much lesser extent.[265]

Thus monolayers of polyorganosiloxanes possess a series of interesting features. Despite the low collapse pressure, the PDMS monolayers are stable on the surface of water. An increase in the length of the side chains in polyorganosiloxanes does not lead to the formation of more expanded monolayers and to an increase in the collapse pressure, in contrast to the acrylic and methacrylic polymers. The conversion of the PDMS macromolecules into the helical form, which can be regulated by varying the area of the monolayer or the surface energy of the subphase, is an important structural transition, the dynamics of which require detailed analysis. Polydimethylsiloxane forms stable thin films on the surface of a liquid. Questions concerning the transfer of these films onto solid supports and the study of their structure and properties have not so far been investigated.

Ladder polymers and functionalised polyorganosiloxanes form stable monolayers with high collapse pressures. The properties of the monolayers of these polymers depend to a large extent on the substituents in the side chain.

The nontoxicity and thermal stability of polyorganosiloxanes as well as the large set of functionalised polymers of this class[266] give rise to the hope that they will be investigated more vigorously in monolayers and LBF.

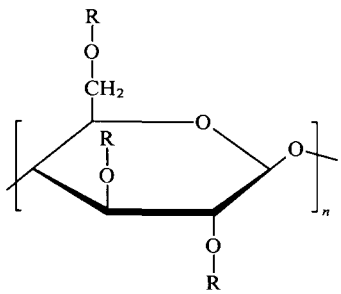


30

R = CH_3, R′ = $(CH_2)_7CH3$; R = CH_3, R′ = $(CH_2)_6CH=CH_2$.

XI. Polysaccharides

Cellulose ethers and esters are classical objects with which systematic studies on polymer monolayers began. It has been shown[267] that cellulose acetate **31a** (n = 0) does not form a stable monomolecular film on the surface of water but a monolayer is formed on the siloxane – water interface, its limiting area corresponding to the model in which the average plane of the glucose rings is arranged parallel to the surface. The influence of molecular mass on the compression isotherms for cellulose acetate has been studied.[33] Despite the fact that the limiting areas of the monolayers of three different fractions of cellulose triacetate were only $^1/_7-^1/_{10}$ of the values of A_0 specified by the high-molecular-mass model, the authors[33] calculated their molecular masses from the $\pi A-\pi$ relations. The molecular masses extrapolated from the region of low π were 3–6 times greater than the control values (57000, 45000, and 29000), while on extrapolation from the region π = 2–6 mN m^{-1} the molecular masses of the first two fractions proved to be close to the control values. The authors explained the better agreement in the latter case by the fact that, in contrast to a domain monolayer (for low values of π), in a dense monolayer account is taken of the contribution of the vibrational motions of the macromolecules to π.



31a: R = $-\overset{\overset{O}{\|}}{C}-(CH_2)_nCH_3$

31b: R = $-(CH_2)_3-OH$.

31c: R = $-(CH_2)_2-OH$.

31a–c

Recently this problem again attracted attention as a result of a study[268] in which monolayers and adsorption layers of hydroxypropylcellulose **31b** with molecular masses of 60000, 100000, 300000, and 1000000 and of hydroxyethylcellulose **31c** with molecular masses of 100000 and 900000 were investigated. Fig. 48 presents the dependence of the surface pressures of the monolayers of these polymers on the monolayer concentration. The molecular mass does not affect the compression isotherms for both polymers, while an increase in the length of the side chain by one CH_2 group increases the value of π corresponding to the plateau from 7 mN m^{-1} for compound **31c** to 28 mN m^{-1} for compound **31b**. It is of interest to note that this plateau is

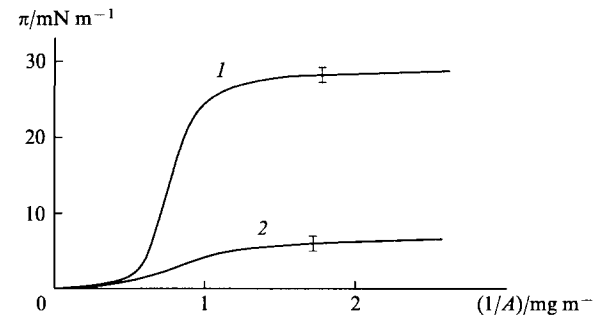


Figure 48. Dependence of the surface pressure (π) on the surface concentration ($1/A$) of monolayers of hydroxypropylcellulose (curve *1*) and hydroxyethylcellulose (curve *2*) specimens with different molecular masses, obtained by spreading from a solution at 25 °C.[268]

reproduced also for adsorption layers of polymers: after a change in concentration by a factor of 300–600, the surface pressure changes by not more than 5%. According to light scattering data, the viscoelastic properties of the monolayers and adsorption layers are also identical.

The importance of these results consist in the fact that they apparently demonstrated clearly for the first time the similarity of the structures and properties of polymers in monolayers obtained by a forced organisation procedure (compression) and in self-organised adsorption layers on the surface of water.

The compression isotherms for cellulose ethers (esters) with different lengths and numbers of side chains are presented in Fig. 49.[269,270] Cellulose triacetate **31a** (n = 0) and cellulose tripalmitate **31a** (n = 14) form condensed monolayers. The limiting area of cellulose triacetate (54 Å^2 per residue) is greater than the value 40–48 Å^2 per residue obtained by Zografi and coworkers[58,268] but is smaller than for compounds **31b** (119 Å^2 per residue) and **31c** (137 Å^2 per residue).[271] For ester groups of moderate length [in the trioctanoate **31a** (n = 6), tridecanoate **31a** (n = 8), and trilaurate **31a** (n = 10)], the liquid-expanded state obtains. The transition from this state to the condensed state is characterised by the constancy of the surface pressure. Monolayers of diesters (cellulose dilaurate) are more compressible and have smaller areas in the expanded and condensed states compared with the triester analogues (Fig. 49, curve *5*). The increase in secondary cohesion in the monolayer with increase in the length of the side chain to 16 carbon atoms (cellulose tripalmitate) leads to the formation of a condensed monolayer in which the glucose residues are arranged parallel to the surface of water, while the hydrocarbon chains are

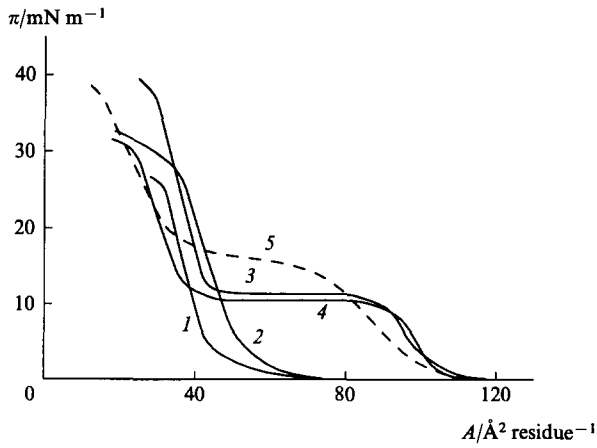


Figure 49. Compression isotherms for the triesters (curves *1*–*4*) and diester (curve *5*) of cellulose **31a**.[269] *n*: (*1*) 0; (*2*) 14; (*3*) and (*5*) 10; (*4*) 6 and 8.

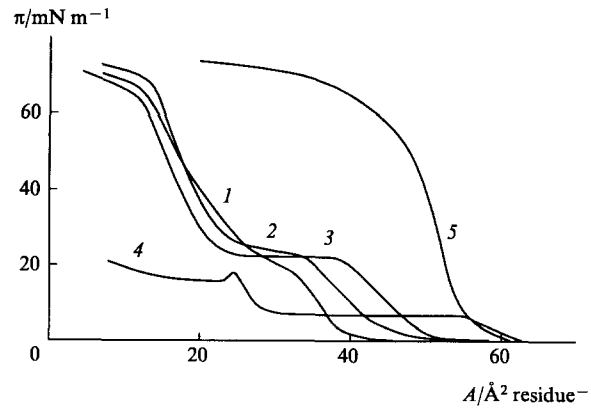


Figure 50. Compression isotherms for amylose esters at 24 °C:[273] (*1*) acetate; (*2*) propionate; (*3*) butyrate; (*4*) laurate; (*5*) palmitate.

arranged perpendicular to the surface of the subphase. Cellulose trioctadecanoate forms a condensed monolayer with a limiting area of 71 Å^2 per residue.[272]

The LBF films of cellulose esters are formed by the horizontal transfer method. X type cellulose trilaurate films with up to 60 layers have been obtained[269] from both expanded (9.5 mN m^{-1}) and condensed (20 mN m^{-1}) regions of the monolayer. Although the authors note that the cellulose trilaurate monolayers were too brittle to be transferred onto a solid support, in another study[272] it proved possible to obtain 10-layer Y type LBF from cellulose trioctadecanoate with even longer chains (horizontal transfer). For LBF of the same polymers into the side chains of which pyrene labels had been introduced, it was shown by fluorescence analysis that energy transfer or the formation of excimers within or between the layers are not observed in films containing up to 7% (percentage substitution of the side groups) of the label. This is associated with the fact that the thickness of the layers (24 Å) is smaller than the Forster radius between the pyrenyl groups localised in the middle part of the LBF layers. If the concentration of the pyrenyl fragments exceeds 7%, then the formation of two types of excimers with different structures and emission times can be detected by time-resolved fluorescence spectroscopy.

The change in the β-structure of the elementary unit of cellulose to the α-glucoside structure leads to amylose derivatives. Extensive studies on amylose esters have been carried out.[273] Monolayers and LBF of amylose acetate, propionate, butyrate, laurate, and palmitate were investigated. The compression isotherms for these polymers up to a degree of substitution in excess of 2.6 are presented in Fig. 50. It is seen that polymers with short, moderately long, and long side chains correspond to three types of isotherms. For short-chain derivatives, neither the temperature (10–37 °C) nor the rate of compression of the monolayer (1–10Å^2 per residue per minute) affect the compression isotherms in the region $\pi \leqslant 10$ mN m^{-1}. Comparison of model and experimental areas per elementary unit and also allowance for data[274] on the crystal structures of the homologous series of amylose esters led the authors[273] to the conclusion that mono-layers comprising helices are formed by short-chain amylose esters. In the region of the plateau, there is a transition from the helical monolayer to a bilayer. Unfortunately, the bilayers decompose on transfer of the film to a solid support and it was therefore not possible to determine their structural parameters.

An amylose ester with side chains of moderate length (laurate) also formed layers comprising helices on the surface of water. Finally, amylose palmitate, the long side chains of which are capable of crystallising, formed a true monolayer with a vertical disposition of the hydrocarbon chains.

Thus the properties of amylose ester monolayers with short side chains are determined by the conformation of the main chain, while those of the compounds with ester alkyl groups of moderate and great lengths are determined by the side chains. Comparison of the data in Figs 49 and 50 for monolayers of isotypical cellulose and amylose esters shows that both series of derivatives form expanded and condensed monolayers, but in the case of amylose esters the isotherms are displaced towards smaller areas.

Furthermore, in contrast to LBF of cellulose esters, those of amylose ester (up to 50 monolayers) can be obtained on solid hydrophobic surfaces by the vertical transfer method. In the case of amylose triacetate molecules, *Z*-layers are then formed whereas *Y*-layers are produced for other homologues. Amylose palmitate can be transferred only from the liquid state, the product being disubstituted derivatives. The arrangements of the LBF comprising monolayers of amylose esters with short and long side chains are compared in Fig. 51. These arrangements were obtained on the basis of polarisation IR spectroscopic, X-ray diffraction, and ellipsometric studies.[273]

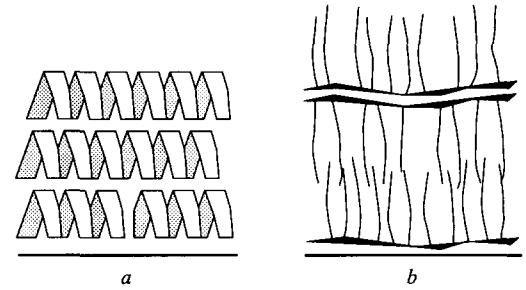


Figure 51. Schematic illustration of the arrangement of LBF of amylose esters with short (*a*) and long (*b*) side chains.[273]

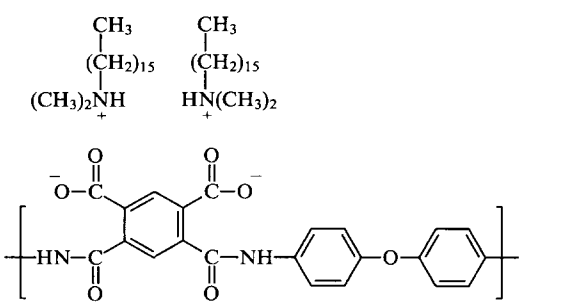
It has been suggested that amylose triacetate monolayers be used[275] as matrix layers for the immobilisation of a chromophore—the active element in a nonlinear optical system. A specially synthesised dye, the ester of palmitic acid and 4-nitro-4′(3R-hydroxypyrrolidino)-1,1′-azobisbenzene, does not afford at 23 °C stable monolayers on the surface of water suitable for use in LBF. Mixed monolayers of the dye and amylose triacetate are stable for a high dye content (up to 50%) and can be transferred onto solid supports by the horizontal and vertical methods. The mixed monolayers consist of amylose acetate domains and two-dimensional dye crystallites. The interfaces between the two types of structures play an appreciable role in increasing the stability of the monolayers. It is of interest that the

stabilisation of monolayers of the above dye by the formation of its mixed monolayers with other amylose esters cannot be achieved. On heating the LBF above the melting point of the dye (129 °C) and subsequent cooling to room temperature, the layered structure becomes more pronounced and virtually all the dye molecules are arranged in hydrogen-bonded aggregates.[276]

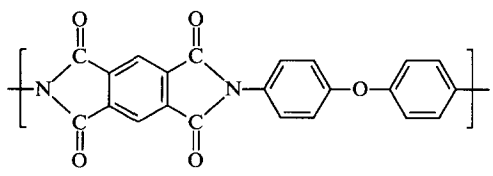
Thus, in relation to esters of cellulose and amylose, it is possible to follow the evolution of views on monolayers of these polymers and to demonstrate yet again the existence of discrepancies between data obtained by different workers in the study of identical polymers. The most interesting results presented in this section are the differences in the behaviour of monolayers of identical cellulose and amylose esters differing only in the configuration of the junctions between the glucose units and the similarity of the properties of monolayers of hydroxyalkyl derivatives of cellulose formed by spreading from solution and by adsorption from the subphase.

XII. Polyimides

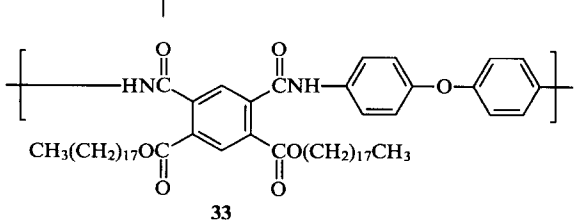
The effective dielectric and mechanical characteristics and the chemical and mechanical stabilities of polyimides have led to their extensive application in various branches of engineering and primarily in electronics.[277] The minimum thickness of films of polyimides obtained on a rotating support from solutions of a polyamidoacid with subsequent thermal or chemical conversion into the imide form is 25 Å.[278] Polymer films with a thickness from 4–6 to 1000 Å can be obtained with the aid of monolayers and LBF. Owing to the insolubility of polyimides in organic solvents, the LBF are formed in several stages. Monolayers of the alkylammonium salt of the polyamidoacid **32** or its long-chain ester **33** are obtained initially on the surface of water. After their transfer to a solid support, they are converted into the imide form by the thermal (~300 °C) or chemical (with a mixture of acetic anhydride and pyridine) methods. LBF of poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] **34** have been investigated most fully.[279–284]



32



34



33

The salt **32** forms stable monolayers of the liquid-expanded type on the surface of water. The limiting area of the monolayer (138 Å^2 per residue) agrees well with the area calculated from a model,[279] while the thickness of one layer, found ellipsometrically for a 50-layer LBF, is 16.5 Å.[285] The quantitative transfer of the polyamidoacid onto the solid support (Z type LBF) is indicated by the degree of transfer, which is unity, and also by the linearity of the dependences of the optical absorption and the reciprocal of the capacity on the LBF thickness. According to IR spectroscopic data for 200-layer LBF, the chemical imide formation process goes virtually to completion and aliphatic products are eliminated from the film. After this, the thickness of a single polyimide monolayer is 4 Å.[279]

The imide formation process depends on the type of the ammonium component of the salt, on the solvent in which the imide formation is carried out, and on the support on which it takes place. It has been shown with the aid of a piezoquartz microbalance that higher-quality Y type LBF are formed when *N*,*N*-dimethyloctadecylamine is used instead of *N*-octadecylpyrrolidine. The initial rate of imide formation, carried out using acetic anhydride and pyridine, is higher in hexane than in benzene, but the conversion is more complete in the latter.[286]

The structure and conformation of the main chain, the number of hydrophobic side chains, and the way in which they are attached to the main chain exert a significant influence on the arrangement of the molecules in the LBF. In particular, the presence of only one hydrocarbon chain in the unit does not allow the formation of an ordered LBF from the polyimide, while two hydrophobic chains attached to different parts of the polymer unit increase the capacity of the polymer for being ordered so much that the layered structure of the polyimide persists also on deposition of the polyamidoacid salt by casting from solution.[287] The influence of the chemical structure and of the flexibility of the main chain of the polyimide on the properties of the LBF has also been investigated by Nishikata et al.[288] LBF of the polyimide **34**, having a zigzag configuration, and also of a rigid linear polyimide containing the phenylenediamine group instead of the oxydianiline group have been investigated by scanning tunnelling microscopy (STM).[281–283,289] Individual polymer chains and their fragments were identified with the aid of STM. The LBF of both polyimides have an ordered structure. The geometrical parameters of the film structure on the surface of highly oriented pyrolytic graphite, evaluated with the aid of STM, agree with data on the orientation of the molecules and their fragments obtained by the molecular dynamics method[289] and EXAFS spectroscopy.[283]

Interesting data concerning the influence of the nature of the support and of the thickness of the LBF on the degree of imide formation have been published.[290] The authors established that the first monolayer of the octadecylammonium salt of the polyamidoacid interacts chemically with the surface of silicon and its molecules are not involved in the imide formation process. According to X-ray electron spectroscopy, the degree of conversion is fairly high in thicker three- and five-layer LBF, although alkyl chains still remain in the film up to 300 °C (annealing for 15 min *in vacuo*). The inhibition of imide formation in thin films of the polyamidoacid, obtained from solution on the surface of nickel and chromium, has been explained by the intense adhesion interactions between the carboxy-groups and the surface. The SiO_2 surface does not hinder the imide formation reaction.[278]

The disordered arrangement of the alkylammonium hydrocarbon chains of the polyamidoacid salt in the LBF and also the retention of these chains in the film at high annealing temperatures[290] are closely related to the question of the defectiveness of the polyimide films arising as a result of the removal of the initial hydrocarbon components. These problems are of key importance in the preparation of high-quality polyimide LBF and require further study.

The change in the orientation of the hydrocarbon chains in the monolayer of the dimethyloctadecylammonium salt of the polyamidoacid has been investigated[291] by the method based on the measurement of the displacement current generated on compression of the monolayer.[292,293] Fig. 52 presents the dependence of the surface pressure, the displacement current, and the dipole moment calculated[294] with its aid on the area of the polyamidoacid salt monolayer. Two peaks may be identified on the $I-A$ relation: one in the region of zero surface pressure and the other in the region of increasing π. With increase in the first peak in I, the dipole moment also increases. Both displacement current peaks can be accounted for by condensation of the polymer molecules in the monolayer.

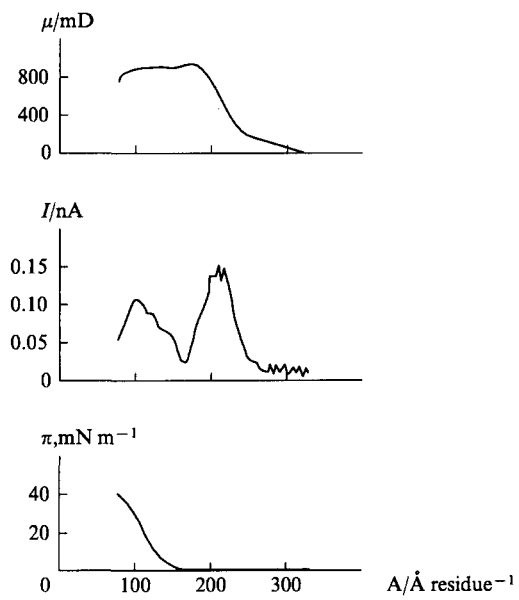


Figure 52. Dependence of the dipole moment (μ), the displacement current (I), and the surface pressure (π) on the area of a monolayer of an alkylammonium salt of a polyamidoacid on the surface of water.[291]

The photoinduced molecular 'switching' in monolayers of the polyamidoacid salt containing the azobenzene group instead of the phenoxyphenyl group has been detected from measurements of the displacement current.[259–297] It was established from molecular spectroscopic data that, on irradiation of the monolayer with UV light (λ_1 = 380 nm), the *trans–cis* isomerisation of the azobenzene group is observed, while on subsequent irradiation with visible light (λ_2 = 450 nm) the reverse *cis–trans* transition occurs. Fig. 53 presents the time variation of the displacement current and of the charge generated for the monolayer on the surface of water. It is seen that the photoisomerisation induces a sharp alteration of the displacement current. The absence of a displacement on irradiation of the monolayer with visible light alone shows that the current is generated precisely by the *trans–cis* isomerisation. Single-layer LBF of the same polyamidoacid salt deposited onto a mixed indium oxide–tin oxide electrode behave similarly.[298] Evidently these results are likely to find a practical application in molecular electronics.

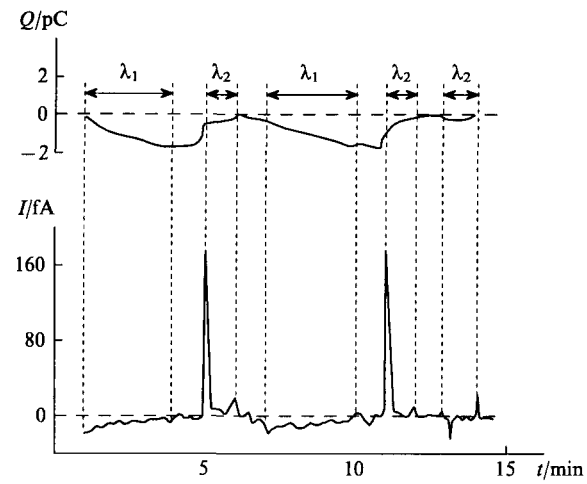


Figure 53. Time variation of the displacement current (I) and the charge (Q) for a monolayer of an alkylammonium salt of a polyamidoacid, containing azobenzene groups, on the surface of water.[295] The time intervals during which the specimen was irradiated with light at wavelengths of 380 nm (λ_1) and 450 nm (λ_2) are indicated.

A design has been proposed for a three-layer photodiode, each layer of which is a polyimide LBF.[299] The donor layer (D) consists of a polyimide containing triphenylamine groups. The sensitiser layer (S) incorporates tetraphenylporphyrin groups. The polyimide **34** LBF was used as the acceptor layer (A). Two types of photodiodes, differing in the position of the layers relative to a semitransparent gold electrode (E), were formed: E/D/S/A and E/A/S/D. The principle of the operation of such photodiodes is as follows: on irradiation with light, the excited electrons are transferred from the sensitiser layer S to the acceptor layer A; the electron deficiency in the S layer is made good from the donor D layer. Z Type LBF were formed in each layer in conformity with the procedure described above, i.e. from monolayers of polyamidoacid salts with subsequent chemical conversion into the imide form. The number of monolayers in each LBF was varied from 0 to 12. It was established that, on irradiation with monochromatic light at a wavelength of 430 nm, cathodic and anodic currents are generated in the photodiodes of the first and second types respectively. With increase in the number of monolayers in each LBF, the current also increases but that for the D layer reaches saturation while the current for the S and A layers passes through a maximum. On the basis of these data as well as the quantum yields, it was concluded that the D layer exhibits a high hole mobility and that the electron mobilities are low in the S and A layers.

LBF comprising the salt of a polyamidoacid based on pyromellitic dianhydride and bis(4-aminophenyl)tetramethyldisilane can be used as positive resists.[300] The quality of the LBF then depends significantly on the type of alkylamine used to obtain the polyamidoacid salt. Among the four dialkylamines selected for this purpose, a high-quality Y type LBF, containing 101 monolayers, could be formed only with *N*-eicosylpyrrolidine. With the aid of the three other alkylamines (*N,N*-dimethyloctadecylamine, *N*-octadecylpyrrolidine, and *N*-octadecylmorpholine), it is possible to obtain LBF the thickness of which does not exceed ten monolayers. After chemical or thermal conversion into the imide form, the LBF were irradiated with UV light through a photomask and were then treated in a mixture of organic solvents. The irradiated sections of the LBF were fully removed, whereas the polyimide on the covered sections of the LBF did not swell and did not dissolve. The use of such a LBF as a positive resist makes it possible to obtain a lithographic picture with a resolution of 0.25 μm.

The polyamidoacid ester **33** has also been used for photolithographic purposes.[301] A 31-layer LBF comprising mixed 1 : 1 monolayers of compound **33** and stearyl alcohol was formed on a silicon surface which had been rendered hydrophilic. The image was created by irradiating the LBF with UV light (254 nm) through a template followed by treatment in 2% KOH solution. The sensitivity, contrast, and resolution of the positive resist were 3.5 J cm^{-2}, 5.5, and 0.4 μm respectively. A characteristic feature of this resist is a low rate of etching in a CF_4/O_2 plasma and a high thermal stability (400 °C). The rates of etching of the LBF and of the silicon support were 1 and 350 nm min^{-1}. The high resistance of the polyamidoacid ester to etching can be accounted for by the presence of aromatic groups in the polymer and the perfection of the LBF structure. Unfortunately, Uekita et al.[301] do not consider the influence of stearyl alcohol, which may be washed out of the LBF on treatment in the liquid and may be desorbed during heat treatment. This should result in an increase in the effectiveness of the LBF and in the impairment of its structure.

Polyimide LBF are used as orienting layers in liquid crystal cells.[302,303] In this case, the liquid crystals are oriented parallel to the direction of transfer of the monolayers from the surface of water onto the supporting surfaces of the cells; rubbing of the film is not then required.

A combination of conducting and orienting properties has been achieved recently on pyrolysed polyimide LBF based on biphenyl dianhydride [biphenyldicarboxylic acid dianhydride? (Translator)] and oxydianiline.[304,305] The pyrolysis of the 31-layer Y type LBF was carried out under a nitrogen atmosphere for 60 min. Fig. 54 illustrates the dependence of the conductivity of the specimens obtained on the pyrolysis temperature. The sharpest increase in conductivity is observed for specimens obtained in the temperature range up to 800 °C. At 1000 °C, the conductivity of the LBF reaches 120 S cm^{-1}. The orienting properties of the films obtained were determined in a liquid crystal cell, arranging the supporting surfaces in such a way that the directions of transfer of the monolayers on them made an angle of 90° ('twist' structure). The cell was filled with a nematic liquid crystal and the optical and electrooptical properties of the system were analysed with the aid of a polarisation microscope. Fig. 55 presents the dependence of the transmittance on the angle between the analyser and the polariser for the twisted nematic structure in liquid crystal cells with supporting surfaces in the form of untreated quartz plates, a rubbed polyimide film, and a pyrolysed polyimide LBF. It is seen that the pyrolysed and rubbed polyimide films have similar orientation properties. However, the mechanism of the orienting effect of the pyrolysed LBF still remains obscure, since, according to polarisation optical spectroscopic data, the film has no planar anisotropy.[304]

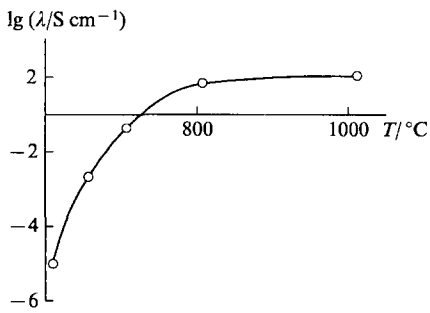


Figure 54. Dependence of the conductivity of specimens of pyrolysed polyimide LBF on the pyrolysis temperature.[305]

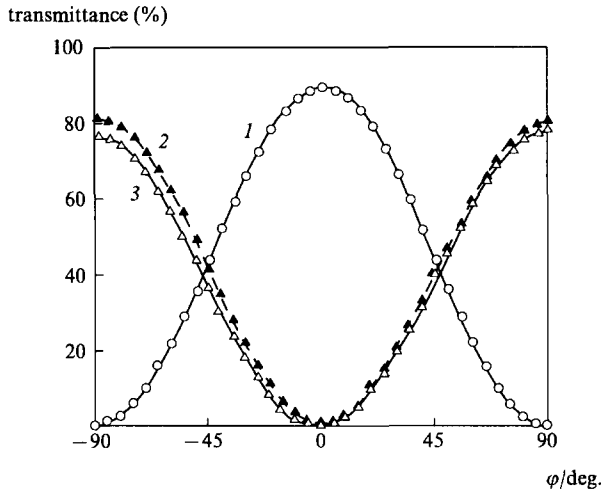


Figure 55. Dependence of the transmittance on the angle between the analyser and the polariser (φ) for a twisted nematic structure in liquid crystal cells with supporting surfaces in the form of untreated quartz plates (curve *1*), a rubbed polyimide film (curve *2*), and a pyrolysed polyimide LBF (curve *3*).[304]

The electrooptical properties of two liquid crystal cells with supporting surfaces comprising pyrolysed LBF and rubbed polyimide film are presented in Fig. 56. Both cells have similar characteristics. The response times to the switching on and switching off of an alternating potential are respectively 200 and 200 ms for the pyrolysed polyimide LBF and 100 and 200 ms for the rubbed film. Consequently, pyrolysed polyimide LBF can be used as more effective orienting layers and transparent electrodes in liquid crystal cells and also in ferroelectric liquid crystal cells.[304,306]

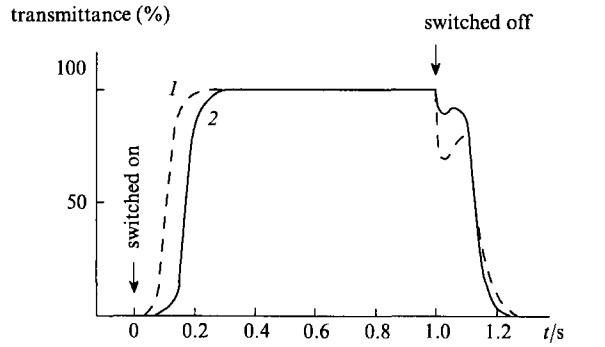


Figure 56. The electrooptical properties of a twisted nematic structure in liquid crystal cells with supporting surfaces comprising a rubbed polyimide film (curve *1*) and a pyrolysed polyimide LBF (curve *2*).[304]

Thus the possibility of obtaining insoluble polymer LBF has been demonstrated in relation to polyimides. In contrast to insoluble polymer LBF obtained by polymerising monomer and oligomer monolayers on a solid support, in the present instance the polymer retains the degree of polymerisation of the prepolymer — the polyamidoacid salt or ester. The imide formation process and the arrangement and quality of the LBF obtained depend on the type of amine component of the polymeric acid, on the solvent in which the chemical imide formation is carried out, and on the nature of the solid support.

The photoswitching effect, based on the *trans – cis* isomerisation of the chromophoric fragment of the main chain, can be achieved with the aid of LBF comprising polyimides containing the azobenzene group. There are also prospects for the application of polyimide LBF as positive photoresists, photodiodes, and orienting layers in liquid crystal cells.

XIII. Conclusion

On the basis of the above analysis of the behaviour of polymer monolayers and LBF, it is possible to arrive at general conclusions concerning the present state of this field of study and the trends in its development.

Among the theoretical aspects, questions concerning the two-dimensional state of macromolecules and the phase and structural transitions in systems with a reduced dimensionality are of greatest current interest. Unfortunately, it must be admitted that there has been no appreciable progress in the study of these fundamental problems of the two-dimensional state of macromolecules. The experimental studies on homopolymer and copolymer monolayers and mixed monolayers comprising polymers and low-molecular-mass compounds are developing more successfully. These involve the investigation of the packing of macromolecules on the surface of a liquid and the influence of the size and orientation of the side groups on the state of the monolayers, the elucidation of the structural correspondence between the components of the mixed monolayers, and the determination of the stability of monomolecular films. However, whereas previously these studies, traditional for monolayers, were of independent character and were sufficiently detailed, in recent years they have played an auxiliary role in most cases and reduce to the determination of the compression isotherms as an essential stage in the formation of LBF. Specific conclusions for each type of polymers considered, based on the results of these investigations, were presented in the appropriate sections of the review. These also contain information about the prospects for the practical employment of polymer LBF. The use of polymer LBF is based, as in the case of LBF comprising low-molecular-mass compounds, on the possibility of assembling multilayer planar structures with a controllable film thickness and orientation of the molecules in layers. Together with the independent role of functionalised polymer LBF in molecular devices, they can be used as matrices for the immobilisation of low-molecular-mass compounds (necessarily diphilic) carrying a specified physical function.

In order to realise these possibilities, it is essential to carry out extensive studies on polymer monomers and LBF, among which the following are of greatest current interest: the determination of the viscoelastic and relaxation properties of polymer monolayers, the establishment of criteria for the preparation of LBF of a specified type, the study of the structural-chemical correlations in the arrangement of monolayers on liquid and solid surfaces.

In conclusion we may note that the studies on monolayers and LBF are not restricted to the objects considered in the present review. Other polymers, the properties of the monolayers and LBF of which the author proposes to consider in subsequent publications, will include conducting high-molecular-mass compounds, water-soluble ionogenic polymers, and certain other functionalised polymers.

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References

1. J-M Lehn *Angew. Chem., Int. Ed. Engl.* **27** 89 (1988)
2. R Maoz, J Sagiv *J. Colloid Interface Sci.* **100** 465 (1984)
3. J Gun, J Sagiv *J. Colloid Interface Sci.* **102** 457 (1986)
4. D L Allara, R G Nuzzo *Langmuir* **1** 45 (1985)
5. D L Allara, S V Atre, C A Elliger, R G Snyder *J. Am. Chem. Soc.* **113** 1852 (1991)
6. R G Nuzzo, D L Allara, F A Fusco *J. Am. Chem. Soc.* **109** 2358 (1987)
7. E B Troughton, C D Bain, G M Whitesides, R G Nuzzo, D L Allara, M D Porter *Langmuir* **4** 365 (1988)
8. C D Bain, E B Troughton, Y T Tao, J Evall, G M Whitesides, R G Nuzzo *J. Am. Chem. Soc.* **111** 321 (1989)
9. M A Bryant, J E Pemberton *J. Am. Chem. Soc.* **113** 3629 (1991)
10. P Laibinis, G M Whitesides, A N Parikh, Y T Tao, D L Allara, R G Nuzzo *J. Am. Chem. Soc.* **113** 7152 (1991)
11. D M Collard, M A Fox *Langmuir* **7** 1192 (1991)
12. P E Laibinis, J J Hickman, M S Wrighton, G M Whitesides *Science* **245** 845 (1989)
13. M H Möhwald *Angew. Chem.* **100** 750 (1989)
14. M G Mneyan *Fizika Mashinnoi Pamyati* (The Physics of Machine Memory) (Moscow: Vysshaya Shkola, 1990)
15. J F Nagle, D A Pink *Can. J. Biochem. Cell. Biol.* **62** 760 (1984)
16. J F Nagle *Annu. Rev. Phys. Chem.* **31** 157 (1980)
17. V V Arslanov *Usp. Khim.* **60** 1155 (1991) [*Russ. Chem. Rev.* **60** 584 (1991)]
18. H Devaux *C. R. Hebd. Seances Acad. Sci.* **201** 109 (1935)
19. J R Katz, P J P Samwel *Liebigs Ann. Chem.* (472) 241; (474) 296 (1929)
20. N K Adam *Trans. Faraday Soc.* **29** 90 (1933)
21. S E Sheppard, R L Keeman *Nature (London)* **121** 938 (1928)
22. J R Katz, P J P Samwel *Naturwissenschaften* **16** 592 (1928)
23. S A Moss *J. Am. Chem. Soc.* **56** 41 (1934)
24. W D Harkins, E F Carman, H F Ries *J. Chem. Phys.* **3** 692 (1935)
25. D J Crisp *J. Colloid. Sci.* **1** 49 (1946)
26. D J Crisp *Surface Phenomena in Chemistry and Biology* (London: Pergamon Press, 1958)
27. H C Saraswat, A Kalyanasundaram *J. Polym. Sci.* **7** 325 (1951)
28. Y S Obeng, A J Bard *J. Am. Chem. Soc.* **113** 279 (1991)
29. T Nakamura, H Tachibana, M Yumura, M Matsumoto, R Azumi, M Tanaka, Y Kawabata *Langmuir* **8** 4 (1992)
30. G L Gaines, Jr *Langmuir* **7** 834 (1991)
31. A Pokels *Nature (London)* **46** 418 (1892); **48** 152 (1893)
32. V A Ogarev, V V Arslanov, A A Trapeznikov *Izv. Akad. Nauk SSSR, Ser. Khim.* **9** 1960 (1972)
33. J Parker, J L Shereshefsky *J. Phys. Chem.* **58** 850 (1954)
34. P G De Gennes *Scaling Concepts in Polymer Physics* (New York: Cornell Univ. Press, 1979)
35. T M Birshtein, O V Borisov, A A Mercurieva, E B Zhulina *Prog. Colloid Polym. Sci.* **85** 38 (1991)
36. R Aveyard, B P Binks, N Carr, A W Cross *Thin Solid Films* **188** 361 (1990)
37. R D Smith, J C Berg *J. Colloid Interface Sci.* **74** 273 (1980)
38. B A Pethica *Thin Solid Films* **152** 3 (1987)
39. W Retting, F Kuschel *J. Colloid Interface Sci.* **140** 169 (1990)
40. M Iwahashi, N Maehara, Y Kaneko, S R Middleton, N R Pallas, B A Pethica *J. Chem. Soc., Faraday Trans. 1* **81** 973 (1985)
41. W D Harkins *The Physical Chemistry of Surface Films* (New York: Reinhold, 1952)
42. N K Adam *Physics and Chemistry of Surfaces* (Translated into Russian; Moscow, Leningrad: Gostekhizdat, 1947)
43. G L Gaines, Jr *Insoluble Monolayers at Liquid-Gas Interfaces* (London: Interscience , 1966)
44. Y M Hifeda, G W Rayfield *J. Colloid Interface Sci.* **104** 209 (1985)
45. N R Pallas, B A Pethica *Langmuir* **1** 509 (1985)
46. S R Middleton, M Iwahashi, N R Pallas, B A Pethica *Proc. R. Soc. London, A. Math. Phys. Sci.* **396** 143 (1984)
47. N R Pallas, B A Pethica *J. Chem. Soc., Faraday Trans. 1* **83** 585 (1987)
48. Y M Hifeda, G W Rayfield *Langmuir* **8** 197 (1992)
49. O Albrecht *Thin Solid Films* **178** 93 (1989)
50. A A Trapeznikov *Zh. Fiz. Khim.* **20** 61 (1946)

51. A A Trapeznikov, Doctoral Thesis in Chemical Sciences, Institute of Chemical Physics, Academy of Sciences, Moscow, 1955
52. V V Arslanov, Candidate Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1973
53. H Huehnerfuss *J. Colloid Interface Sci.* **107** 84 (1985)
54. K Helperin, J B Ketterson, P Dutta *Langmuir* **5** 161 (1989)
55. A G Bois *J. Colloid Interface Sci.* **105** 124 (1985)
56. T Kato *Langmuir* **6** 870 (1990)
57. K C O'Brien, J B Lando *Langmuir* **1** 433 (1985)
58. E J McNally, G Zografi *J. Colloid Interface Sci.* **138** 61 (1990)
59. H W Fox, P W Taylor, W A Zisman *Ind. Eng. Chem.* **39** 1401 (1947)
60. M J Newing *Trans. Faraday Soc.* **46** 755 (1950)
61. A A Trapeznikov, T N Zatsepina, T A Gracheva, R N Shcherbakova, V A Ogarev *Dokl. Akad. Nauk SSSR* **160** 174 (1965)
62. J E Sutherland, M L Miller *J. Colloid Interface Sci.* **32** 181 (1970)
63. A E Fainerman, Yu S Lipatov, V K Maistruk *Dokl. Akad. Nauk SSSR* **178** 1129 (1968)
64. J Guastalla *C. R. Hebd. Seances Acad. Sci.* **208** 1078 (1939)
65. V A Ogarev, Candidate Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1963
66. K Ariga, Y Okahata *J. Am. Chem. Soc.* **111** 5618 (1989)
67. A M Bibo, C M Knobler, I R Peterson *J. Phys. Chem.* **95** 5591 (1991)
68. C M Knobler *J. Phys. Condens. Mater.* **3** 17 (1991)
69. M Engel, H J Merle, I R Peterson, H Riegler, R Steitz *Ber. Bunsenges. Phys. Chem.* **95** 1514 (1991)
70. D Dervichian *J. Chem. Phys.* **7** 931 (1939)
71. S Stillberg-Stenhagen, E Stenhagen *Nature (London)* **156** 239 (1945)
72. M Lundquist *Chem. Scr.* **1** 5 (1971)
73. B Lin, M C Shin, T M Bohanon, G E Ice, P Dutta *Phys. Rev. Lett.* **65** 191 (1990)
74. P Le Barny *Thin Solid Films* **152** 99 (1987)
75. S W J Kuan, C W Frank, C C Fu, D R Allee, P Maccagno, R F W Pease *J. Vac. Sci. Technol. B* **6** 2274 (1988)
76. N Beredjick, H E Rice, Jr *J. Polym. Sci.* **62** 64 (1962)
77. M J Schick *J. Polym. Sci.* **25** 465 (1957)
78. N Beredjick, R A Ahlbeck, T K Kwei, H E Ries *J. Polym. Sci.* **46** 268 (1960)
79. S Wu, J R Huntsberger *J. Colloid Interface Sci.* **29** 138 (1969)
80. A Labbauf, J R Zack *J. Colloid Interface Sci.* **35** 569 (1971)
81. G Gabrielli, M Puggelli, R Faccioli *J. Colloid Interface Sci.* **41** 63 (1972)
82. A Blumstein, H E Ries *J. Polym. Sci., Part B, Polym. Phys.* **3** 927 (1965)
83. M Puggelli, G Gabrielli *Colloid Polym. Sci.* **263** 879 (1985)
84. E Bringuier, R Vilanove, Y Gallot, J Selb, F Rondelez *J. Colloid Interface Sci.* **104** 95 (1985)
85. H Hotta *J. Colloid. Sci.* **9** 504 (1954)
86. T Nakahara, K Motomura, R Matuura *Bull. Chem. Soc. Jpn.* **40** 495 (1967)
87. S J Mumby, J D Swalen, J F Rabolt *Macromolecules* **19** 1054 (1986)
88. T Arndt, C Bubeck, A J Schouten, G Wegner *Microchim. Acta* 7 (1988)
89. J F Rabolt *J. Chim. Phys.* **85** 1027 (1988)
90. C J Drummond, P Elliott, D N Furlong, G T Barnes *Thin Solid Films* **210/211** 69 (1992)
91. S Yoshikawa, M Ueno, K Meguro *Bull. Chem. Soc. Jpn.* **51** 3136 (1978)
92. D Naegele, H Ringsdorf *J. Polym. Sci., Polym. Chem. Ed.* **15** 2821 (1977)
93. M Ueno, S Yoshikawa, K Meguro *J. Polym. Sci., Polym. Chem. Ed.* **17** 334 (1979)
94. N Beredjick, W J Burlant *J. Polym. Sci., Part A-1* **8** 2807 (1970)
95. G Gabrielli, M Puggelli, P Bagloni *J. Colloid Interface Sci.* **86** 485 (1982)
96. M Puggelli, G Gabrielli *Colloid Polym. Sci.* **261** 166 (1983)
97. M Hatada, M Nishii, K Hirota *J. Colloid Interface Sci.* **45** 502 (1973)
98. T Nakahara, K Motomura, R Matuura *J. Polym. Sci., Part A-2* **4** 649 (1966)
99. C S Winter, R H Tredgold, A J Vickers, E Khoshdel, P Hodge *Thin Solid Films* **134** 49 (1985)
100. M Avrami *J. Chem. Phys.* **8** 221 (1940)
101. G Caminati, G Gabrielli, M Puggelli, E Ferroni *Colloid Polym. Sci.* **266** 775 (1988)
102. G Caminati, G Gabrielli, M Puggelli, E Ferroni *Colloid Polym. Sci.* **267** 237 (1989)
103. K Naito *J. Colloid Interface Sci.* **131** 218 (1989)
104. H Matsuda, H Kawada, K Takimoto, Y Morikawa, K Eguchi, T Nakagiri *Thin Solid Films* **178** 505 (1989)
105. S Okada, H Nakanishi, H Matsuda, M Kato, T Abe, H Ito *Thin Solid Films* **178** 313 (1989)
106. R Elbert, A Laschewsky, H Ringsdorf *J. Am. Chem. Soc.* **107** 4134 (1985)
107. A Laschewsky, H Ringsdorf, J Schneider *Angew. Makromol. Chem.* **145/146** 1 (1986)
108. S Hironaka, K Meguro *J. Colloid Interface Sci.* **35** 367 (1971)
109. V A Kargin, Yu M Malinskii, S S Medvedev *Dokl. Akad. Nauk SSSR* **96** 307 (1954)
110. S Yoshikawa, M Ueno, K Meguro *Colloid Polym. Sci.* **256** 422 (1978)
111. S Yoshikawa, M Ueno, K Meguro *J. Colloid Interface Sci.* **69** 334 (1979)
112. S Yoshikawa, M Ueno, K Meguro *J. Polym. Sci., Polym. Chem. Ed.* **17** 2491 (1979)
113. H Kumehara, T Kasuga, T Watanabe, S Miyata *Thin Solid Films* **178** 182 (1989)
114. R Vilanove, F Rondelez *Phys. Rev. Lett.* **45** 1502 (1980)
115. M B Biddle, J B Lando, H Ringsdorf, G Schmidt, J Schneider *Colloid Polym. Sci.* **266** 806 (1988)
116. H Ringsdorf, G Schmidt, J Schneider *Thin Solid Films* **152** 207 (1987)
117. H Ringsdorf, B Schlarb, J Schneider *Polym. Prepr.* **27** 127 (1986)
118. P Stroeve, G J R Spooner, P J Bruinsma, L B Coleman, C H Erdelen, H Ringsdorf *ACS Symp. Ser.* **447** 177 (1991)
119. P J Bruinsma, C Sturesson, G J R Spooner, L B Coleman, P Stroeve *Polym. Prepr.* **32** 242 (1991)
120. P J Bruinsma, G J R Spooner, L B Coleman, R Koren, C Sturesson, P Stroeve *Thin Solid Films* **210/211** 440 (1992)
121. L B Coleman, T G Fiske, P Stroeve, M A N Coelho, S Dong, H Ringsdorf, J Schneider *Thin Solid Films* **178** 227 (1989)
122. P Stroeve, M A N Coelho, S Dong, P Lam, L B Coleman, T G Fiske, H Ringsdorf, J Schneider *Thin Solid Films* **180** 241 (1989)
123. K Kurihara, T Kunitake, N Higashi, M Niwa *Thin Solid Films* **210/211** 681 (1992)
124. J N Israelachvili *Intermolecular and Surface Forces* (London: Academic Press, 1985)
125. J N Israelachvili *Surf. Sci. Rep.* **14** 109 (1992)
126. R M Pashley, P M McGuiggan, B W Ninham, J Brady, D F Evans *J. Phys. Chem.* **90** 1637 (1986)
127. P Kekicheff, H K Chistenson, B W Ninham *Colloid Surf.* **40** 31 (1989)
128. K Kurihara, S Kato, T Kunitake *Chem. Lett.* 1555 (1990)
129. H Hsiung, J Rodriguez-Parada, R Bekerbauer *Chem. Phys. Lett.* **182** 88 (1991)
130. B K Mandal, T Takahashi, M Maeda, S Kumar, A Blumstein, S K Tripathy *Makromol. Chem.* **192** 1009 (1991)
131. T Takahashi, Y M Chen, A K Rahaman, J Kumar, S K Tripathy *Thin Solid Films* **210/211** 202 (1992)
132. P Tao, L Xu, G Chen, X Yang, G Wang, J Zheng, Z Zhang, W Wang *Thin Solid Films* **179** 381 (1989)
133. W Hickel, G Appel, D Lupo, W Prass, U Scheunemann *Thin Solid Films* **210/211** 182 (1992)
134. W Meisel, P Tippmann-Krayer, H Möhwald, P Gütlich, J Fresenius *Anal. Chem.* **341** 289 (1991)
135. K Kobayashi, K Takaoka, S Ochiai *Thin Solid Films* **178** 453 (1989)
136. P Tippmann-Krayer, H Möhwald *J. Phys. Chem.* **96** 5220 (1992)
137. B Hagenhoff, A Benninghoven, H-U Siegmund, D Holtkamp *Thin Solid Films* **210/211** 601 (1992)
138. B Hagenhoff, M Deimel, A Benninghoven, H-U Siegmund, D Holtkamp *J. Phys. D* **25** 818 (1992)
139. M Shimomura, K Song, J F Rabolt *Langmuir* **8** 887 (1992)

140. G Gabrielli, M Puggelli, R Faccioli *J. Colloid Interface Sci.* **37** 213 (1971)
141. G Gabrielli, M Puggelli, E Ferroni *J. Colloid Interface Sci.* **47** 145 (1974)
142. F C Goodrich, in *Proceedings of 2nd Int. Congr. Surface Activity, London, 1957* Vol. 1, p. 85
143. S J Singer *J. Chem. Phys.* **16** 872 (1948)
144. H L Frisch, R Simha *J. Chem. Phys.* **27** 702 (1957)
145. G Gabrielli, M Puggelli, E Ferroni *J. Colloid Interface Sci.* **32** 242; **33** 133 (1970)
146. J T Davies, E K Rideal *Interfacial Phenomena* (New York: Academic Press, 1963)
147. P Joos *Kolloid. Z.* **238** 499 (1970)
148. G Gabrielli, M Puggelli, P Baglioni *J. Colloid Interface Sci.* **86** 490 (1982)
149. M L Huggins *Kolloid. Z.* **251** 449 (1973)
150. G Gabrielli, G G T Guarini *J. Colloid Interface Sci.* **64** 185 (1978)
151. M Puggelli, G Gabrielli *Colloid Polym. Sci.* **263** 885 (1985)
152. G Gabrielli, A Maddii *J. Colloid Interface Sci.* **64** 19 (1978)
153. G Gabrielli, P Baglioni, A Fabbrini *Colloid Surf.* **3** 147 (1981)
154. E G Cocbain, K J Day, A J McMullen, in *Proceedings of 2nd Int. Congr. Surface Activity, London, 1957* Vol. 1, p. 56
155. T Isemura, H Hotta, T Miwa *Bull. Chem. Soc. Jpn.* **26** 380 (1953)
156. G Gabrielli, M Puggelli *J. Colloid Interface Sci.* **35** 460 (1971)
157. H E Ries, D C Walker *J. Colloid Sci.* **16** 361 (1961)
158. J Lopis, D V Rebollo *J. Colloid Sci.* **11** 543 (1956)
159. G Gabrielli, M Puggelli *J. Colloid Interface Sci.* **37** 503 (1971)
160. F H Müller *Z. Electrochem.* **59** 312 (1955)
161. D J Crisp *Research Suppl. Surf. Chem. (London)* **17** 23 (1947)
162. J Heller, D J Lyman *J. Polym. Sci., Polym. Phys. Ed.*, **1** 317 (1963)
163. H E Ries, Jr, R A Ahlbeck, J Gabor *J. Colloid Sci.* **14** 354 (1959)
164. G C Benson, R L McIntosh *J. Colloid Sci.* **3** 323 (1948)
165. F M Fowkes, M J Schick, A Bondi *J. Colloid Sci.* **15** 531 (1960)
166. J Gottlieb *J. Phys. Chem.* **64** 427 (1960)
167. H Schuller *Z. Elektrochem.* **60** 147 (1956)
168. K Huff, F H Müller *Kolloid. Z.* **120** 49 (1952)
169. R H Tredgold *Rep. Prog. Phys.* **50** 1609 (1987)
170. G Gabrielli, P Baglioni, E Ferroni *Colloid Polym. Sci.* **257** 121 (1979)
171. M Puggelli, G Gabrielli *J. Colloid Interface Sci.* **61** 420 (1977)
172. A Labbauf *J. Appl. Polym. Sci.* **10** 865 (1966)
173. J B Peng, G T Barnes *Langmuir* **6** 578 (1990)
174. S A Letts, T Fort, J B Lando *J. Colloid Interface Sci.* **56** 64 (1976)
175. K Fukuda, T Kato, S Machida, Y Shimizu *J. Colloid Interface Sci.* **68** 82 (1979)
176. G Gabrielli, C D'Aubert *Colloid Polym. Sci.* **56** 258 (1980)
177. G Gabrielli, P Baglioni, A Maddi *J. Colloid Interface Sci.* **79** 268 (1981)
178. N Beredjick *Newer Methods of Polymer Characterization* (Ed. K Bacon) (New York: Interscience, 1964)
179. M Puggelli, G Gabrielli *Colloid Polym. Sci.* **82** 261 (1983)
180. K Oguchi, T Yoden, Y Kosaka, M Watanabe, K Sanui, N Ogata *Thin Solid Films* **161** 305 (1988)
181. M Watanabe, Y Kosaka, K Oguchi, K Sanui, N Ogata *Macromolecules* **21** 2997 (1988)
182. T P Kenigsberg, N G Ariko, V E Agabekov, N I Mitskevich *Acta Chim. Hung.* **129** 545 (1992)
183. N Ogata, K Sanui, K Oguchi, T Nakada, Y Takahashi *J. Appl. Polym. Sci.* **28** 2433 (1983)
184. S Ito, H Okubo, S Ohmori, M Yamomoto *Thin Solid Films* **179** 445 (1989)
185. S Ito, T Ueno, M Yamomoto *Thin Solid Films* **210/211** 614 (1992)
186. J P Rabe, J F Rabolt, C A Brown, J D Swalen *J. Chem. Phys.* **84** 4096 (1986)
187. J P Rabe, J F Rabolt, C A Brown, J D Swalen *Thin Solid Films* **133** 153 (1985)
188. S Lee, B Hillebrands, G I Stegeman, L A Laxhuber, J D Swalen *J. Chem. Phys.* **91** 1882 (1989)
189. C S Winter, R H Tredgold, A J Vickers, E Khoshdel, P Honge *Thin Solid Films* **134** 49 (1985)
190. R H Tredgold, A J Vickers, P Hodge, A Hoorfar, E Khoshdel *J. Phys. D* **18** 1139 (1985)
191. B P Binks, P D I Fletcher, A Price, P Hodge *Thin Solid Films* **207** 273 (1992)
192. R H Tredgold, C S Winter *J. Phys. D* **15** 155 (1982)
193. R H Tredgold, C S Winter *Thin Solid Films* **99** 81 (1983)
194. M R Buhaenko, J W Goodwin, R M Richardson *Thin Solid Films* **159** 171 (1988)
195. L Ter-Minassian-Saraga, S J Abitboul *J. Colloid Interface Sci.* **48** 32, 42 (1974)
196. M Niwa, E Matsuyoshi, N Higashi *Langmuir* **5** 1256 (1989)
197. P DeKeyser, P Joos *J. Phys. Chem.* **88** 274 (1984)
198. E S Nikomarov *Langmuir* **6** 410 (1990)
199. H E Ries, Jr, H Swift *Langmuir* **3** 853 (1987)
200. A W Adamson *Physical Chemistry of Surfaces* (New York: Wiley, 1982)
201. B M Abraham, J B Ketterson *Langmuir* **1** 461 (1985)
202. P Ekwall, R Ekholm, A Norman *Acta Chem. Scand.* **11** 703 (1957)
203. H Sobotka, M Demeny, M Arnaki *J. Colloid Interface Sci.* **14** 281 (1959)
204. V N Izmailova, G P Yampol'skaya, B D Summ *Poverkhnostnye Yavleniya v Belkovykh Sistemakh* (Surface Phenomena in Protein Systems) (Moscow: Khimiya, 1988)
205. G P Yampol'skaya, P V Nuss, G Ts Raznikova, V N Izmailova, in *Uspekhi Kolloidnoi Khimii* (Advances in Colloid Chemistry) (Leningrad: Khimiya, 1991) p. 292
206. K S Birdi *Lipids and Biopolymers in Monolayers at Liquid Interfaces* (New York: Plenum, 1989)
207. S J Singer, G L Nicolson *Science* **175** 720 (1972)
208. V Erokhin, L A Feigin *Prog. Colloid Polym. Sci.* **85** 47 (1991)
209. T Isemura, K Hamaguchi *Bull. Chem. Soc. Jpn.* **25** 40 (1952)
210. B R Malcolm *Proc. R. Soc. London, A. Math. Phys. Sci.* **305** 363 (1968)
211. B R Malcolm *Prog. Surf. Membr. Sci.* **7** 183 (1973)
212. G I Loeb, R E Baier *J. Colloid Interface Sci.* **27** 38 (1968)
213. B R Malcolm *Polymer* **7** 595 (1966)
214. D W Goupil, F C Goodrich *J. Colloid Interface Sci.* **62** 142 (1977)
215. B R Malcolm *Thin Solid Films* **134** 201 (1985)
216. B R Malcolm *J. Colloid Interface Sci.* **104** 520 (1985)
217. G Gabrielli, E Ferroni, M L Huggins *Prog. Colloid Polym. Sci.* **58** 201 (1975)
218. P Baglioni, L Dei, E Ferroni, G Gabrielli *Colloid Surf.* **60** 399 (1991)
219. P Baglioni, L Dei, G Gabrielli *J. Colloid Interface Sci.* **93** 402 (1983)
220. B R Malcolm *Thin Solid Films* **178** 191 (1989)
221. B R Malcolm *Thin Solid Films* **178** 17 (1989)
222. S Egusa, T Nakayama, N Gemma, A Miura, M Azuma *Thin Solid Films* **178** 165 (1989)
223. T Yamashita, A Shibata, S Yamashita *Bull. Chem. Soc. Jpn.* **51** 2751 (1978)
224. G Gabrielli, P Baglioni, E Ferroni *J. Colloid Interface Sci.* **81** 139 (1981)
225. G Gabrielli, P Baglioni *J. Colloid Interface Sci.* **83** 221 (1981)
226. A Albert, J Corboda *Colloid Polym. Sci.* **262** 811 (1984)
227. F Kimura, S Uematsu, H Sakurai, Y Akahori, M Nakagaki. *J. Colloid Interface Sci.* **124** 290 (1988)
228. P Baglioni, L Dei, E Ferroni, G Gabrielli *J. Colloid Interface Sci.* **109** 109 (1986)
229. W Hickel, G Duda, M Jurich, T Kröhl, K Rochford, G I Stegeman, J D Swalen, G Wegner, W Knoll *Langmuir* **6** 1403 (1990)
230. H Motschmann, R Reiter, R Lawall, G Duda, M Stamm, G Wegner, W Knoll *Langmuir* **7** 2743 (1991)
231. K Mathauer, A Mathy, C Bubeck, G Wegner, W Hickel, U Scheunemann *Thin Solid Films* **210/211** 449 (1992)
232. T Takenaka, K Harada, M Matsumoto *J. Colloid Interface Sci.* **73** 569 (1980)
233. F Takeda, M Matsumoto, T Takenaka, Y Fujiyoshi *J. Colloid Interface Sci.* **84** 220 (1981)
234. F Takeda, M Matsumoto, T Takenaka, Y Fujiyoshi, N Uyeda *J. Colloid Interface Sci.* **91** 267 (1983)
235. H W Fox, P W Taylor, W A Zisman *Ind. Eng. Chem.* **39** 1401 (1947)
236. W Noll, H Steinbach, C Sucker *Ber. Bunsenges Phys. Chem.* **67** 407 (1963)
237. W H Banks *Nature (London)* **174** 365 (1954)
238. A H Ellison, W A Zisman *J. Phys. Chem.* **60** 416 (1956)
239. V A Ogarev, V V Arslanov, A A Trapeznikov *Kolloid. Zh.* **34** 372 (1972)

240. V V Arslanov, V A Ogarev *Dokl. Akad. Nauk SSSR* **196** 1105 (1971)
241. Y Kakihara, D M Himmelblau, R S Schechter *J. Colloid Interface Sci.* **30** 200 (1969)
242. W Noll *Pure Appl. Chem.* **13** 101 (1966)
243. W Noll, H Steinbach, C Sucker *J. Polym. Sci., Part C, Polym. Lett.* **34** 123 (1971)
244. H Steinbach, C Sucker *Adv. Colloid Interface Sci.* **14** 43 (1980)
245. V A Ogarev, V V Arslanov, A A Trapeznikov, in *Makromolekuly na Granitse Razdela Faz* (Macromolecules at a Phase Interface) (Kiev: Naukova Dumka, 1971) p. 155
246. G L Gaines *J. Polym. Sci., Part C* **34** 115 (1971)
247. M J Owen, T C Kendrick *J. Colloid Interface Sci.* **27** 46 (1968)
248. W Noll *Z. Elektrochem.* **67** 407 (1963)
249. K Motomura, R Matuura *J. Colloid Interface Sci.* **18** 52, 295 (1963)
250. V A Ogarev, V V Arslanov, A A Trapeznikov, in *Poverkhnostnye Yavleniya v Zhidkostyakh i Zhidkikh Rastvorakh* (Surface Phenomena in Liquids and Liquid Solutions) (Leningrad: Izd. Leningr. Univ., 1972) p. 79
251. M Matsumoto, H Yoshimura, V S Kulkarni, K Nagayama *Colloid Polym. Sci.* **268** 1174 (1990)
252. P Ekwall, R Ekholm, in *Proceedings of 2nd Int. Congr. Surface Activity London, 1957* Vol. 1, p. 23
253. J F Joany, P-G De Gennes *C. R. Acad. Sci., Ser. 2* **299** 279 (1984)
254. A A Vavkushevskii, V V Arslanov, V A Ogarev *Kolloid. Zh.* **50** 1180 (1988)
255. E K Mann, S Henon, D Langevin, J Meunier *J. Phys. France* **2** 1683 (1992)
256. S Granick, D J Kuzmenka, S J Clarson, J A Semlyen *Langmuir* **5** 144 (1989)
257. T Richardson, G G Roberts, S Holder, D Lacey *Thin Solid Films* **210/211** 299 (1992)
258. E Orthmann, G Wegner *Angew. Chem.* **98** 1114 (1986)
259. A A Kalachev, T Sauer, V Vogel, N A Plate, G Wegner *Thin Solid Films* **188** 341 (1990)
260. K S Schwieg, H Fisher, Y Xu, F Kremer, G Wegner *Macromol. Chem. Macromol. Symp.* **46** 211 (1991)
261. K Yase, K S Schwieg, G Lieser, G Wegner *Thin Solid Films* **213** 130 (1992)
262. G L Gaines, Jr *Adv. Chem.* **144** 338 (1975)
263. G L Gaines, Jr *J. Polym. Sci., Part C* **34** 115 (1971)
264. A A Trapeznikov, M A Kolobov *Kolloid. Zh.* **44** 277 (1982)
265. M A Kolobov, A A Trapeznikov *Kolloid. Zh.* **44** 690 (1982)
266. A Bachrach, A Zilkha *Eur. Polym. J.* **5** 493 (1984)
267. N K Adam *Trans. Faraday Soc.* **29** 108 (1933)
268. B A Johnson, J Kreuter, G Zografi *Colloid Surf.* **17** 325 (1986)
269. T Kawaguchi, H Nakahara, K Fukuda *J. Colloid Interface Sci.* **104** 290 (1985)
270. T Kawaguchi, H Nakahara, K Fukuda *Thin Solid Films* **133** 29 (1985)
271. M Hittmeier, L S Sandell, P Luner *J. Polym. Sci., Part C* **36** 267 (1971)
272. Y Tsujii, T Itoh, T Fukuda, T Miyamoto, S Ito, M Yamamoto *Langmuir* **8** 936 (1992)
273. M A Schoondorp, E J Vorenkamp, A J Schouten *Thin Solid Films* **196** 121 (1991)
274. P Zugenmaier, H Steinmeier *Polymer* **27** 1601 (1986)
275. M A Schoondorp, A J Schouten, B E Hulshof, B L Feringa, G T Ostergetel *Langmuir* **8** 1817 (1992)
276. M A Schoondorp, A J Schouten, B E Hulshof, B L Feringa *Langmuir* **8** 1825 (1992)
277. K L Mittal (Ed.) *Polyimides — Synthesis, Characterization and Application* (New York: Plenum, 1982) Vol. 1; (1984) Vol. 2
278. F Iacona, M Garilli, G Marletta, O Puglisi, G Pignatazo *J. Mater. Res.* **6** 861 (1991)
279. M Kakimoto, M Suzuki, T Konishi, Y Imai, M Iwamoto, T Hino *Chem. Lett.* 823 (1986)
280. M Suzuki, M Kakimoto, T Konishi, Y Imai, M Iwamoto, T Hino *Chem. Lett.* 395 (1986)
281. H Sotobayashi, T Schilling, B Tesche *Langmuir* **6** 1246 (1990)
282. T Schedel-Niedrig, H Sotobayashi, A Ortega-Villamil, A M Bradshaw *Surf. Sci.* **247** 83 (1991)
283. T Schedel-Niedrig, M Keil, H Sotobayashi, T Schilling, B Tesche, A M Bradshaw *J. Phys., Condens. Mater.* **3** 23 (1991)
284. M Sugi *Molecular Electronic Devices* (Ed. F Carter) (Amsterdam: Elsevier, 1988) p. 441
285. M Kakimoto, A Morikawa, Y Nishikata, M Suzuki, Y Imai *J. Colloid Interface Sci.* **121** 599 (1988)
286. Y Nishikata, K Kamatsu, M Kakimoto, Y Imai, K Ariga, Y Okahata *J. Chem. Soc. Jpn., Chem. Ind. Chem.* **10** 1150 (1990)
287. V P Kukhar', N I Mishchenko, V V Tsukruk, S Yu Petrash, E V Shelud'ko, A V Tolmachev, I P Krainov *Dokl. Akad. Nauk USSR* **13** 119 (1991)
288. Y Nishikata, T Konishi, A Morikawa, M Kakimoto, Y Imai *Polymer J.* **20** 269 (1988)
289. I Fujiwara, C Ishimoto, J Seto *J. Vac. Sci. Technol. B* **9** 1148 (1991)
290. A Killinger, C Thümmler, M Grunze, W Schrepp *J. Adhesion* **36** 229 (1992)
291. M Iwamoto, Y Majima, A Watanabe *Thin Solid Films* **210/211** 101 (1992)
292. M Iwamoto, Y Majima *Jpn. J. Appl. Phys.* **28** 721 (1988)
293. M Iwamoto, Y Majima *Thin Solid Films* **178** 67 (1989)
294. M Iwamoto, Y Majima *J. Chem. Phys.* **94** 5135 (1991)
295. Y Majima, H Naruse, M Iwamoto *Thin Solid Films* **210/211** 82 (1992)
296. Y Majima, M Iwamoto *Rev. Sci. Instrum.* **62** 2228 (1991)
297. M Iwamoto, T Kubota *Repts Asahi Glass Found.* **61** 195 (1992)
298. M Iwamoto, T Noguchi, H Fuwa, Y Majima *Jpn. J. Appl. Phys.* **30** 1020 (1991)
299. Y Nishikata, S Fukui, M Kakimoto, Y Imai, K Nishiyama, M Fujihira *Thin Solid Films* **210/211** 296 (1992)
300. M Iwamoto, S Kasahara, Y Yoneda, K Iriyama, Y Nishikata, M Kakimoto, Y Imai *Thin Solid Films* **210/211** 461 (1992)
301. M Uekita, H Awaji, M Murata, S Mizunuma *Thin Solid Films* **205** 109 (1991)
302. H Ikeno, A Oh-saki, M Nitta, N Ozaki, Y Yokoyama, K Nakaya, S Kobayashi *Jpn. J. Appl. Phys.* **27** L475 (1988)
303. S Baker, A Seki, J Seto *Thin Solid Films* **180** 263 (1989)
304. T Akatsuka, H Tanaka, J Toyama, T Nakamura, M Matsumoto, Y Kawabata *Chem. Lett.* 1351 (1991)
305. T Akatsuka, H Tanaka, J Toyama, T Nakamura, M Matsumoto, Y Kawabata *Thin Solid Films* **210/211** 458 (1992)
306. K Nakaya, B Y Zhang, M Yoshida, I Isa, S Sindoh, S Kobayashi *Jpn. J. Appl. Phys.* **28** L116 (1989)