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Polymer monolayers and Langmuir–Blodgett films. Polymerisation reactions in organised molecular ensembles; structural transformations and properties

V V Arslanov
Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The method of preparation, structure, and properties of monolayers on the surface of a liquid and of Langmuir–Blodgett films on surface-active monomers are discussed. The influence of the chemical composition and structure of monomer molecules, the conditions for the preparation of organised ensembles, and the conditions in polymerisation reactions for the structural-morphological transformations in monolayers and Langmuir–Blodgett films are considered.

The bibliography includes 128 references.

Contents

I.	Introduction	584
II.	Preparation of monolayers on the surface of a liquid and of Langmuir–Blodgett films	585
III.	Polymerisation reactions in monolayers	585
IV.	Polymerisation reactions in Langmuir–Blodgett films	596
V.	Prospects for the application of polymeric Langmuir–Blodgett films	601

I. Introduction

Polymer monolayers and Langmuir–Blodgett films (LBF) should occupy in the next few years a position in the problem of multilayer two-dimensional structures consistent with their scientific and applied importance. This refers both to the unique possibilities of the assembly and study of two-dimensional polymer systems with controlled orientation and distances between the chains and their elements and to the prospects for the application of Langmuir–Blodgett (LB) ensembles in modern technology. The study of the specific characteristics of the behaviour of organised ensembles of macromolecules at interfaces between two fluids or at a solid/fluid interface makes it possible not only to achieve in practice the advantages of polymeric LBF already recognised (thermal and mechanical stability, resistance to the action of corrosive media) but also to construct new generation superstructures taking into account the chain structure of the polymers.

Polymeric LBF are nowadays obtained by three procedures which provide for (1) the formation of polymer monolayers on the surface of a liquid (usually water) and their transfer to a solid support, (2) the formation of monolayers made up of monomers, their polymerisation, and their transfer to a solid support, and (3) the formation of monomer monolayers, their transfer to a solid support, and their polymerisation in the LBF.

It is important to emphasise that, for compounds having the same chemical composition, LBF differing in structural organisation can be obtained depending on the method of formation. This is associated, for example, with different conditions in the polymerisation reactions carried out on liquid and solid surfaces, with the rotation of the monomer molecules in the preparation of the LBF, etc. For this reason, the current stage (in many respects, the initial stage) of the development of studies in the field of polymer LBF should include in the first place the comparative analysis of the three procedures for their formation indicated above. In the first case, attention should be concentrated on the study of the thermodynamic, structural-morphological, and molecular-kinetic features of the behaviour of polymer monolayers on the surface of a liquid which distinguish them from low-molecular weight analogues. A striking example of the existence of such differences is the possibility of obtaining stable monolayers from water-soluble polymers.

The regulation of the structure and properties of LBF during their preparation by the second method reduces mainly to the selection of known or the construction of new diphilic monomer molecules with a definite disposition of hydrophilic and hydrophobic fragments and their polymerisation, which is achieved preferentially with the aid of UV irradiation. Here so far little attention has been devoted to the use of the possibilities of a liquid support, the variation of the composition of which makes it possible to influence both the structure of the monolayer and the polymerisation process.

The third procedure for the formation of LBF has become most widely known in connection with the wide-scale employment of diacetylene derivatives. Photopolymerisation is carried out in two ways: either each transferred monolayer or the multilayer LBF as a whole is polymerised. The first method leads to the breakdown of the correlation between neighbouring LBF layers, while the second involves the retention of the three-dimensional crystal lattice of the monomer. The main problem arising in this method for the preparation of LBF is associated with the shrinking of the polymer which leads to the formation of defects (cracks, cavities, and folds).

Together with the increase in the thermal and mechanical stability of polymer LBF noted above, it is possible to realise with their aid also other, hitherto unused, possibilities of molecular architecture: the controlled phase separation in a mixed monolayer with immobilisation of the low-molecular-weight compound carrying a definite functional group; the fixation of additives introduced into the support; the formation of stable multilayers of polymers on a liquid surface and their transfer to a solid support, etc.

Polymer LBF are nowadays used in microelectronics as resistors and insulating layers with high specific characteristics. There are good prospects for the application of polar and alternating non-centrosymmetrical LBF in non-linear optics. Conducting polymers (for example, polyalkylthiophenes) are not inferior as regards their parameters to the known LBF consisting of charge-transfer complexes. Photochromic transformations (reversible *cis–trans* isomerisation and aggregation) can be used in the recording and representation of information. Molecular electronics, different types of sensors, multilayer selective membranes, and many other self-evident and merely predicted applications of polymer LBF require a significantly more vigorous investigation of these unique objects.

Langmuir's brilliant studies on the chemistry surfaces, for which he was awarded the Nobel Prize in 1932, served as a basis for the current spurt in the research into the monolayers (ML) and multilayer films obtained by the method also proposed by Langmuir (1920) and developed by his colleague Blodgett (1935). A historical survey of the studies on these unique objects has been given by Tredgold.[1] The present interest of physicists in the LBF was initiated by the elegant studies of Kuhn and his school on molecular architecture.[2] By virtue of Blinov's reviews,[3,4] the Soviet reader was able to become acquainted with the latest advances in the physics of LBF. Problems of the physical chemistry and mechanics of monolayers of low-molecular-weight surfactants and polymers have been described by Trapeznikov[5] and his students. The methodological problems of the formation of monolayers and LBF have been dealt with in reviews[1–4] and in the monographs of Adam,[6] Harkins,[7] Izmailova et al.,[8] and Gaines[9] and also in other communications.[10–12]

It is surprising that, despite the wide-scale research into monomer and polymer monolayers and LBF, reviews devoted to the present state of this problem are still lacking. The only exception is the publication by Tieke,[13] in which the properties of films of butadiynes and butadienes on the surfaces of water and solids are discussed.

In connection with the differences in the behaviour of polymer and monomer monolayers mentioned above and also with the abundance of data on this problem, the present review is devoted solely to the analysis of the polymerisation reactions of monomers on the surface of a liquid and in a LBF and the phase and structural-morphological transformations in these systems caused by these reactions. In addition, owing to the existence of a sufficient number of publications describing the methodological aspects of the problem under discussion, the latter have been excluded from the present review together with studies in the field of organised protein structures, which require independent analysis.

II. The preparation of monolayers on the surface of a liquid and of Langmuir–Blodgett films

The monolayers on the surface of a liquid (water, glycerol, dioxane, mercury, and gallium) consist of films of usually diphilic compounds one molecule thick. The monolayer is formed when a dilute solution of the surfactant in a volatile solvent spreads. In many instances, such films can be produced by the spreading of the bulk phase of the given substance. The phase state of the monolayer is recorded with the aid of compression isotherms: the dependence of the surface pressure (π) on the area per molecule or the monomer residue (A). In the general case, when the area is diminished, the gaseous, liquid, and solid states of the monolayer are produced. Each state of the monolayer is characterised by a definite orientation (thickness) of the molecules, which depends on the available area and the cohesive and adhesive properties of the system.

When the solid support is moved slowly through the surface of the liquid with the monolayer, the latter is deposited on the support. Successive upward and downward movements of the support lead to the formation of a Y-type centrosymmetrical LBF. Polar X- and Z-type LBF are obtained with the aid of special procedures. In X-type layers, the hydrophobic components of the molecule are directed towards the support, while in the Z-type layers they are turned in the opposite direction. Alternating LBF consist of layers of two and more compounds alternating in a specified sequence. They were obtained using several Langmuir baths. The LBF are usually formed from the monolayer in the liquid state. Solid monolayers are transferred by Shaefer's method, bringing into contact the surfaces of the solid support and the monolayer (horizontal transfer). In the course of the deposition of the monolayer, a specified surface pressure is maintained.

III. Polymerisation reactions in monolayers

One of the causes of the wide-scale interest in LBF is the possibility of reproducing the structure of the monolayer when it is transferred from the surface of the liquid to a solid support. The construction of a monolayer with the required structure on the surface of a liquid is a simpler problem than its construction on the surface of a solid. Indeed, slight changes in the chemical composition or structure of the molecules (increase in chain length, introduction of multiple bonds, change from single-chain to multichain lipids, change from an alcohol to an acid or ester, etc.) are instantly reflected in the compression isotherm. The structure of the monolayer is also extremely sensitive to changes in the pH and the temperature of the support, the introduction into the latter of electrolytes or other special additives, and the presence of slight admixtures of surfactants in the monolayer. Since the influence of these factors on the structure and properties of monolayers of low-molecular-weight compounds, such as the monomers, has been studied in fair detail, we are able to devote more attention to the characteristics of the behaviour of these systems associated with polymerisation reactions in monolayers.

1. Polymerisation of diphilic monomers containing multiple bonds in the polar component

Systematic studies on the influence of the chemical composition and structure of monomer molecules on the properties of monolayers and polymerisation reactions have been carried out recently by Ringsdorf and co-workers.[14–18]

The aim of the polymerisation of monomeric lipids (models of biomembranes) in organised systems (monolayers, bilayer lipid membranes, vesicles) is to increase their stability. However, polymerisation frequently leads to such an increase in the rigidity of the system that the formation of liquid phases is ruled out. To prevent this and to make sure that the main chains do not hinder the self-organisation of the side groups, flexible hydrophilic spacers are introduced into the monomer molecules. This leads to the formation of polymers of three types containing a spacer in the side chain (Fig. 1*a*), the main chain (Fig. 1*b*), and in both chains (Fig. 1*c*).[19,20] Such architecture makes it possible to achieve in the polymerised lipid an adequate degree of independence of the movements of the side chains. It is essential to note that a flexible spacer, leading

normally to the expansion of the monolayers, does not always increase their stability and hence the possibility of their transfer to a solid support.

The length of the spacer introduced between the lipid component and the polymer chain (Fig. 1*a*) influences the properties of the monolayer of not only the monomer but also of the polymerised system.

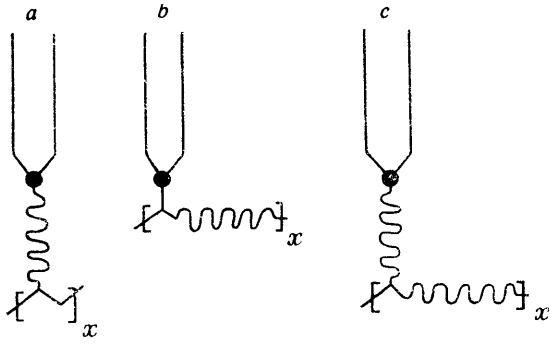
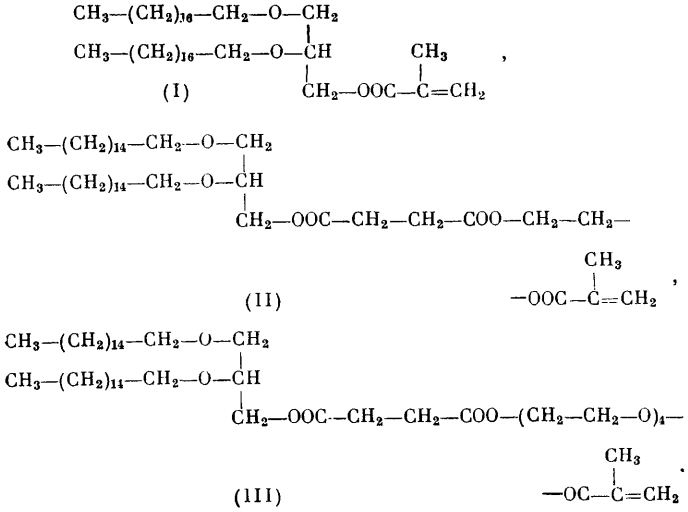


Figure 1. Three types of polymers containing a hydrophilic spacer in the side chain (*a*), the main chain (*b*), and the side and main chains (*c*).[20]

Fig. 2 illustrates the $\pi-A$ relations for the monolayers of two-chain methacrylate lipids (I), (II), and (III) with an increasing length of the spacer.[19,20]



An increase in the length of the hydrophilic spacer leads to the expansion of the monolayers: regions of expanded liquid and transition states appear for compounds (II) and (III). Nevertheless the monolayers of all the monomers retain a solid state with identical limiting areas and high decomposition pressures.

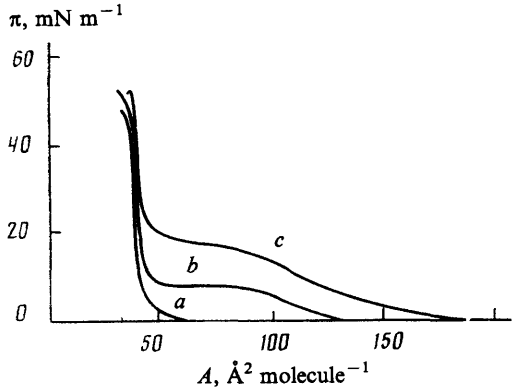


Figure 2. Surface pressure (π)/area (A) isotherms for monomeric lipids: *a*, (I), 20 °C; *b*, (II), 30 °C, *c*, (III), 30 °C.[19,20]

The compression isotherm for compound (I) photopolymerised in the monolayer virtually repeats the $\pi-A$ relation for the monomer,[20] i.e. the highly organised structure of the monolayer is retained during polymerisation (Figs. 3*a* and 3*b*). However, for the polymer obtained by the homopolymerisation of the lipid (I) in solution and then deposited on the surface of water, the $\pi-A$ relation (Fig. 3*c*) has a different form: there is no solid state and the monolayer decomposes at low surface pressures. This indicates a low capacity of the monomer without a spacer for self-organisation. In the presence of even a short spacer [the monomer (II)], the picture changes (Fig. 3*d*). The $\pi-A$ isotherm for the homopolymer obtained in solution from the lipid (II) is characterised by the presence of only the solid state, which indicates a high capacity of the macromolecules for self-organisation in the monolayer.

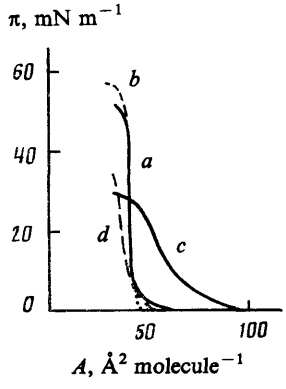
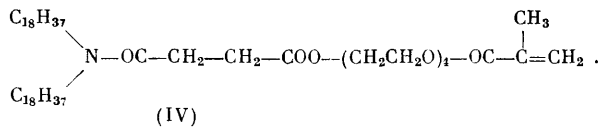


Figure 3. Surface pressure/area isotherms for monomeric (*a*) and polymeric (*b*–*d*) lipids: *a*, (I); *b*, (I), polymerised in the monolayer; *c*, (I), polymerised in solution; *d*, (II), polymerised in solution.[20]

Evidently, on polymerisation of the lipid (II) in the monolayer, the $\pi-A$ relation has a similar form. Finally, in the polymerisation of a monomer containing a fairly long spacer [the lipids (III) and (IV)] the condensation of the monolayer is much less marked (Fig. 4): the

isotherms for the polymers obtained by polymerisation in the monolayer (Fig. 4*b*) and in solution (Fig. 4*c*) have an expanded state region:[19]



(IV)

The incorporation of a flexible spacer in the main chain (Figs. 1*b* and 1*c*) is achieved as a rule by the copolymerisation of the corresponding monomers in solution. For example, the monomer (II) and 2-hydroxyethyl acrylate have been used for this purpose.[20]

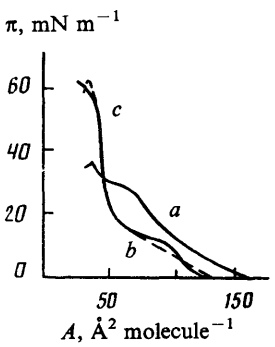
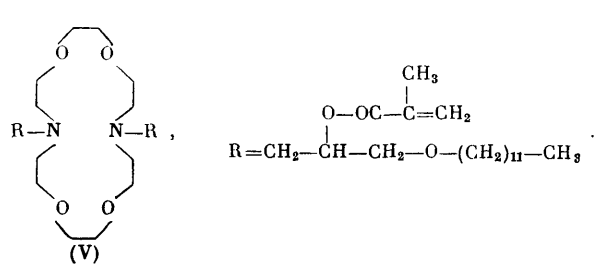


Figure 4. Surface pressure/area isomers for monomeric (*a*) and polymeric (*b*, *c*) lipids: *a*, (IV); *b*, (IV), polymerised in the monolayer; *c*, (IV), polymerised in solution.[19]

Thus the introduction of a flexible spacer with a definite link between the main chain and the lipid group intensifies the tendency of the polymers to undergo self-organisation in the monolayer and provides a possibility of choice: the formation of monolayers from the monomer and its subsequent polymerisation or the formation of the monolayer from the homopolymer.

The first steps have been taken in the study of polymerisation processes in monolayers of crown-ethers, which are important compounds.[21] Fig. 5*a* illustrates the compression isotherm for the monolayer of 1,10-bis(3-dodecyloxy-2-methacryloyloxypropyl)-1,10-diaza-18-crown-6 (V).



(V)

The isotherm, which is typical for the liquid state, is characterised by low decomposition pressures. The photopolymerisation of the crown-ether (V) under a nitrogen atmosphere leads to the shrinkage of the monolayer (Figs. 5*a* and 5*b*) and to a steeper $\pi-A$ relation.

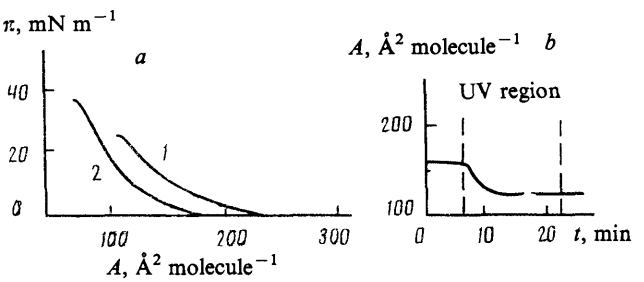
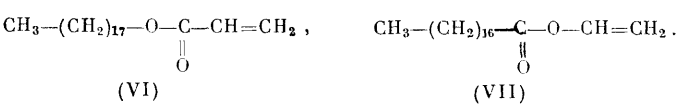


Figure 5. Surface pressure/area (*a*) isotherms for monomeric (curve *1*) and polymeric (curve *2*) crown-ether (V) and the dependence of the area of the monolayer of compound (V) on the duration of UV irradiation (*b*).[21]

The preparation of stable monolayers of LBF from polymerised crown-ethers leads to prospects for a more effective utilisation of these compounds as selective membranes and also as models of biomembranes. The success in the development of the latter aspect of this field is guaranteed by the fact that crown-ethers [for example, the monomer (V)] form bilayer lipid membranes and stable vesicular solutions.[21]

Generally speaking, a decrease in the area of the monolayer on polymerisation is not obligatory. As a result of the polymerisation of classical systems such as octadecyl acrylate (VI) and vinyl stearate (VII), the area of the monolayer increases, the degree of expansion depending on the area over which polymerisation has been carried out.



(VI) (VII)

Fig. 6 presents the $\pi-A$ relations for the octadecyl acrylate monolayer at a water/nitrogen interface before its irradiation with electrons and after exposure to an electron beam (30 s, 70% conversion). Evidently an increase in the area over which polymerisation has been carried out leads to an increase in the limiting area A_0.[22] Two facts are also of interest: the degeneracy of the point of inflection corresponding to the transition from the liquid state of the monolayer to the solid state and the possibility of polymerisation for large areas (42 Å^2 molecule^{-1}, π = 0). The first result reflects the structural changes in the monolayer associated with the fact that the polymerisation of the heat groups prevents close packing of the hydrocarbon chain and the second indicates a domain structure of the monolayer for large areas. Comparison of the data obtained for the water/air and water/nitrogen interfaces permits the conclusion that the polymerisation reaction is initiated by the products formed in the aqueous phase on irradiation of the system:[22] the reaction does not occur (remains unchanged during

irradiation) in the first case owing to the presence of atmospheric oxygen, which suppresses the activity of the hydrated electron, while in the second it does not occur when a compound (*N,N'*-dimethyl-*p*-nitrosoaniline), binding these products, is introduced into the aqueous support. Since the nitrosoaniline reacts with both water radiolysis products—the hydrated electon and the OH radical—it is so far not clear which of these species initiates the polymerisation.[22]

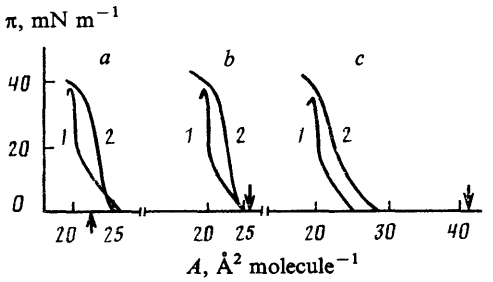


Figure 6. Surface pressure/area isotherms for the octadecyl acrylate (VII) monolayer on the water/nitrogen interface before (curve *1*) and after (curve *2*) 30 s UV irradiation; area for which the polymerisation was carried out (indicated by arrows (Å^2 molecule^{-1}): *a*, 22; *b*, 26; *c*, 42.[22]

The expansion of the monolayer is observed in the photopolymerisation of vinyl stearate.[23] The polymerisation reaction does not take place in air owing to the formation of ozone, which converts vinyl stearate into stearic acid. However, in circulating air, which reduces the time of contact between ozone and the monolayer, it is possible to achieve 50% conversion (in nitrogen, the conversion is 80%). The rate constant for the polymerisation reaction of vinyl stearate in the monolayer (N_2) for large areas (40 Å^2 molecule^{-1}) exceeds by a factor of 3 the rate constant for the polymerisation of the monolayer having an area of 22 Å^2 molecule^{-1}. This is apparently associated with the higher self-organisation of the monomer molecules in the domains[24] on the surface of water compared with the close-packed monolayer subjected to forced compression. However, the polymerisation of vinyl stearate on the surface of water leads in all cases to a more regular structure of the polymer and to a less effective monolayer than for the polymer obtained in solution.

Beredjick and Burlant,[25] who investigated the polymerisation of octadecyl methacrylate (VIII) in the monolayer on the surface of water, arrived at a similar conclusion.

$$CH_3-(CH_2)_{17}-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2 \quad .$$

(VIII)

It is of interest that the photopolymerisation occurring at the interface with argon and air can be accompanied both by the shrinkage (argon) and expansion (air) of the monolayer (Fig. 7). Fig. 8 illustrates the compression isotherms for octadecyl methacrylate and its polymers obtained under various conditions. Evidently, in contrast to the isotherm for the compression of the octadecyl acrylate monolayer (Fig. 6), the $\pi-A$ relation for the octadecyl methacrylate monolayer has no break point corresponding to the transition to the solid state. Furthermore, the decrease in the slope of the isotherm beyond A = 25 Å^2 molecule^{-1} indicates the onset of the decomposition of the true monolayer[26] in this range of areas. Such behaviour is associated not only with the steric hindrance to the formation of a close-packed monolayer[25] but also with its low stability. The bulk-phase or two-dimensional polymerisation of the monomer alters sharply the properties of the monolayer. The expansion of the monomer monolayer in the polymerisation reaction in air can be explained by the formation of a polymeric peroxide (copolymerisation with oxygen). The rate of this reaction is three times higher than the rate of polymerisation of the monomer in the monolayer at the water/argon interface.

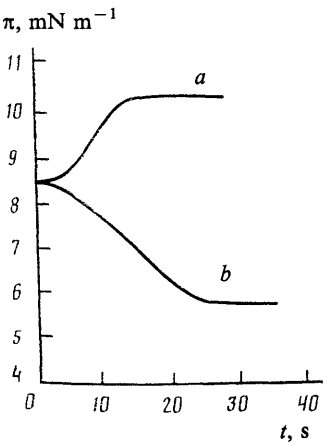


Figure 7. Dependence of the surface pressure on the duration of UV irradiation of the octadecyl methacrylate monolayer on the water/air (*a*) and water/argon (*b*) interfaces.[25]

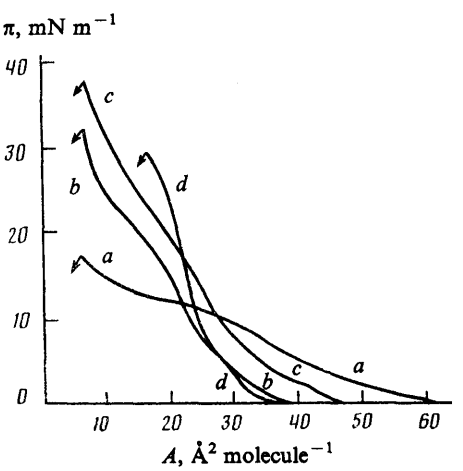


Figure 8. Surface pressure/area isotherms for octadecyl methacrylate (*a*) and poly(octadecyl methacrylate) (*b*–*d*) obtained by polymerising the monomer in the monolayer on the water/argon (*b*) and water/air (*c*) interfaces and in solution (*d*).[25]

Thus inappreciable changes in the structure and composition of the monomers [position of the oxygen bridge in the polar part of the molecules of the monomers (VI) and (VII), transition from the acrylic to the methacrylic monomer] lead to a significant alteration of the structural organisation of the monomer monolayers and induce differences in their response to the polymerisation conditions.

The results of studies on the monolayers of the two isomeric monooctadecyl esters of fumaric (ODF) and maleic (ODM) acids reflect in a clear-cut form the high susceptibility of the monolayers to the molecular structure. The isotherms for the cadmium salts of ODF and ODM, illustrated in Fig. 9, are clearly distinguishable.[27,28] The larger areas of the *cis*-isomer (ODM) compared with the *trans*-compound (ODF) reflect the fact that the head group of the ODM molecule occupies a larger area. The polymerisation induced by UV irradiation on the surface of water increases the area of the monolayer for ODF and decreases it for ODM, but the compression isotherms are identical for both polymers (Fig. 9).

$$CH_3-(CH_2)_{17}-OCOCH=CHCOOH.$$
(IX)

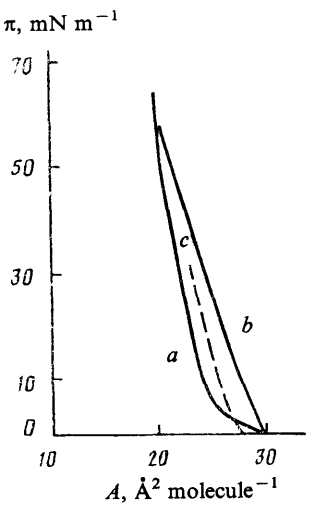


Figure 9. Surface pressure/area isotherms for the cadmium salts of octadecyl fumarate (*a*), octadecyl maleate (*b*), and the polymer (*c*) obtained by polymerising the salts in the monolayer.[27]

By varying the ratio of the components in mixed monolayers, it is possible to achieve a definite change or constancy (for a 25% content of ODF) of the area in polymerisation which gives rise to the hope that LBF free from cracks may be prepared. We may note that, whereas the structures of the films of polymeric ODF and ODM differ both on the surface of water and in the LBF, the polymeric monolayers and the LBF (subjected to UV and thermal polymerisation) have identical organisations and a higher thermal stability. The dimerisation of ODM and ODF with formation of cyclobutane rings was not observed.[27,28] Nevertheless, a cyclisation process, leading to the formation of an extremely unusual polymer structure, takes place in monolayers starting with compounds analogous to compound (IX) but containing a more complex central group: aliphatic monoesters of phenylenediacrylic acid:

$$C_nH_{2n+1}OCOCH=CHC_6H_4CH=CHCOOH,$$
(X)

$n = 7$, 10, 12, 14, and 18.

A characteristic feature of the behaviour of these compounds on the surface of water is that an increase in the length of the hydrocarbon group leads not to the condensation but to the expansion of the monolayer.[29] Thus the limiting area of the monolayer of compound (X) with $n = 14$ is 27 Å^2 molecule^{-1}, which corresponds to A_0 for unsaturated aliphatic acids: $A_0 = 24$ Å^2 molecule^{-1} for $n = 12$ and $A_0 = 34$ Å^2 molecule^{-1} for $n = 18$. On photopolymerisation in the monolayer ($\pi = 20$ mN m^{-1}), the area of the latter ($n = 12$) increases by 20% and the surface pressure increases from 20 to 50 mN m^{-1} for A = const. Such appreciable changes of the parameters of the monolayer are due to the alteration of its structure during polymerisation, which leads to the breakdown of the parallel orientation of the benzene rings and the formation of chains of cyclobutane rings with mirror symmetry (Fig. 10).

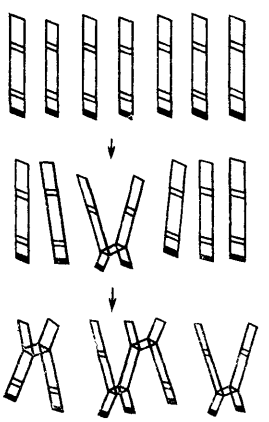


Figure 10. The change in the structure of the monolayer on photopolymerisation of an aliphatic monoester of phenylenediacrylic acid (X).[29]

A similar structure is formed also on polymerisation of these monoesters in the LBF (Z-type, 20 layers), It has been shown by UV spectroscopy[29] that the organisations of the molecules in the LBF and in the bulk-phase crystal differ significantly: in the bulk phase, the molecular packing resembles that in a Y-type LBF. As a result of these differences, the monoesters (X) with $n = 14$ and 18, which are photostable in the crystalline state, readily polymerise in the monolayer under the influence of UV radiation. The latter fact demonstrates the notable possibilities of monolayers and LBF in molecular engineering.

The degree of shrinkage or expansion of the monolayer as a result of polymerisation, which is a function of many parameters, depends also on the area of the monolayer for which the process takes place. For example, in the photopolymerisation of a two-chain lipid, as in

that of compound (X), containing the styrene group (XI), the shrinkage of the monolayer diminishes with increase in the area over which the polymerisation reaction takes place and disappears altogether when a close-packed monomer monolayer is polymerised.[30]

$$(C_{18}H_{37})_2\overset{+}{N}(CH_3)(CH_2C_6H_4{=}CH_2)Cl^- .$$
(XI)

This factor complicates in many respects the studies of the kinetics of polymerisation reactions in monolayers which are in any case not simple and therefore not popular. Evidently, the most reliable data on the rate of consumption of the monomer can be obtained with the aid of optical spectroscopy. In their absence, the reaction order and rate constant are found from the change in the area of the monolayer[30] or the surface potential,[23] specifying at the same time the type of function describing the variation of the surface concentration of the monomer.

2. Polymerisation of diphilic monomers containing multiple bonds in the hydrophobic component. Diacetylenes

Among the surface-active monomers investigated in monolayers and in LBF, diacetylene derivatives have firmly retained leading positions. This is explained by the interest in the study of two-dimensional solid-phase photopolymerisation and by the prospects for the application of thin layers made up of macromolecules with long chains of conjugated bonds oriented in the plane of the monolayer.

Tieke's review,[13] published in 1985, on the monolayers and LBF of diacetylene surfactants summarises the brief but extremely vigorous periods of their investigation. In recent years, there has been a significant expansion of the geography of these studies, the ideas concerning the behaviour of traditional diacetylene monomers and polymers have been deepened, and new compounds have been synthesised.

The properties of the monomer monolayers examined above are characteristic also of diacetylene surfactants on the surface of water. The interest in compounds of this class and in particular in the diynoic acid (XII), encouraged by the synthesis of homologous series of the latter,[31,32] is due to the possibility of studying the influence of the chain length and of the position of the diacetylene group relative to the carboxy-group on the stability[33] and other properties of the monolayers.

$$CH_3{-}(CH_2)_{m-1}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_n{-}COOH \text{ or } C_mC_n .$$
(XII)

Fig. 11 illustrates the dependence of the decomposition pressure of the monolayers of long-chain diynoic acids on the surface of water as a function of the overall chain length $L = m + n + 5$.[34] The parameter m, with increase of which (or with increase in L) the decomposition pressure π_c increases linearly, plays an important role in increasing the stability of the monolayers. For low values of n, this increase is steeper and the influence of n on the variation of the stability is manifested to a lesser extent than the influence of m. With decrease in n, i.e. as the diyne group approaches the head group, the stability increases appreciably both as a consequence of the decrease in the perturbation of the packing of the hydrocarbon chains of the diyne group[33] and by virtue of the activation of the carboxy-group by the diyne group. The stability of the monolayer increases greatly after the introduction of $CdCl_2$ (10^{-3} M) into the aqueous subphase.[35] The acid $C_{12}C_0$ forms a condensed film only on a support of this kind. The increase in stability can be explained in this instance by the formation of a salt which is controlled by the pH of the support. According to IR spectroscopic data, the transfer of the acid to the cadmium salt is completed at pH 6.5.[36] The concentration of Cd^{2+} ions in the support influences the stability of the monolayer in two ways.[33,37] High $CdCl_2$ concentrations greatly increase the decomposition pressure of the monolayer and diminish A_0 while low ones promote a decrease in stability owing to the formation in the monolayer of small amounts of a polymer, this effect intensifying when other divalent ions are employed (Ba^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}). On the other hand Collins[38] showed that, compared with the stability of the monolayers of $C_{16}C_8$ and $C_{16}C_0$ acids on different supports, the first monomer forms more stable monolayers on the surface of water while the second forms them on the surface of an aqueous $CdCl_2$ solution.

In this instance one must emphasise that inadequate attention has

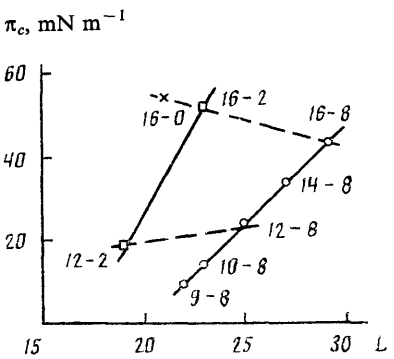


Figure 11. Dependence of the decomposition pressure (π_c) of solid monolayers of diynoic acids C_mC_n on the overall chain length L (T = 12 °C).[34]

In this instance one must emphasise that inadequate attention has been devoted to problems of stability in modern studies on monomer monolayers and the very concept is treated in a narrow sense, although more than 40 years ago Cris[39] proposed reliable criteria for the determination of this important characteristic of the monolayer. We may note the results of studies by Owens et al.,[33] who investigated the influence of the rate of compression of the monolayer of the $C_{12}C_8$ acid on the $\pi-A$ relations. At a rate of compression of the monolayer of 1.3 Å^2 molecule^{-1} min^{-1}, the isotherms hardly differ from relations obtained by other workers and have values of π_c reaching 30 mN m^{-1}. When the rate of compression is reduced by a factor of 4, π_c diminishes to 1 mN m^{-1}. The authors[33] attribute such behaviour to the loss of molecules from the monolayer. The cause of this effect, observed for diynoic acids also in other investigations,[38,40] still remains unexplained. However, if one assumes that the molecules cannot pass from the monolayer to the support, the only cause of such low values of the surface pressure may be a high rate of three-dimensional crystallisation. In order to elucidate the mechanism of the instability of the monolayer, it is essential to carry out more detailed investigations: the determination of the equilibrium pressure of the spreading and hysteresis of the compression isotherm at different temperatures and rates of compression. The high rigidity of the monolayers of diacetylenes gives rise also to other problems associated with the

measurement of the surface pressure of Wilhelmy's method. In this case, and also for rigid monolayers of other monomers and especially polymers, important information can be obtained from data for the viscoelastic behaviour of the monolayer.

Polymerisation of diacetylenic carboxylic acids in monolayers on the surface of water has been studied in greatest detail by Tieke[13] and Day and Ringsdorf.[41] The architecture of the acid molecule influences the course of the photopolymerisation reaction in the following way. Monomers with L from 25 to 29 (m = 12, 14, and 16) polymerise at 20 °C in nitrogen; for L = 23 and m = 10, polymerisation occurs at 2 °C and for m = 5 and 8 the acids in the monolayer do not polymerise at all.[41] If polymerisation occurs, then it proceeds at any surface pressure from 0 to π_c. Consequently the degree of orientation is higher even at π = 0. In the latter case, domains, formed on spreading of the acid as a result of the interaction between the hydrocarbon chains, are present on the surface of water. Clearly, despite the low values of π, fragments of the monolayer are in the solid state because in the liquid state of the monolayer, as in solution, in a melt, and in the liquid crystal state, the polymerisation of diynoic acids is impossible.[42,43] The polymerisation of the acid $C_{12}C_8$ at π = 0 leads to a decrease in area by 10% and at π = 10 mN m^{-1} the decrease is by 15%. The degree of conversion of the monomer can be judged from the degree of shrinkage. However, kinetic studies are difficult owing to the lack of reliable calibration methods. It is believed[38,41] that the degree of conversion of diyne surfactants in the monolayer reaches 100%.

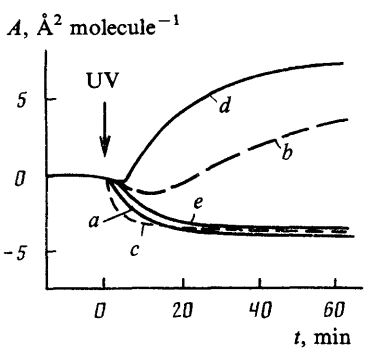


Figure 12. Dependence of the area per molecule of the monolayer of the acid $C_{12}C_8$ on the duration of UV irradiation; polymerisation conditions: π = 10 mN m^{-1}, T = 0–2 °C: *a*, water, pH 6.0, N_2; *b*, water, pH 6.0, air; *c*, 3 × 10^{-4} M M^+, pH 10.5, N_2; *d*, 3 × 10^{-1} M M^{2+}, pH 10.5, N_2; 3 × 10^{-4} M dM^{2+}, pH 5.5, N_2.[41]

other hand, for all the divalent ions (Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, and Cd^{2+}) at high pH (10.5) a perturbation of the packing is observed. Under these conditions, there is a possibility of the occurrence of side reactions, for example, the formation of carbenes by reaction with water. The decrease of the pH to below 6 restores the ability of the salts to polymerise with topochemical control.

Following the procedure of Day and Ringsdorf,[41] we shall compare the compression isotherms for polymer monolayers obtained from the acid $C_{14}C_8$ under different conditions. As can be seen from Fig. 13, the polymerisation in the monolayer at π = 10 mN m^{-1} leads to a system which is rigid to the maximum extent. A less rigid monolayer is formed when the polymerisation is carried out at π = 0 and A = 60 Å^2 molecule^{-1}. These differences are understandable since close packing of the monomer domains is observed in the polymerisation of the first system, while in the polymerisation of the second the domains are distributed over a larger area and regions with a free water surface are present between them. On compression of the smaller layer, close packing cannot be achieved. The monolayer of a specimen polymerised in block, dissolved and deposited on the surface of water, is unstable and has a low decomposition pressure (Fig. 12). Evidently, the self-organisation of the monomer molecules on the surface of water is more effective than that of the molecules linked to one another into a long chain.

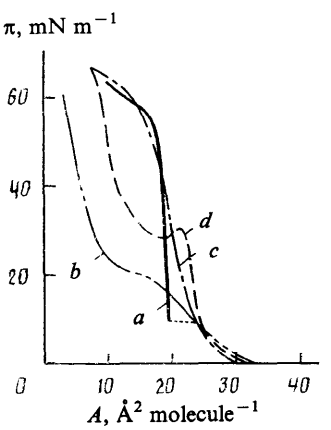


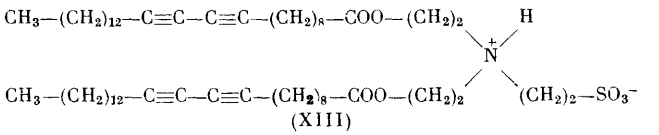
Figure 13. Compression isotherms for the $C_{14}C_8$ polymer at 20 °C: *a*, polymerisation at π = 10 mN m^{-1}; *b*, polymer obtained in block; *c*, polymerisation at π = 0 and A = 60 Å^2 molecule^{-1}; *d*, monomer.[41]

Fig. 12 illustrates the kinetics of the shrinkage of the monolayers for different polymerisation conditions.[41] Polymerisation in the presence of O_2 leads initially to a slight shrinkage, after which appreciable expansion is observed. Evidently, the formation of the polymer is followed by the ozonolysis of the conjugated bonds with formation of hydrophilic groups. This is shown by IR spectroscopic data indicating the appearance of bands at 1255, 1020, and 800 cm^{-1}. As can be seen from Fig. 12, the polymerisation is influenced by the ionic charge and the pH of the subphase. The salts of singly charged ions (Li^+, Na^+, and K^+) polymerise at high pH with shrinkage, by analogy with acids on the surface of water. On the

Consequently, the highly organised rigid two-dimensional structure of polydiacetylenes can be obtained only by the polymerisation of the monomer on the surface of the liquid.

The topochemical control of the polymerisation reaction in the monolayer imposes fairly rigid conditions of the packing of the monomer molecules.[14,44,45] It would appear that, if diynoic acids polymerise in the monolayer and at π = 0, then the photopolymerisation of the monolayer in the solid state should be achieved without obstacles. However, the acid $C_{12}C_8$ does not exhibit photoreactivity at high degrees of compression (A_0 = 23 Å^2 molecule^{-1}, pH 6.8),[44] while the two-chain diyne lipid (XIII)

polymerises only in one of two solid phases, namely in the less condensed phase A at $\pi \leqslant 20$ mN m^{-1} (Fig. 14).[14,43]



(XIII)

The causes of such behaviour are revealed by the schematic disposition of the lipid molecules in phases A and B illustrated in Fig. 14. The vertical displacement of the molecules relative to one another prevents the topochemical polymerisation reaction. By varying the composition of the support and temperature, it is possible to influence the region corresponding to the existence of each phase. The data of Tamura et al.,[44] who established the decrease of the reactivity of the acid $C_{12}C_8$ with decrease in the area of the monolayer, are consistent with these ideas. However, in his study of the behaviour of the two acids with different positions of the diyne group ($C_{16}C_8$ and $C_{16}C_0$), Collins[38] arrived at the opposite conclusion. The acid containing the unsaturated bonds in the centre of the chain was distinguished by a much lower reactivity in the monolayer.

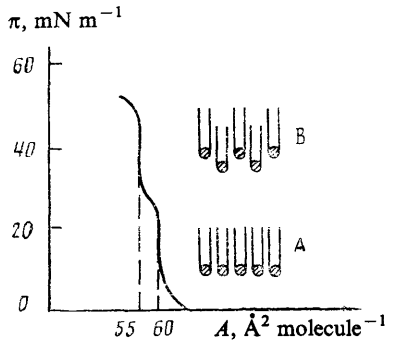


Figure 14. The surface pressure–area relation for the monolayer of the diyne lipid (XIII) at 41 °C at pH 2.[43]

The combination of data obtained by means of the Langmuir balance with UV spectroscopic data,[46] which presents no serious technical difficulties, makes it possible to follow *in situ* the polymerisation in the monolayer on the surface of water. In contrast to monomer monolayers, the polymerised monolayers of diacetylenes strongly adsorb in the visible region. For this reason, the observation of the variation of the optical density with increase in the duration of UV irradiation yields information about the degree of conversion of the monomer. Differences between the reflection spectra of the monolayer of the acid $C_{14}C_8$ on the surface of pure water and on that of an aqueous $CdCl_2$ solution have been recently established.[47] In the former case (254 nm; 0.4 mW cm^{-2}; 15 °C; 20 mN m^{-1}; 26.5 Å^2 molecule^{-1}; N_2) (Fig. 15*a*), the blue form of the acid (610 nm), formed in the initial stages of the polymerisation reaction, is converted into the red form (529 nm) with increase in the duration of UV irradiation. Similar spectra have been published in another communication,[46] where it is noted that the red form can be obtained also after prolonged heating of the blue form at temperatures above that of the phase transition of the monomer. In the polymerisation of the monomer on the surface of the $CdCl_2$ solution (4×10^{-4} M; pH 6.5; 20 mN m^{-1}; 22.3 Å^2 molecule^{-1}) on which it is more close-packed, only the red form can be detected (Fig. 15*b*). This effect can be explained by the differences between the mechanical stresses arising in the polymerisation of monolayers having different limiting areas. Indeed, as can be seen from Fig. 16, an increase in surface pressure is accompanied by an increase in the intensity of the band corresponding to the red form of the partly polymerised monolayer of the acid $C_{14}C_8$ on the surface of water and a decrease in the intensity of the band due to the blue form.[47] These stages are reversible and are reproduced in a large number of cycles (Fig. 17).

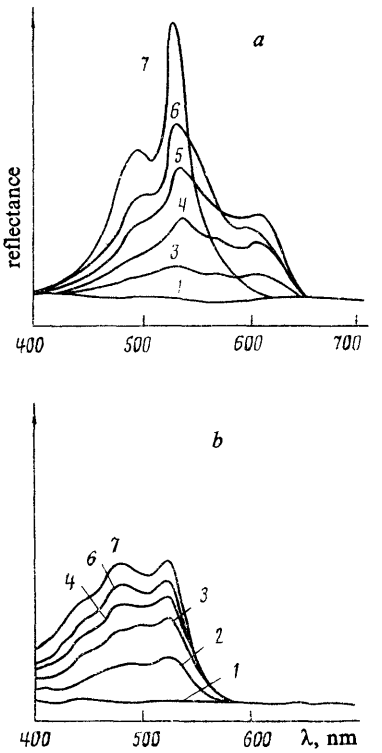


Figure 15. The reflectance spectra of monolayers of the diynoic acid $C_{14}C_8$ on the surface of water (*a*) and of an aqueous $CdCl_2$ solution (*b*); UV irradiation time (min): *1*, 0; *2*, 10; *3*, 20; *4*, 30; *5*, 40; *6*, 50; *7*, 100.[47]

The reversibility of the photochromism is based on the deformation of the monomer monolayer lattice, i.e. is determined by the phase transition induced by the change in surface pressure. It has been noted[44] that the reversible transition between the red and blue forms of the acid $C_{12}C_8$ in the monolayer, observed when the pH of the support is varied between 5 and 6, is not associated with the

isomeric changes in the main polymer chain (transformation of the diacetylene bonds into butatriene bonds) but is related to the structural disordering of the side chain. For the monolayer of the symmetrical diacetylene containing urethane groups [compound (XIV)], reversible photochromism is not observed owing to the strong interactions between the side chains.[47]

$$R{-}C{\equiv}C{-}C{\equiv}C{-}R,$$

(XIV)

$$R = -(CH_2)_4{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2)_3{-}CH_3 \ .$$

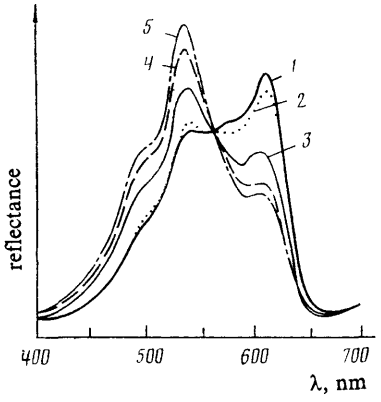


Figure 16. Reflectance spectra of a partly polymerised monolayer of the diynoic acid $C_{14}C_8$ at the nitrogen/water interface for different surface pressures (mN m^{-1}): *1*, 3; *2*, 14; *3*, 20; *4*, 24; *5*, 25.[47]

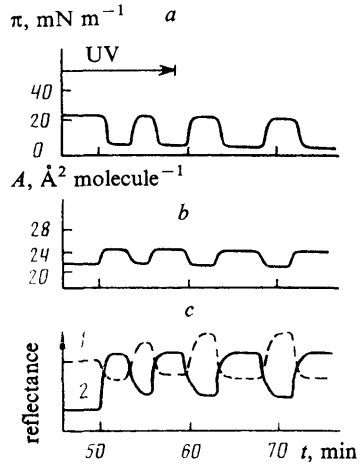
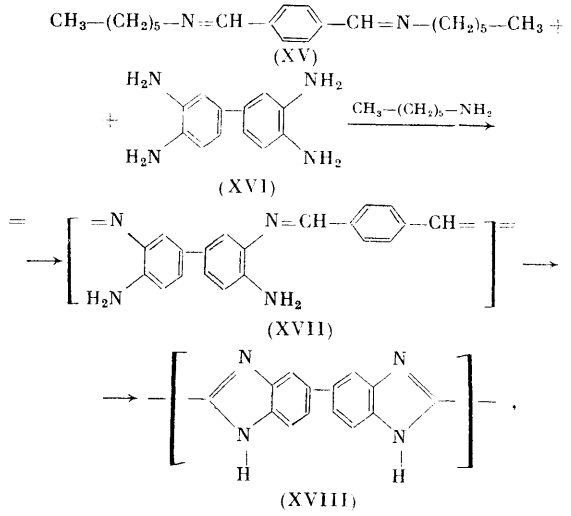


Figure 17. Reversibility of the photochromism of the partly polymerised monolayer of the diynoic acid $C_{14}C_8$ at the nitrogen/water interface in compression–expansion cycles: *a*, surface pressure; *b*, area per molecule of the monolayer; *c*, reflectance at the band maxima with different λ (nm); *1*, 535; *2*, 610.[47]

3. Polycondensation reactions and polymer-analogue transformation.

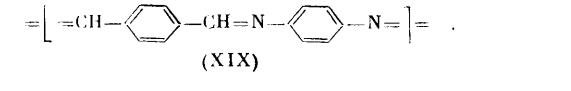
The polycondensation reactions in monolayers have not so far become very common owing to the more rigid requirements as regards the reacting compounds and the conditions of the synthesis: the compatibility of the components in the binary monolayer, the solubility in the support of one of the reactants and its adsorption on the monolayer of the other, desorption of low-molecular-weight reaction products from the monolayer, etc. One can state confidently that much more attention will be devoted to these reactions in the immediate future because with their aid it is possible to obtain two-dimensional ensembles with unique properties.

The synthesis of aromatic polybenzimidazoles in accordance with the scheme[48]



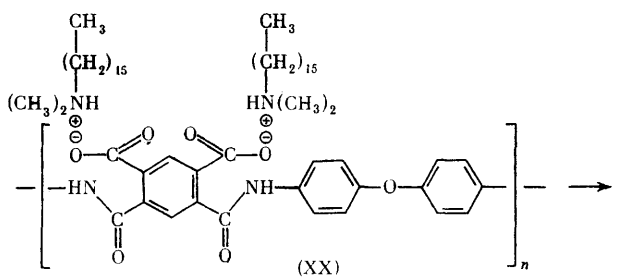
is instructive in this respect. The monolayer of dialkylterephthalaldimine (XV), which, as can be seen from the scheme above, contains no long alkyl chain, is formed on an acidified aqueous support containing the tetramine (XVI). The polyanil (XVII) formed, is converted into the polybenzimidazole (XVIII) as a result of the oxidative cyclodehydrogenation reaction. The latter reaction, controlled by the transport of oxygen and occurring in the monolayer on the surface of water at room temperature, does not occur in a LBF (21 layers) even at 120 °C. This can be readily demonstrated by the absence of changes in the colour of the LBF and is confirmed by optical spectroscopic data. The complete conversion in the LBF is attained at temperatures above 220 °C and such films are stable in air at 420 °C.

A similar approach has been used in the synthesis of thermostable aromatic Schiff bases from dioctadecylterephthalaldimine, forming the monolayer, and *p*-phenylenediamine introduced into the support.[49] The polycondensation reaction leads to a significant expansion of the monolayer and, with increase in the concentration of the diamine in the support, this effect intensifies and the resulting polymer [polyphenylterephthalaldimine (XIX)] has a higher molecular weight.

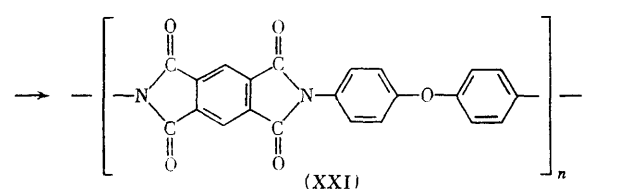


(XIX)

It is of interest to note that this synthesis cannot be carried out in solution owing to the rapid crystallisation of terephthalaldimines, while the polymer (XIX), synthesised by an alternative procedure from the corresponding aldehyde and the diamine, does not dissolve in solvents suitable for deposition and does not form a monolayer on the surface of water. Consequently, the polycondensation in the monolayer and subsequent formation of the LBF (Z-type, 25 layers) is the only procedure for the preparation of organised ensembles of the polymeric aromatic azomethine (XIX), whose thermal stability is high. The foregoing refers to ultrathin films of polyimides. Hitherto, the minimum attainable thickness of such films, obtained on a rotating support from solutions of a polyamidoacid with subsequent conversion into the imide form (thermal at 300 °C or chemical in a mixture of acetic anhydride and pyridine) was 0.1 μm.[50] Films with a thickness corresponding to between one and two hundred layers can be obtained with the aid of monolayers and LBF. For this purpose, one obtains initially monolayers of the alkylamine salt of the polyimidoacid (XX) on the surface of water and then, after the transfer to a solid support, the chemical conversion into the imide form is carried out:[50,51]



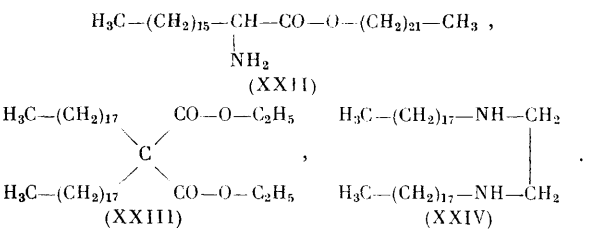
(XX)



(XXI)

The structure and electrical and mechanical properties of the LBF of poly *N,N'*-bis(phenoxyphenyl)pyromellitimide (XXI) have been investigated,[52] while in another study[53] it was demonstrated by scanning tunnel microscopy that the structural organisation of the monolayer on the surface of water is retained also after its transfer to the surface of highly oriented pyrolytic graphite.

Polycondensation in monolayers of long-chain α-aminoacids, diamines, and diesters has been described.[14,54] Naturally, together with the head group and the alkyl chain, the pH of the support exerts a major influence on the structure of the monolayer. The ionisation of the amino-group on an acid subphase leads to a more expanded state of the monolayer with a lower decomposition pressure than on an alkaline subphase. In the polycondensation of docosyl 2-aminooctadecanoate (XXII), the expansion of the monolayer was observed, while the monolayer of the polymer formed on reaction of diethyl 2,2-dioctadecylmalonate (XXIII) with *N,N'*-dioctadecylethylenediamine (XXIV) occupies a smaller area than the initial 1 : 1 mixture of compatible monomers.



(XXII)

(XXIII) (XXIV)

The oriented polypeptide films thus formed served as models of biomembranes.[54]

One of the effective ways of constructing new macromolecules and their organised ensembles with various functions involves carrying out polymer-analogue reactions in monolayers. However, with the exception of the elegant studies by Fariss et al.,[55] there have been virtually no studies on this aspect of the field. This confirms yet again the considerations put forward above concerning the low degree of utilisation of the possibilities of the subphase for reactions in monolayers.

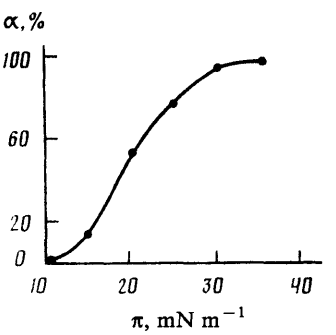


Figure 18. Dependence on surface pressure of the degree of conversion (α) of octadecyl acrylic acid in the monolayer on the surface of water.[55]

The aim of the study mentioned above was to increase the resulting capacity of an electronic resistor based on polyoctadecylacrylic acid by grafting aromatic ester groups to it. Since monomeric esters do not polymerise in the monolayer, a monolayer of octadecylacrylic acid (XXV) was formed initially on the surface of water and photopolymerised. Next benzyl alcohol (XXVI) was introduced into the support and a polymer-analogue reaction (esterification) was carried out. The degree of conversion α of the polymeric acid depends on the degree of polymerisation, the unpolymerised acid being apparently incapable of esterification. The degree of conversion of the monomer (XXV) is in its turn determined by the surface pressure at which it is polymerised in the monolayer, reaching 100% at $\pi = 35$ mN m^{-1} (Fig. 18). The degree of conversion of the acid groups of the polymer depends in a

complex manner on the pH of the subphase and varies from 0 to 70% with decrease in pH (Fig. 19), the degree of conversion of the monolayer greatly exceeding the maximum degree of conversion attained in aqueous solution. The linear resolution achieved by Schaefer's method of the 20 layer LBF of the polyester (electron-beam resistor) reaches 80 nm.

$CH_3-(CH_2)_{17}-C(=CH_2)-COOH$ (XXV); $HO-CH_2-C_6H_5$ (XXVI).

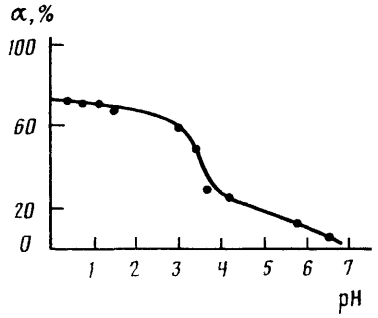


Figure 19. Dependence of the degree of conversion of the acid groups into ester groups of poly(octadecylacrylic acid) in the monolayer on the surface of water on the pH of the support.[55]

The high sensitivity of the organisation of the monolayer to changes in a large number of system parameters facilitates the control of their assembly and can be used for molecular switching. We shall consider the switching mechanism based on a phase transition in monolayers of silane lipids containing different numbers of hydrocarbon chains:[56] [γ-(*N*-octadecylsuccinylamino)-propyl]-triethoxysilane (XXVII), [γ-(*N*, *N*-dioctadecylsuccinylamino)-propyl]-triethoxysilane (XXVIII), and tris(octadecanoyloxy-methoxy)({[γ-(triethoxysilyl)propyl]succinyl}amino)methane (XXIX).

$CH_3(CH_2)_{17}-NHCO-CH_2-CH_2-CONH-(CH_2)_3-Si(OC_2H_5)_3$ (XXVII).

$(CH_3(CH_2)_{17})_2N-CO-CH_2-CH_2-CONH-(CH_2)_3-Si(OC_2H_5)_3$ (XXVIII).

$(CH_3(CH_2)_{16}COO-CH_2)_3C-NHCO-CH_2-CH_2-CONH-(CH_2)_3-Si(OC_2H_5)_3$ (XXIX).

Fig. 20 demonstrates the influence of the number of chains and of the pH of the support on the state of the monolayers of silane lipids. On an acid support (pH 2), all lipids form solid monolayers. At pH 5.8, the monolayers of compounds (XXVII) and (XXVIII) expand, while the monolayer of the three-chain lipid (XXIX) remains in the solid state. According to IR Fourier spectroscopic data,[56] at these pH the monolayers of the monomers do not hydrolyse. The lipids are therefore subjected to polycondensation at pH 2. The polymerisation on the surface of water leads to the formation of a brittle monolayer of the single-chain silane (XXVII) and of an elastic monolayer, suitable for transfer to a solid support, of the two-chain lipid (XXVIII). The three-chain lipid (XXIX) does not polymerise on the surface of water due to steric hindrance. The monolayer method makes it possible to determine directly the molecular weight of the polymer during the reaction. The molecular weights of the silane lipids, calculated by the equation

$$M_w = RT/(\pi A)_{\pi \to 0},$$

for $\pi < 0.2$ mN m^{-1} amounted to $(6-15) \times 10^4$ after 60 min from the start of the polymerisation. On heating the monolayer of the polymerised compound (XXVIII), a phase transition is observed from the solid to the liquid-crystal state, whose temperature (T = 44 °C) agrees with the transition temperature found by differential scanning calorimetry for an aqueous solution of this lipid. At this temperature, the permeability of the monolayer of the polymerised lipid (XXVIII), deposited on the surface of porous glass by the Langmuir–Blodgett method, to NaCl and a fluorescent probe charges by an order of magnitude.[56]

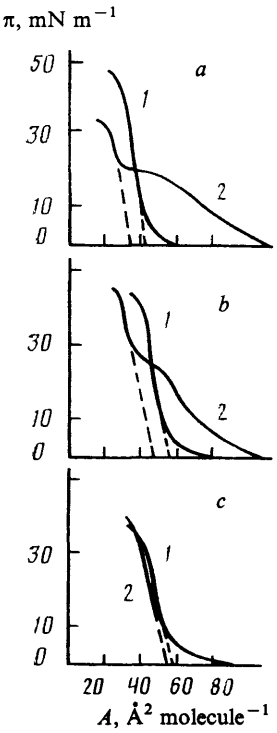


Figure 20. The surface pressure/area isotherms for the monolayers of single-chain (*a*), two-chain (*b*), and three-chain (*c*) silane lipids: *1*, pH 2; *2*, pH 5.8.[56]

Evidently, the possibilities of molecular switching based on a phase transition, predicted to occur in the stage involving the formation of the polymer monolayer, are not restricted by permeability. Another important aspect of the studies of monolayers and LBF of silane compounds is the modelling of decorative layers (of γ-aminopropyltriethoxysilane, etc.) for adhesion polymer systems,[57] the mechanism of the action of which still remains unexplained[58] despite vigorous investigations.

IV. Polymerisation reactions in Langmuir–Blodgett films

1. Diacetylenes

The structure of the LBF of monomers is determined by the transfer conditions, the organisation of the monolayers on the surface of water, and the properties of the solid support.

On the geometrically and energetically uniform surface of water, it is impossible to create an extended monolayer of diacetylenes with identical orientation of the monomer molecules. The attempts to increase the area of the domains in the monolayer, which are of great practical interest, have been at the centre of attention of investigators. The reported formation of regions in the monolayer with a uniform orientation having an area of several square centimetres[59] on spreading a 1:1 mixture of diacetylenic acid and hexadecane from a solution in chloroform was checked.[40] The author also used benzene as the solvent and together with hexadecane applied octadecane (from 1 to 33 mol%) for the formation of the binary monolayer. The largest domains (100 × 500 μm) are formed in a monolayer of the pure acid $C_{12}C_8$, deposited from benzene, and the smallest (from 1 × 1 to 1 × 10 μm) are produced in the system subjected to the test. The morphology of the monolayer on the surface of water is appreciably influenced by the solvent, admixtures and additives, the temperature and composition of the support, and the surface pressure.[40] Impurities in chloroform (ethanol) diminish the size of the domains.[60] The use of hexane, octane, cyclohexane, or aromatic hydrocarbons as the solvent instead of chloroform increases the size of the domains by a factor of 10. The dynamic annealing of the monolayer of the acid $C_{14}C_8$ leads to the transformation of the structure of the monolayer and the formation of domains whose size amounts to several square millimetres.[61]

As in the monolayer on the surface of water, the polymerisation of diacetylenes in the LBF is topochemically controlled. This type of reaction takes place without diffusion and with minimal movements of the molecules forming the crystal lattice.[62] Since the reaction zone is characterised by a definite size and form, which depend on the structure of the lattice, the topochemical control presupposes minimal changes in the form and size of the zone (minimal deformation of the surface zone) during and at the end of the polymerisation reaction.[63,64]

Fig. 21 illustrates schematically the topochemical polymerisation reaction.[64] The transformation from the monomeric to the polymeric single crystal is accompanied by the concerted rotation of the monomer units. This transformation can be regarded as a special case of a phase transition. Bubeck[64] divided topochemical reactions into two subtypes—homogeneous and heterogeneous. In the former case (Fig. 22*a*), the products form a solid solution with a statistical distribution in the lattice of the initial material. This case occurs in the absence of causes increasing the reactivity of the monomer (lattice defects, traps, etc.). With increase in the degree of conversion and with a significant difference between the lattice parameters of the monomer and the polymer, the limit of solubility may be reached. This leads to the formation of a new phase, which may induce perturbations in the structure of the initial lattice and hence arrest further polymerisation.

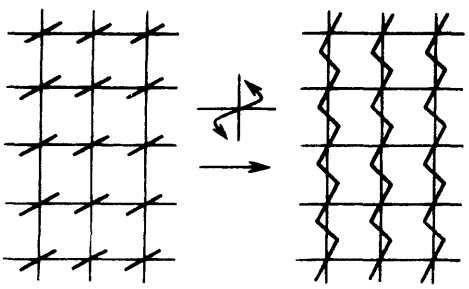


Figure 21. Schematic illustration of topochemical polymerisation.[64]

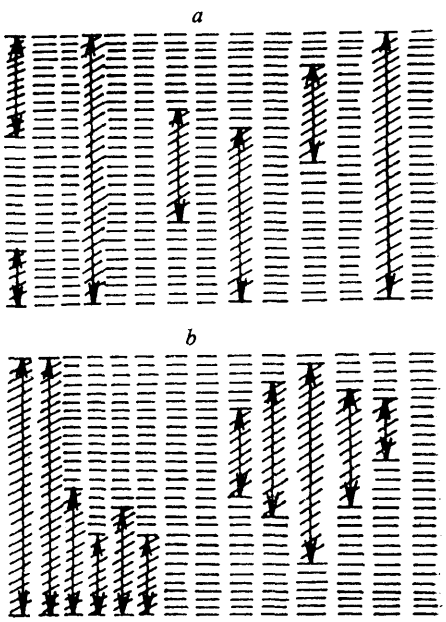


Figure 22. Schematic illustration of homogeneous (*a*) and heterogeneous (*b*) topochemical polymerisation.[64]

The heterogeneous subtype of the reaction (Fig. 22*b*) presupposes the presence of a phase structure in the reaction products within the monomer matrix already in the initial stages of conversion. It occurs when the product formed is capable of increasing the reactivity of the monomer. Evidently, the nucleation of the phase regions can also be induced by the presence of random impurities or special additives in the monomer lattice.

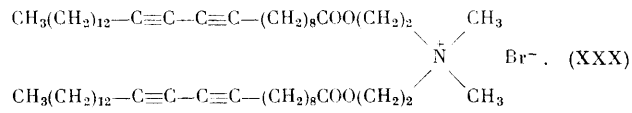
The high transparency of the LBF of diacetylenes and the change in their colour on polymerisation make it possible to monitor visually the course of the polymerisation and quantitative studies of photochemical processes. Significant differences in the photochemistry of the polymerisation of diyne surfactants on the surface of water and in the LBF are not usually observed. Admittedly, differences in the behaviour of these two systems have been inferred[13,65] from the fact that the absorption spectra of the monolayer on the surface of water have an isosbestic point, in contrast to the LBF. This point reflects the presence of a direct transition between the electronic structures of the blue and red forms of the polymers without passage through any intermediate states. Its existence in the spectra of the monolayers might be associated with the greater mobility and capacity for reorganisation of the molecules on the surface of the liquid.[13] However, the latest data for the acids $C_{14}C_8$ (Fig. 15)[47] and $C_{12}C_8$[44] do not confirm the presence of an isosbestic point in the spectra of monolayers on the surface of water. The incomplete clarity of the picture as regards photochromic transitions in monolayers and LBF is also indicated by the wide variety of interpretations of these transitions. Among the causes responsible for the photochromic transformations, the following have been discussed: the influence of the isomerisation of bonds,[66] the conformational transformations,[67] aggregation effects,[68] disordering of the side chains,[44] and the stresses arising in the polymerisation process.[69] Probably the above effects make different contributions to the photochromic transformations of polyacetylenes in monolayers and LBF. Here it is necessary to take into account the fact that in the case of LBF oxygen hardly affects the polymerisation reaction and also data[44] indicating the reversibility of the photochromic transitions in monolayers and their irreversibility in LBF.

Monochromatic light with the wavelength $\lambda = 254$ nm is usually employed for polymerisation of LBF of diacetylenic surfactants. The absorption band of the monomer is located in precisely this region of the spectrum and the polymerisation reaction is therefore initiated by the absorption of a photon by the diyne group, the quantum yield ($\Phi = 10$) showing that the absorption of one photon initiates the formation of the entire polymer chain.[70] If the specimen is subjected to preliminary pulsed irradiation by monochromatic light with a short wavelength, then the subsequent polymerisation proceeds on exposure to light with $\lambda \leqslant 500$ nm. Since the photopolymerisation should not occur under these conditions, it has been assumed[13,64] that the oligomer formed on UV irradiation induces the self-sensitised polymerisation. Sensitised polymerisation in the visible region is observed when the LBF of diacetylenes are doped with dye molecules. This process has been investigated in detail by Bubeck et al.[71] in relation to electron-donating and electron-accepting dyes. The quantum yield of this type of polymerisation is extremely low: the dye molecules must absorb a thousand photons for one monomer molecule to react.

The examples of photochemical reactions examined refer to two subtypes of topochemical polymerisation reactions: homogeneous and heterogeneous.[64] When LBF are irradiated with monochromatic light at $\lambda = 254$ nm, the excitation of the monomers and hence the initiation of the reactions assume a statistical character and lead to the homogeneous growth of polymer chains in the lattice. For longer wavelengths at which the sensitisation or self-sensitisation of polymerisation takes place, the reactions involve primarily monomers present near the dye or oligomer molecules. This leads to the heterogeneous growth of the polymer phase in the monomer matrix and to a less perfect morphology of the film.

Annealing exerts an appreciable influence on the structure, the spectroscopic properties, and the polymerisation of diyne surfactants in LBF.[40,44,72] Heating of the LBF of the $C_{10}C_8$ acid at 40–80 °C and the subsequent photopolymerisation result in the appearance of a new intense band in the absorption spectra at $\lambda = 704$ nm (blue form) and also increase the degree of order in the layers (X-ray diffraction). Annealing at $T > 90$ °C leads to the breakdown of orientation in the LBF and precludes its polymerisation.[72] Under these conditions, the band at 704 nm vanishes, which indicates its relation with the organisational structure of the LBF. On the other hand, breakdown of order has been observed[40] in the LBF of $C_{12}C_8$ together with a decrease in reactivity at an annealing temperature exceeding only 59 °C. If one bears in mind that the melting points of these monomers differ by only 4 K,[13] then the differences in the behaviour of the acids cannot be explained from the standpoint of the given phase transition.

The degree of conversion of the monomer and the rates of the polymerisation reactions, which determine their effectiveness, have remained little investigated and there are no reliable data for the molecular weights of the polymers obtained in LBF. For example, the M_w for diyne surfactants, obtained from viscosity data,[73] proved to be 200 000, while according to the view of Göbel et al.,[45] based on diffraction studies, in the polymerisation of dimethylbis(2-hexacosa-10,12-diynoyloxyethyl)ammonium bromide (XXX) the chain length does not exceed 50 units.



(XXX)

Evidently these parameters are affected by the same factors which determine the photochemistry of the polymerisation reactions described above and the morphology of the LBF considered below. The complete conversion in the LBF is not attained in photopolymerisation with topochemical control and the approach to the maximum degree of conversion is asymptotic.[16] This is associated with the fact that either the packing of only some of the molecules in the layers corresponds to the topochemical control, or that the structural organisation of the layers breaks down in the course of the reaction, or is caused by both factors. The complete conversion is attained on irradiation of diacetylenes with X-rays or γ-rays,[74] whereupon the quantum yield is 10^{12} [sic. (Ed. of Translation)].

The polymerisation of diynes containing a second functional group [for example, compound (XXXI)] is of interest because it can be carried out in two stages by irradiating the LBF with light at different wavelengths characteristic of each type of reactive group.[16] By alternating the irradiation, it is possible to vary the architecture of the change in the LBF at will.

$$CH_3(CH_2)_{13}—C\equiv C—C\equiv C—(CH_2)_8—CH_2—OOC—CH=$$
$$= CH—COOH.$$
(XXXI)

Structural-morphological studies on LBF are carried out by X-ray diffraction (small angle scattering, fine structural analysis in the vicinity of the edge of the X-ray absorption), electron diffraction,

different versions of optical spectroscopy, electron and polarisation-optical microscopy, scanning tunnel microscopy, X-ray photoelectron spectroscopy, surface plasma resonance, etc.

LBF made up of diacetylenes have as a rule a Y-structure with hydrocarbon chains inclined relative to the normal to the support at an angle of 30–50°.[16,65,75] The preparation of polar LBF of diacetylenes (X- and Z-types) requires special procedures.[76] Like the sublayers of aliphatic acids, diacetylenic LBF can crystallise spontaneously with formation of a three-dimensional lattice.[13] This tendency intensifies with decrease in the overall length of the acid chain.[77] The crystal structures of the monomeric and polymeric LBF of diynoic acids and the alcohol $C_{10}C_2$ are identical with the structures of these specimens in bulk-phase crystals.[78]

The polymerisation of diyne surfactants leads to an increase in the repeat period and to a decrease in the angle of inclination of the chains to the normal. The increments in the repeat period depend on the surfactant structure and reach 30% for the acid $C_{16}C_0$.[65] However, comparison of the structures of the LBF and a sputtered film of the acid $C_{10}C_8$ [79] led to the unexpected conclusion that the degree of order in the LBF is smaller and that on polymerisation the angle of inclination to the normal increases for the LBF and diminishes for the sputtered films. These differences may be caused by the instability of the polymerisation LBF on exposure to X-rays: in the determination of the structures of the films by fine structural analysis near the edge of the X-ray absorption (EXAFS), the blue form of the LBF is converted into the red form, whereas the sputtered films remains unaltered in the visible part of the spectrum. Polymerisation takes place in each layer (with the exception of ω-derivatives) and the macromolecular chain is arranged parallel to the support. The cations distributed between the head groups of neighbouring monolayers do not form an intrinsic lattice. As a result of the polymerisation, the initial domain texture of the monomeric LBF is established. In the domains, the macromolecular chains are packed parallel to one another but the orientations of the chains in different domains differ. The shrinkage accompanying the polymerisation of the LBF predicates the appearance and growth of cracks and cavities. The sharp difference between the changes in the volume of the unit cell on polymerisation, found[78] for the acid $C_{10}C_2$ and the alcohol $C_{10}C_2$ (388 and 217 Å^3 respectively) is reflected in the texture of the LBF: in contrast to the polymeric acid, the diyne polymeric alcohol forms significantly less effective polymer structures. The thickness of the LBF, the number of layers, and the changes in the repeat period also influence the degree of defectiveness of the polymeric LBF.[76] The mechanical properties of the LBF are determined on the basis of their ability to cover the pores of solid supports without being ruptured.[16]

In conclusion it must be emphasised that at the present time a fairly detailed analysis of the behaviour of monolayers and LBF of diphilic monomers can be achieved only for diacetylenic surfactants because none of the monomers of other classes have been subjected to such intensive and comprehensive studies in organised systems.

2. Polymerisation of diphilic monomers containing multiple bonds in the ω-position

The bias in the studies on the polymerisation of monomeric surfactants in LBF is in many respects due to their use as resistors. This applies fully to ω-tricosenoic acid (XXXII) and its salts.

$$CH_2{=}CH{-}(CH_2)_{20}{-}COOH\,.$$
(XXXII)

The polymerisation of ω-tricosenoic acid in Y-type LBF (electron beam) takes place via an ionic mechanism, which is indicated by the low activation energies, the insensitivity to the presence of free radicals and oxygen, and the first order of the reaction.[80] The angle of inclination of the aliphatic chains to the normal for the monomeric LBF depends on the surface pressure at which the monolayer is transferred to a solid support (π_{tr}). According to X-ray diffraction data,[81] this angle is 33°, 30°, and 27° for π_{tr} = 20, 25, and 30 mN m^{-1}. During polymerisation, the angle of inclination increases by 4° and the film itself becomes less ordered.[80] There is a close relation between the structure of the LBF of the polymerised acid (XXXII) and the characteristics of its multilayer ensembles used as electronic resistors in microlithography. The high contrast and sensitivity of the negative resistors based on the acid are due to the monodispersity of the polymer and the coherence of the LBF. The first fact can be explained by the appearance of mechanical stresses in the solid-phase polymerisation of the monomer, which limits the growth of the chains, and the second is caused by the high packing density of the hydrocarbon chains.[82,83] It is of interest to compare the properties of multilayers of ω-tricosenoic acid obtained by the Langmuir–Blodgett method and vacuum sputtering. The larger repeat period for the LBF (56.3 Å at π_{tr} = 30 mN m^{-1} compared with 49.6 Å) and the smaller angle of inclination of the chains (27° and 38° respectively) indicate a more organised structure of the acid in the LBF.[81] Peterson and Russell[84] do not rule out the possibility of the epitaxial growth of the multilayers when ω-tricosenoic acid is deposited on a solid support.

The high interlayer adhesion in the LBF of ω-tricosenoic acid shows that polymerisation is possible not only in the plane of the layers but also between them. It is of interest[85] that the solid-phase polymerisation is initiated by the defects of the crystallites in the vicinity of which the orientation of the atoms readily changes. The interface between the layers of the LBF can be regarded as a controlled defect.[86] Therefore in this particular region with a low structural organisation the initiation and growth of the chains are most likely. Furthermore, the interlayer polymerisation in Y-type LBF of ω-compounds can be facilitated by the penetration of the ends of the chains into neighbouring layers. This feature is apparently characteristic of all ω-monomers forming Y-type LBF and, depending on the purpose of the LBF, the high interlayer adhesion can play both a positive and a negative role. In order to eliminate polymerisation between the layers, it is useful to generate polar X- or Z-structures, although this can be by no means always achieved, or to obtain alternating LBF separating the monomer monolayers by inert (for example, aliphatic acid) intervening layers.[80,86] In order to prevent the interlayer polymerisation of the diynoic ω-acid C_0C_{20} in a LBF (Y-type, 135 monolayers), alternating polymeric structures with arachidonic acid have been obtained.[87]

3. Polymerisation of monomers containing multiple bonds in the polar component

The study of the monolayers and LBF of vinyl stearate and octadecyl acrylate has a long history.[88] Nevertheless, these classical subjects still remain within the range of interests of investigators.

In the radiation-induced polymerisation (^{60}Co) of vinyl stearate, there is no interlayer poymerisation problem because, regardless of the method of preparation of the LBF (Y- or X-transfer), only X-type multilayers are formed. The irradiation is carried out at low temperatures ($T \leqslant 0$ °C) at which the degree of conversion is low and then, after the removal of the radiation source, the post-polymerisation is carried out and its kinetics are investigated.[89] The

reaction proceeds via a free-radical mechanism, oxygen inhibiting the process as in polymerisation in a monolayer. At low pressures π_{tr} = 10–12 mN m^{-1}, the degree of conversion is low, which can be explained by the low packing density of the molecules. The increase of π_{tr} to 17–19 mN m^{-1} makes it possible to achieve 100% conversion of the monomer, which depends in its turn on temperature, the irradiation time and dose, and the temperature and duration of the post-polymerisation reaction. As a result of the polymerisation reaction, the orthorhombic structure of the monomer in the LBF is converted into the hexagonal structure of poly(vinyl stearate).[90] Mixed monolayers of vinyl and ethyl stearate are solid solutions for any component ratio.[88,90] These systems can be used to construct fairly thick (1000 layers) polar (X-type) skeletised LBF.

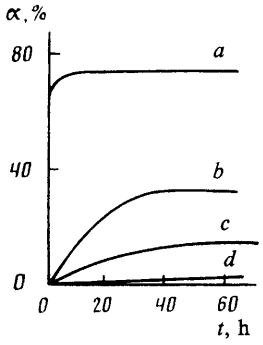


Figure 23. Dependence of the degree of conversion on the duration of the radiation-induced post-polymerisation of octadecyl acrylate in block (*a*, *d*) and in LBF (*b*, *c*): *a*, hexagonal lattice; *d*, triclinic lattice; *b*, X-type LBF; *c*, Y-type LBF; T = 20 °C.[91]

The slight differences between the chemical structures of the vinyl stearate (VII) and octadecyl acrylate (VI) molecules influence significantly the behaviour of these monomers in the LBF. Fig. 23 illustrates the dependence of the degree of conversion on the post-polymerisation time at 20 °C (^{60}Co irradiation at −196 °C) for X- and Y-type octadecyl acrylate LBF and also a block monomer in the hexagonal and triclinic crystal forms. Evidently the rate and limiting conversion depend on the type of LBF, the parameters assuming intermediate values between those for bulk-phase crystals of the two modifications.[91] The less dense packing of the X-type LBF obtained at low π_{tr} promotes higher rates of polymerisation and higher degree of conversion compared with Y-type LBF. The relative disposition of the curves in Fig. 23 of Ref. 91 led to the conclusion that hexagonal and triclinic packing corresponds to the X-type and Y-type LBF respectively. On comparing these results with the data presented above for vinyl stearate, it can be seen that the degree of conversion of the acrylic monomer is appreciably lower for the same X-type LBF and, in contrast to vinyl stearate, a higher rate and a higher degree of conversion correspond to smaller values of π_{tr}, affording LBF with less dense packing. However, the picture changes sharply in the photopolymerisation of octadecyl acrylate and vinyl stearate and the copolymerisation of their mixtures (Fig. 24). The rate of polymerisation and the degree of conversion of vinyl stearate in X-type LBF are much lower than for octadecyl acrylate in the same vinyl stearate LBF subjected to radiation-induced polymerisation.[92] With increase in the content of octadecyl acrylate in the mixture with vinyl stearate, the degree of conversion rises and reaches 95% for the LBF of the acrylic monomer (Fig. 24). The differences in the behaviour of these monomers have been explained[92] by differences between their structures, ensuring, in the case of octadecyl acrylate, the conjugation of the C=C and C=O bonds, which increases the reactivity of the monomer.

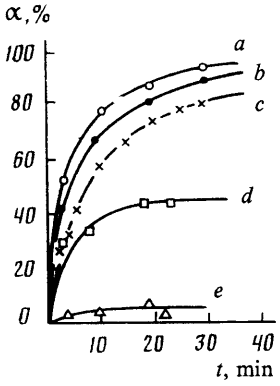


Figure 24. Dependence of the degree of conversion on the duration of the photopolymerisation of octadecyl acrylate (*a*), vinyl stearate (*e*), and their mixtures (*b*–*d*) in X-type LBF: *b*, 8:2; *c*, 1:1; *d*, 2:8; T = 10 °C, N_2.[92]

An exceptionally large increase (30%) in the repeat period has been observed[93] in the photopolymerisation of 2-eicosenoic acid (XXXIII) in a LBF (Y-type, up to 30 layers).

$$CH_3-(CH_2)_{16}-CH=CH-COOH\,.$$
(XXXIII)

The increase in this parameter during polymerisation reaction is accompanied by a phase transition between the monomer and polymer matrices. Since the phase separation in the concluding stage of the polymerisation reaction takes place via the migration of the monomer molecules and the formation of their clusters in the polymer matrix, it has been suggested[93] that the molecules in the layers possess a much higher mobility than has been assumed hitherto. The question of the possible involvement of the molecules of neighbouring layers of the LBF in the phase separation therefore requires elucidation.

An important difference between the photopolymerisation of 2-eicosenoic acid and vinyl monomers, examined above, is the absence of the influence of atmospheric oxygen on the polymerisation reaction, which is explained by the close packing of the hydrocarbon chains, preventing the diffusion of oxygen.[93] Although in our view this conclusion conflicts with the author's claim that the monomer molecules possess a high mobility, the fact itself is of undoubted practical interest.

The radiation-induced polymerisation[94] or photopolymerisation[95,96] of octadecylacrylamide (XXXIV) results in the formation of high-quality Y-type LBF which can be used as negative resistors.

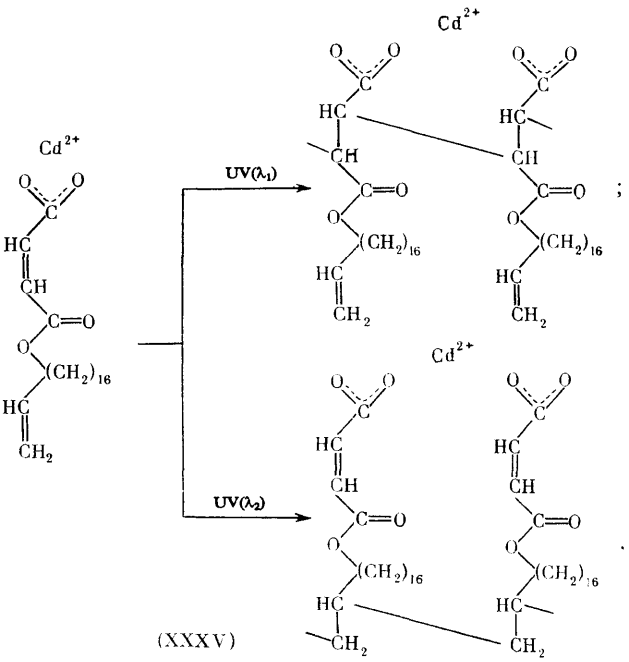
$$CH_3-(CH_2)_{17}-NH-CO-CH=CH_2\,.$$
(XXXIV)

According to X-ray diffraction, electron diffraction, and IR spectroscopic data,[94] phase transitions are not observed in the polymerisation process and the side chains retain their orientation.

A convenient object for the study of the influence of the configuration of the double bond or the organisation of monomers in the LBF and their polymerisation is provided by the isomers octadecyl fumarate (ODF) and octadecyl maleate (ODM) (IX). A thorough analysis was carried out by the low-angle IR transmittance and reflectance spectroscopy of the structures of the LBF (Y-type, 9 and 20 layers) obtained by transferring the ODF and ODM monomers from the surface of water onto a KRS-5 prism and an aluminium support and then polymerised, and of the LBF of polymers transferred from an aqueous support.[27] It was established that the molecular structure of the LBF is independent of the support on which the polymerisation has been carried out. The molecules of the cadmium salt of ODF are oriented along the normal to the surface of the support, whereas the molecules of its analogue have an appreciable angle of inclination, which is associated with the conformational limitations of the *cis*-configuration of the double bond of ODM. On polymerisation, a profound reorganisation of the molecules of the *cis*-isomer in the LBF takes place, as a result of which the aliphatic chains are arranged along the normal to the surface. Both monomers ultimately give rise to polymers whose IR spectra are indistinguishable. Two important features distinguish the LBF of these compounds. Firstly, there is a possibility of thermopolymerisation (up to 145 °C). Although it leads to a less ordered structure (thermally induced disorder accompanying polymerisation) compared with photopolymerisation, it has definite prospects. Secondly, the formation of non-shrinking LBF for a 1 : 3 ratio of ODF and ODM prevents the appearance of cracks and stresses in the multilayer structure. For these systems, it is of interest to determine the molecular weight of the polymer obtained in the LBF. It was noted above that the cessation of chain growth on polymerisation in two-dimensional structures and the formation of monodisperse polymers are associated with the appearance of stresses. If this mechanism is valid, then the molecular weights of the polymers obtained in the LBF from individual compounds and their mixture should differ.

4. Polymerisation of certain other diphilic monomers

The introduction of the double bond in the ω-position in octadecyl fumarate increases the ease of controlling the structure and properties of the LBF. Irradiation of ω-octadecenyl fumarate (XXXV) by UV light at different wavelengths leads to selective polymerisation:[97]



(XXXV)

If we recall that reaction between neighbouring layers is possible in polymerisation of monomers containing terminal double bonds (ω-tricosenoic acid) in Y-type LBF, then one can readily foresee the prospects for such bifunctional surfactants in the preparation of systems with high interlayer and intralayer adhesion. In alternating and polar LBF, compounds of this type are capable of forming polymer networks.

Long-chain derivatives of dienes also polymerise in two stages.[13] When the LBF of docosyl penta-2,4-dienoate (XXXVI), a monobasic dienoic acid ester, is irradiated with UV light (λ = 250 nm), the dimerisation reaction takes place initially in the first stage. It is rapid, the conversion is complete, and it involves only the C(3)=C(4) bonds. The second stage (polymerisation at λ = 210 nm) occurs at low rates and the degree of conversion does not exceed 80%:

$$CH_3-(CH_2)_{21}-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH_2\,,$$
(XXXVI)

$$CH_2=CH-(CH_2)_{21}-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH_2\,.$$
(XXXVII)

It is believed[98] that the differences between the reactivities of the C(3)=C(4) and C(1)=C(2) bonds are due to the different dispositions of these groups relative to the interlayer plane. The end groups have a greater freedom to change their conformation compared with the C(1)=C(2) groups located deeper within the lattice. In the analogous compound ω-tricosenyl penta-2,4-dienoate (XXXVII), containing a third double bond in the ω-position, there is

a possibility of a third polymerisation stage. Despite the fact that the vinyl groups in the ω-position are at the interface between the layers, polymerisation under the influence of the electron beam proceeds with difficulty.[98]

The monoesters of dibasic dienoic acids polymerise in LBF with 100% conversion.[16] Although the rate of the photopolymerisation reaction and the degree of conversion of hydrocarbon [compound (XXXVIII)] and fluorocarbon [compound (XXXIX)] derivatives of muconic acid are identical, their UV absorption spectra differ significantly.

$$CH_3(CH_2)_{16}CH_2-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH-COOH\ ,$$

(XXXVIII)

$$H(CF_2)_{10}-CH_2-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH-COOH\ .$$

(XXXIX)

This shows that the orientation environments of identical chromophoric groups in the LBF of these compounds are not the same. Evidently, the differences are established in the Y-type LBF formation stage: the fluorine-containing surfactants are transferred to a solid support for areas greater by a factor of 1.5 than the hydrocarbon muconates. The stability of the LBF of these compounds was estimated from their ability to cover pores (0.2 μm) in a polypropylene membrane. The monomeric and polymeric LBF (2–6 layers) of compound (XXXVIII) cover the pores without disrupting the coherence of the film. The LBF of compound (XXXIX) in any form are incapable of covering the pores. Such behaviour of the fluorocarbon muconic monoesters can be explained by the small chain length and by the weak interchain interactions.[16] On the other hand, tridecylpentadienoic acid, a hydrocarbon analogue of compound (XXXIX), does not form a LBF at all.[99]

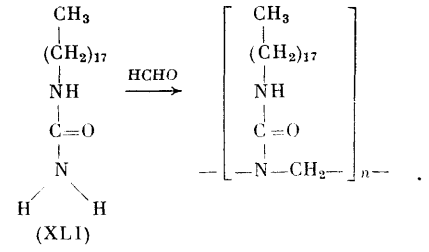
In contrast to diacetylenic derivatives, surfactants of the diene series, containing an unsaturated group at the edge or in the middle of the hydrocarbon chain, have remained uninvestigated. By analogy with diyne and ethylene surfactants, one may claim that the migration of the diene group along the chain in the direction of the polar group can initially reduce the stability of the monolayer and the quality of the LBF and then increase these characteristics of the system. The results of studies on the structure of the LBF made up of mixed monolayers of β-parinaric acid (XL) and stearic acid then lend a definite support to these considerations.[100]

$$\textit{trans}\text{-}C_2H_5(CH=CH)_4(CH_2)_7COOH\ .$$

(XL)

According to X-ray diffraction data the LBF consisting of the individual acid (XL) are amorphous and do not have a layered structure. With increase in the concentration of stearic acid, the degree of order in the LBF increases but polymerisation again disrupts the organised structure of the LBF.

A novel example of a polymerisation reaction in the LBF, leading to the formation of a network polymer, is provided by the polycondensation of octadecylurea (XLI) with formaldehyde, which diffuses into the LBF from the vapour phase:[86,101]



(XLI)

The methylene bridges connecting the polar head groups, do not prevent the close packing of the molecules in the layers. On raising the temperature, a network polymer is formed as a result of the interaction of formaldehyde with the NH groups.[102] Here we again encounter the situation where the reaction is possible only in the organised ensembles but not in the bulk phase.

V. Prospects for the application of polymeric Langmuir–Blodgett films

The prospects for the application of LBF may well satisfy those who indulge in the wildest fantasies. Fairly complete information has been published[1–4,12,103–107] about the possible applications of LBF, low-molecular-weight surfactants, and partly, polymeric surfactants. The majority of the applications of LBF comprising small molecules hold also for polymer systems. The molecular groups carrying a definite functional group are immobilised in the polymer (a network polymer is best) matrix by forming a mixed monolayer with the matrix or are grafted via a spacer of definite length in the side chain or the main chain of the polymer (polymer-analogue transformations, copolymerisation). An important advantage of such systems is that the "guest" molecules may not in fact possess pronounced surface-active properties and may not form their own stable monolayer on the surface of the liquid.

In any case, the application of LBF in both fundamental and applied research is based on the possibility of assembling uniform two-dimensional structures with a controllable thickness and orientation of the molecules in the layers. The controllable structural organisation of monomers in monolayers and LBF (the inclination of the molecules, the distances between them, the influence of the environment, the positions of the functional groups, isomerisation, etc.) make it possible not only to investigate the theoretical questions concerning polymerisation reactions in these systems but also to synthesise new materials, whose preparation is impossible under other conditions (in the melt, in solution, and in the solid phase).

The phase transitions in individual and mixed monomer monolayers, the thermodynamics and kinetics of polymerisation, copolymerisation, polycondensation, and grafting reactions, carried out under different physical influences (UV irradiation, electron beam, radiation, temperature) or under the influence of initiators and cross-linking agents introduced into the aqueous (monolayer) or gaseous (monolayer and LBF) phases, represent the range of

problems requiring nowadays an appreciably greater attention of investigators.

The molecular weights and molecular weight distributions of polymers, obtained when they are synthesised in monolayers, the mechanism of the termination of chain growth and of the formation of monodisperse polymers in LBF, and sensitised and self-sensitised photopolymerisation effects await a more detailed development.

Langmuir–Blodgett films provide a unique possibility of constructing models of boundary layers comprising combined (with polymers) materials, which constitute the basis of modern materials science.[57,108,109] The regulation of intralayer and interlayer polymerisation make it possible to generate gradient boundary structures with different levels and ratios of adhesive and cohesive strengths and a specified free volume, sorption-diffusion properties, stresses within cracks, etc. Consequently, the mechanism of the of adhesion interactions in polymer/metal and polymer/finishing agent/metal systems and the principles governing the protection of metals against corrosion by organic coatings associated with it may not only be comprehended at a deeper level but can also be used to create a new generation of polymeric protective coatings.[58,105,110] After considering reactions at the support/first LBF layer interface, Barraud et al.[86] identified the adhesion problem as the main one. When acids are deposited on an aluminium support coated by the oxide, salts are formed (for example, aluminium stearate) which ensure an effective adhesion to the support. The intensification of adhesion interactions with supports made of noble metals, germanium, and silicon constitute a more complex problem. Studies designed to devise gradient transition zones in polymer/adhesion junctions are being prosecuted at the Institute of Physical Chemistry of the USSR Academy of Sciences.

An important advantage of the organised layered structure of monomers is that certain polymers can be obtained only by polymerising monomers in the monolayer on the surface of a liquid or in a LBF or the formation of the LBF by them is possible only via the stage involving the synthesis of the polymer in the monolayer. In the former case, one is dealing with monomers polymerising under the conditions of a topochemical reaction, while in the latter the problem concerns polymers from which monolayers cannot be formed on the surface of water in view of their negligible solubility (polyimides, dense network polymers).

A wide range of compounds, polymerising in monolayers and in LBF, have been synthesised and used to devise models for biological membranes by Ringsdorf and co-workers.[14–20] The "architects" from Mainz (Federal Republic of Germany) have successively improved lipid molecules by introducing polarisable groups into the hydrophobic and/or hydrophilic parts of the molecules and by altering the length of the spacer in the side chain and/or the main chain. Ultimately the biomembrane models stabilised by photopolymerisation became very similar to the original.

Together with the use of polymer monolayers and LBF in fundamental research, polymers are used nowadays in modern engineering and in the first place as calibrated insulating and active layers in metal–dielectric–metal and metal–dielectric–semiconductor systems and also as optical and electron beam resistors in high-resolution microlithography.[1,76,81–83,95,96,111]

Much attention has been devoted recently to the study of non-linear optical effects in both centrosymmetrical and polar and alternating polymeric LBF.[1,3,4,103,112] The high non-linear susceptibilities in polydiacetylenes are due to the presence of chains of conjugated bonds. The influence of the length of the chain of conjugated bonds on the cubic magnetic susceptibility has been investigated[113] for LBF comprising mixed monolayers of arylbutadienes and hexatriyne with poly(isobutyl methacrylate). The introduction of hexatriyne into LBF makes it possible to obtain a longer chain of conjugated bonds compared with diyne derivatives and hence a greater intensity of the third harmonic signal.[113] The effects associated with the doubling of the frequency of the light (generation of the second optical harmonic) are being investigated using polar and alternating as well as centrosymmetric LBF in an electric field which eliminates the centre of inversion. Together with thin (several bilayers) films, LBF containing hundreds of bilayers began to be used.[114,115] The combination of non-linear optical properties of the LBF with the possibility of using them as light guides [optic fibres?][112,116] has opened up prospects for the application of these systems in integrated optics, in recording devices, and in information storage and reproduction devices.

The iodine-doped diacetylene LBF have a fairly high electrical conductivity. For example, whereas the specific conductances of LBF comprising diacetylenic acids containing a diyne group in the centre of the chain ($C_{16}C_8$)[117] and in the ω-position (C_0C_{20})[87] do not exceed 10^{-2} and 5×10^{-8} Ω^{-1} cm^{-1} respectively, after doping with iodine the specific conductance increases by 3–4 orders of magnitude. However, LBF comprising polythiophenes, whose electrical conductivity and stability are greater, are of major interest nowadays from this point of view.[118,119]

The possibilities of polymeric LBF as partition membranes have perhaps still not been utilised. The regulation of the thickness, structure, and composition of the LBF deposited on a porous support makes it possible to vary within wide limits the productivity and selectivity of membranes. Membrane gas-separation processes and processes involving the reverse-osmotic separation of solutions have been investigated using LBF comprising diacetylenes[120] and organosilicon[56] and other polymers.[121] An appreciable increase in the number of publications on this field is to be expected soon. They will discuss the properties of LBF partition membranes consisting of interesting compounds such as derivatives of cyclodextrins,[122–125] calixarenes,[126,127] crown-ethers,[21] and macrocyclic polyamides.[128]

* * *

In conclusion, it must be emphasised that the monomer polymerisation processes in monolayers and LBF examined in this part of the review together with the associated changes in the structural organisation and properties of these planar systems represent one aspect of the general problem of Langmuir–Blodgett polymer films. The second aspect involves analysis of the behaviour of monolayers and LBF of polymers synthesised by traditional methods. Although studies on the polymer monolayers, which are only part of this aspect, have long been prosecuted, much less attention is devoted nowadays to problems of the preparation of LBF and the relation between the properties of monolayers and LBF comprising macromolecules than to monolayers and Langmuir–Blodgett films comprising monomers. On the other hand, polymer monolayers have a series of specific features. These include the possibility of obtaining stable monomolecular films from water-soluble polymers and polymers without pronounced diphilic properties, a broad relaxation spectrum, and a high kinetic stability of monolayers. The above features of polymer monolayers will apparently attract in the immediate future the attention of specialists using LBF for the solution of applied problems. The author plans to devote his next review to the analysis of these systems.

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