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Polymer monolayers and Langmuir – Blodgett films. Polythiophenes

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Abstract. The structures and properties of monolayers and Langmuir – Blodgett films of conducting oligo- and polythiophenes are analysed. The published data on the influence of the number, size, and composition of substituents in polythiophene molecules and of the pattern of their distribution along the chain on the monolayer stability and Langmuir – Blodgett film quality are generalised. Considerable attention is given to the description of the behaviour of mixed monolayers and Langmuir – Blodgett films composed of polythiophenes and various amphiphilic compounds. The effective conjugation lengths of polymer chains and conductivities of polythiophenes in Langmuir – Blodgett films and cast films are compared. Examples of the use of Langmuir – Blodgett films for scientific and technological purposes are given. The bibliography includes 100 references.

I. Introduction

The Langmuir – Blodgett method is a versatile technique for assembling multilayer planar ensembles. The scope of problems that can be solved with the use of this method has expanded considerably over recent years. Polymer monolayers and Langmuir – Blodgett (LB) films play an important role in fundamental and applied molecular architecture studies. In the author's review,[1] the two-dimensional polymerisation of, mostly, traditional monomers and their analogues with hydrocarbon substituents incorporated in order to increase their amphiphilic properties was discussed. In the majority of cases, polymerisation in monolayers and LB films has been carried out by photo-irradiation of unsaturated compounds such as acrylate and methacrylate lipids, alkyl fumarates and maleates, unsaturated fatty acids, *etc*. Within the latter group of systems, diacetylenes and polydiacetylenic amphiphilic compounds belonging to conducting polymers were considered.

In another paper,[2] the structure and properties of polymer monolayers and LB films have been analysed. This paper dealt with the characteristic features of the packing of macromolecule on the surfaces of liquids and solids, the compatibility of high- and low-molecular compounds in monolayers, the influence of the degree of polymerisation, size and orientation of side groups on the phase states of monolayers, the correspondence between the architectures of Langmuir and LB monolayers, and many other issues. However, this paper did not touch upon the so-called special polymers which include conducting macromolecules with conjugated bonds, polymers synthesised for nonlinear optics, and highly stable multifunctional network polymers. The abundance of recent data on the properties of monolayers and LB films of only conducting polymers does not allow a detailed analysis of these systems to be made in the framework of one publication. Therefore, the author intends to present separate discussions on the most promising conducting polymers in the form of LB films that are studied most extensively.

Polythiophenes occupy a particular place among these polymers (polydiacetylenes, polyaniline, polypyrrole, polyphenylenes, *etc*.), primarily because they are soluble in ordinary solvents, form rather stable monolayers on the surface of water in air and have relatively high stability and conductivity in a doped state.

Extensive studies of polymers with internal conductivity started back in the 1970s when polydiacetylene was synthesised.[3,4] Conducting organic polymers have a quasi one-dimensional structure which, to some extent, is similar to that of charge-transfer complexes (CTC). In the conducting state, both types of materials exist as charged molecules. The conductivity of CTC is much higher along the axial direction of stacked molecules due to overlapping of the π-orbitals of the adjacent complexes. In the case of conducting polymers, charge transfer occurs along the chain due to overlapping of the π-orbitals of the adjacent monomeric units. Due to the chain-like structures of the conducting polymers, strong interactions of the electronic states with the excited conformation states (solitons, polarons, bipolarons) exist, which is typical of one-dimensional systems. The relatively weak interchain interactions provide the diffusion of dopant molecules to the polymeric chain. A decrease in the intensity of interchain interactions in polythiophenes containing substituents at positions 3 and 4 favours the solubility of the polymers in ordinary solvents. This is the most important feature of polythiophenes when deciding whether the Langmuir – Blodgett technique should be used for their organisation. For example, it was noted [4] that the conductivity of non-substituted polythiophenes ranges from 50 to 100 S cm^{-1}, while it is as high as 500 S cm^{-1} in the case of poly(3-methylthiophene) and is close to 1000 S cm^{-1} for some substituted polythiophenes.

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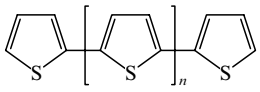
Polythiophenes are synthesised by chemical or electrochemical methods. The former method gives non-conducting polymers which can be transformed to the conducting state by chemical or electrochemical doping. In the latter case, doped (oxidised) polymers formed can be reduced chemically (de-doped) to the insulating state. The doping efficiency is determined from the position and intensity of the characteristic $\pi-\pi^*$ transition absorption band and from the change in the polymer colour. In addition, optical absorption spectra enable determination of the effective conjugation length of the polymeric chains. The longer the conjugation length the higher the polymer conductivity. The conjugation length can be increased by chemical synthesis of polythiophenes with a regular structure. As a result, the electric conductivity can be increased by a factor of 100 (Ref. 3).

The features of polythiophenes noted above are used for obtaining monolayers and LB films that are promising as metal and gas sensors, photoelectric and electrochromic devices, optical switches, solar batteries, *etc* .

The Langmuir – Blodgett method is used for the formation of planar ensembles of conjugated polymers in order to obtain ordered, similarly organised molecular chains, *i.e*., to reach the longest possible conjugation length so as to increase the intramolecular conductivity and provide the transfer of charge carriers between the adjacent molecules. However, the potential of this method can only be realised if true monolayer films with concerted molecular orientation are formed on the surface of a liquid and if these monolayers can be transferred onto solid supports with the formation of multilayered ensembles. The success of these operations is usually judged from the structural or optical spectroscopy studies. The latter method makes it possible to estimate the zone structure features and evaluate the conjugation length of the system formed. Measurement of the conductivity of the LB films obtained is the final step. Depending on the ultimate goal of the studies, other properties of the systems, such as nonlinear optical, photo- and electrophysical properties, can also be determined. The majority of studies on the subject of this review have been carried out according to this scheme, hence it is reasonable to follow it when discussing their results.

It might seem that one glance at the polythiophene chain (**1**) † would suffice to make sure that these polymers cannot form stable monolayers on the surface of water and, even more so, on solid supports.

However, as shown below, not all researchers agree with this viewpoint.



1

The problem of increasing the stability of monolayers of compound **1** can be solved at least by two methods: *viz*., by incorporation of groups that can enhance the surface activity of the molecule and by creation of mixed monolayers with amphiphilic compounds that form stable monolayers. The merits and drawbacks of these two methods for obtaining stable monolayers from molecules that are not 'strictly amphiphilic' are considered elsewhere.[2] It should be emphasised here that for polymers with distinct functions which depend, first, on the presence of certain reactive groups or conjugated bonds, and second, on realisation of a given conformation or structure of side chains determining the operating capabilities of molecules and their ensembles, incorporation of a second component is undesirable because it decreases the density of the key elements (functional groups, molecules, domains) in the layer and, as a consequence, decreases the efficiency of devices based on these elements. Therefore, the efforts of researchers are primarily aimed at synthesising such derivatives of polythiophenes whose spreading does not require dilution with other components, *i.e*. at designing mixed monolayers with the matrix components possessing high surface activities. Let us note the main directions of these studies.

1. Grafting of a polar group to an end of the oligothiophene chain which in this case plays the role of the hydrophobic component of the amphiphilic molecule.

2. Incorporation of a side alkyl chain in each thiophene unit. This method works successfully in the case of linear polymers.[2]

3. Incorporation of one or two hydroxyalkyl groups, which increase the polarity of the thiophene components, in each thiophene unit.

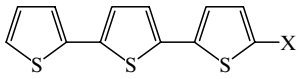
4. Copolymerisation (including block copolymerisation) of thiophene with other monomers that ensure distribution of the thiophene fragments over the subphase surface. In this case it is important that the second component also had conjugated bonds.

5. Synthesis of regioregular poly(3-R-thiophenes), where R is an alkyl, alkoxy or some other group.

However, these methods do not guarantee the desired result; therefore, mixed systems are studied, in which the functional capabilities of the key elements are preserved, provided that the component ratio remains at the optimum level.

II. Oligothiophene monolayers and Langmuir – Blodgett films

The effect of a polar group on the compression isotherms of a monolayer is shown in Fig. 1 for three-membered oligothiophenes **2** – **7** on the surface of water at 10 °C. One can see that compounds **2** and **3** do not form stable monolayers.[2] The esters **4** – **6** form condensed monolayers, in which the limiting area per molecule (A_0) is 27 – 29 Å^2. It is believed that this area corresponds to the vertical arrangement of terthiophene units that are directed towards the air phase, since they are more hydrophobic than the polar components of the oligomer molecules. Taking the parameters of the characteristic points in the compression isotherms of compounds **4** – **6** into account, Nakahara *et al*.[5] concluded that the monolayers of these oligomers are stable up to surface pressures (π) of 20 (**4** and **5**) and 30 mN m^{-1} (**6**).



2 – **7**

X = CHO (**2**), CH_2OH (**3**), CH_2OCOMe (**4**), $CH_2OCOCH=CMe_2$ (**5**), $CH_2OCO(CH_2)_7Me$ (**6**), $CH_2OCO(CH_2)_{16}Me$ (**7**).

For the long-chain derivative **7**, the surface pressure for destruction is as small as several units, while the value of area per molecule extrapolated to zero surface pressure is no higher than 23 Å^2. In this case, a condensed monolayer is formed in

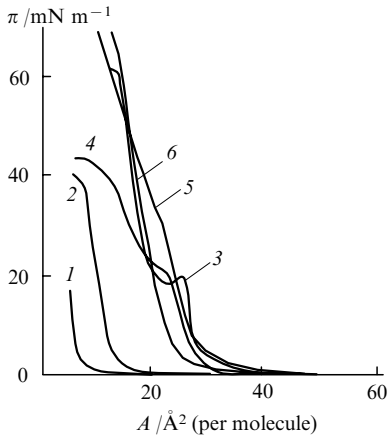


Figure 1. Compression isotherms of terthiophene derivatives at 10 °C;[5] (*1*) **2**, (*2*) **3**, (*3*) **4**, (*4*) **5**, 95) **6**, (*6*) **7**.

† Henceforth, poly(2,5-diylthiophene) is considered in this review.

which dense packing of hydrocarbon chains probably exists, whereas the less hydrophobic terthiophene group can be immersed in the aqueous phase. The U-shaped configuration of molecules in the monolayer can be ruled out because the areas of the molecules are very small. Presumably, the capability of these compounds to give stable monolayers is overestimated: the isotherms of compound **4** are shifted to smaller areas with increase in temperature. Moreover, the possibility of 'immersion into water' of the thiophene groups is determined by interactions of their hydrocarbon substituents with water molecules rather than by the lengths of these substituents. Unfortunately, the data on the changes in the surface pressure following stopping of the mobile barrier of surface balances were not reported.

Monolayers of oligothiophenes with a larger number of units could be obtained only by mixing them with eicosanoic (arachidic) acid.[5]

Monolayers and LB films were obtained from the six-membered oligothiophene **1** ($n = 4$, S_6) using a strategy for the formation of one-dimensional conducting systems.[6] The monolayers were transferred onto a solid support with the surface pressure of 15 mN m^{-1} and surface area per molecule (A) of 25 Å^2. The chain orientation found from the dichroic ratio was vertical relative to the support (Fig. 2). The eighteen-layered LB films were thermally polymerised (270 °C, 2.5 h). Comparison of the electronic spectra of LB films of the original oligomer S_6 and its thermal polymerisation product showed that the conjugation length in the latter was larger. It was also noted that the S_6 oligomer is completely soluble in nitrobenzene and trichlorobenzene, while the polymer synthesised in LB films is insoluble in these solvents.

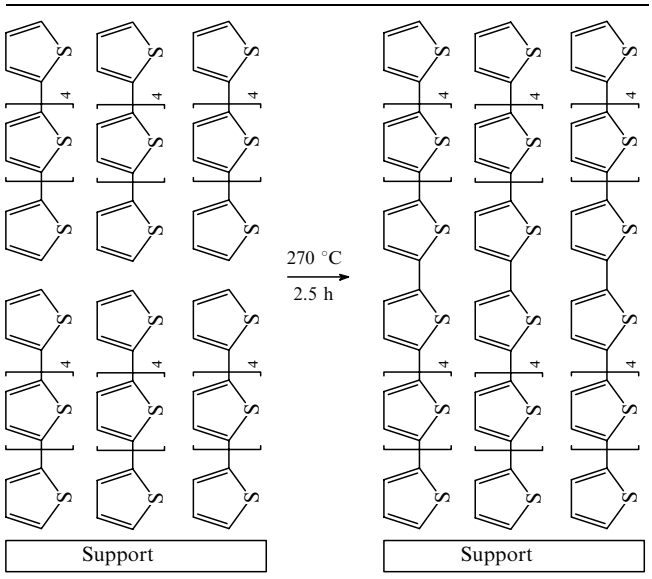
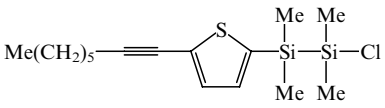
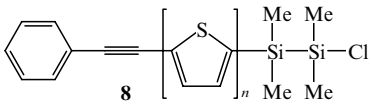


Figure 2. Organisation of six-membered thiophenes **1** (S_6) in LB films before and after thermal polymerisation.[6]

The solubility of oligothiophenes in various solvents and the possibility of coordination of their sulfur atoms with metals [7] are the properties that attract the most attention in relation to the studies in the field of self-assembled monolayers,[8–10] *i.e.*, systems very similar to LB films. A study of this kind was carried out for systems containing (oligo)thiophene unit(s) with 2-chlorotetramethyldisilanyl and phenylethynyl (compound **8**) or oct-1-ynyl substituents.[11, 12]





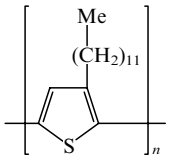
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$n = 1, 2, 4$

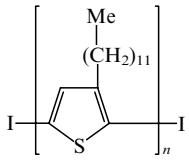
The adsorption of the oligothiophene **8** from its solution in toluene was carried out onto a SiO_2 surface (3000 Å)/Si. The authors succeeded in obtaining self-assembled monolayers the density of which depended on the number of thiophene rings in the molecule and increased with the increase in the length of the oligomeric chain. Obviously, lateral conductivity requires a high density of the surface layer and at least six or seven thiophene units in the oligomer molecule are required for obtaining high transverse conductivity.[13–17]

III. Polythiophene monolayers and Langmuir – Blodgett films

One attempt at obtaining monolayers and LB films from individual polythiophene derivatives has been undertaken by Logsdon *et al.*[18] Poly(3-dodecylthiophene) was synthesised by electrochemical and chemical polymerisation. Electrochemical polymerisation of 3-dodecylthiophene was carried out under galvanostatic conditions at an anodic current density of 2 mA cm^{-2} at 5 °C in an argon atmosphere using nitrobenzene as the solvent.[19] The average molecular mass of the chloroform-soluble fraction of the polymer **9** is 10^5 Da. The chemical synthesis included three steps, *viz.*, synthesis of 3-dodecylthiophene,[20] its conversion to diiodo-3-dodecylthiophene [21] and polymerisation.[22] The molecular mass of the final product (**10**) determined by gel-permeation chromatography was 2.3×10^3 Da.



9 ($n = 400$)



10 ($n = 9$)

The limiting areas per monomeric unit were 14.4 and 11.2 Å^2, respectively, for monolayers of poly(3-dodecylthiophenes) synthesised chemically and electrochemically. The authors believe that, since the first value correlates with that of 14.7 Å^2 calculated using the structural model for thiophene rings arranged at a right angle to the substrate surface, this particular orientation exists in the polythiophene monolayers synthesised chemically. If this is the case, the role of the hydrocarbon chain, the cross-section of which is ~ 18.5 Å^2, remains unclear. We shall return to this problem in the analysis of the structure of monolayers of other thiophene derivatives. It should be noted here that both specimens of poly(3-dodecylthiophene) spread poorly and do not form stable true monolayers on the surface of water.[2] The limiting area of the polythiophene monolayer synthesised chemically was larger than that of the thiophene monolayer obtained electrochemically, but the former monolayers were less stable and could not be transferred onto solid supports. The Langmuir – Blodgett vertical method 'did not work' in the case of the electrochemically polymerised poly(3-dodecylthiophene), either. However, the horizontal method at a surface pressure of 12 mN m^{-1} made it possible to transfer the monolayers and to obtain X-type films several tens layers thick on a solid support hydrophobised with trichlorooctadecylsilane. Unfortunately, diffraction methods were not used for structural studies of the resulting films, therefore the structure quality of these films cannot be judged.

Obviously, the films considered above may be, with caution, classified as LB films with distinct molecular orientation in the layers and alternation of the layers. This should be taken into account when considering the results of analysis of poly(3-do-

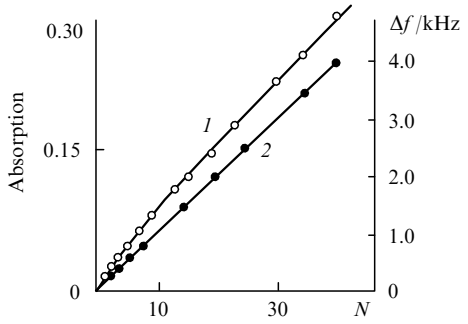


Figure 3. Dependence of optical absorption (*1*) and change in resonance frequency (*f*) of a quartz crystal (*2*) on the number of monolayers (*N*) of polythiophene **9**.[18]

decylthiophene) LB films presented below. Figure 3 shows the dependences of the optical absorption and the change in the quartz resonator frequency on the number of layers of the chemically polymerised poly(3-dodecylthiophene). The small inflexion on the plot of absorption *versus* the number of layers at $N = 10$ can be explained either by incomplete transfer of thick films onto the support due to the non-uniformity of the morphology of the surface formed or by a decrease in the structural correlation due to disordering of the polymeric segments. The monolayer thickness in LB film calculated from optical absorption data was found to be 35 Å. This value is closer to the result of ellipsometric thickness measurement (30 Å) than to the monolayer thickness determined using the structural model (19–24 Å). The linear dependence of the quartz resonator frequency on *N* indicates that the mass of the monolayer transferred onto the solid support is constant (the mass of one layer per 1 cm^2 is 350 ng) and that changes in the slope of the optical absorption on *N* are due to the orientation effects rather than to changes in the mass of the monolayers transferred. The specific electric conductivity of the non-doped film does not depend on the number of layers for $N \leqslant 40$ and equals 9×10^{-10} S cm^{-1}. Doping with iodine increases the conductivity by 8 orders of magnitude, and its minimum value depends on the number of layers: the conductivity for $N = 1$, 20 and 40 equals 0.014, 0.20 and 0.51 S cm^{-1}, respectively. The curves of changes in $\sigma_{\|}$ (lateral conductivity) and absorption at 760 nm during the doping in iodine vapour are presented in Fig. 4. During the first 460 s, $\sigma_{\|}$ increases by 6 orders and then reaches saturation in 4300 s. Flushing the cell with argon, which removes iodine from the system, restores the initial value of conductivity. The cubic susceptibility [$\chi^{(3)}$] of the non-doped film is as high as 1×10^{-9} electrostatic units. After doping, $\chi^{(3)}$ becomes 10% less and acquires its original value upon removal of iodine from the system.[23]

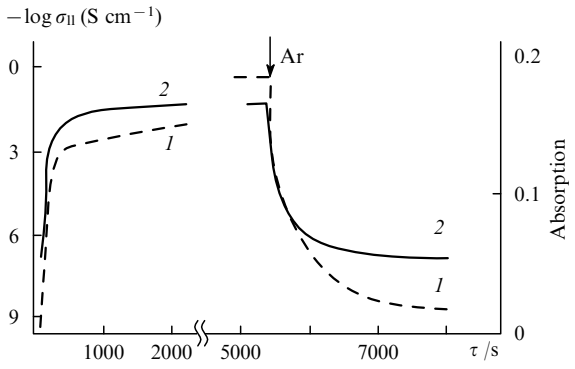


Figure 4. Dependences of the specific electric conductivity (*1*) and optical absorption (*2*) of a 40-layer LB film of polythiophene **9** on the time of exposure in iodine vapour and changes in these parameters after removal of iodine with a flow of argon.[18]

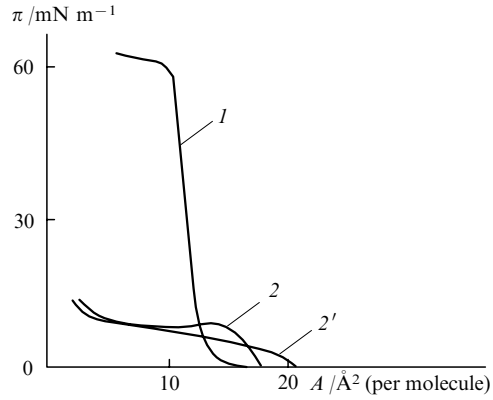
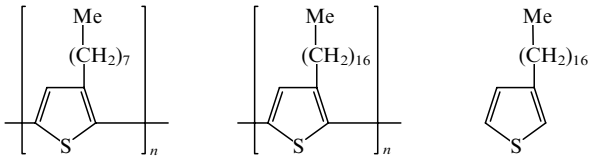


Figure 5. Compression isotherms of monolayers of polythiophene **12** (*1*) and its monomer **13** on the surface of water (*2*) and a 10^{-3} M $CdCl_2$ solution (*2′*).[25]

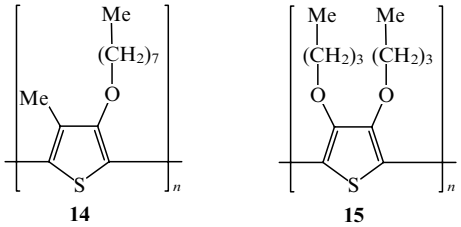
It should be emphasised that complex studies of poly(3-dodecylthiophene) LB films did not reveal any specific features of multilayer structures which would be untypical of this conjugated polymer in the bulk.

A decrease [24] or increase [25] in the length of the alkyl chain at position 3 of the thiophene ring in the polymer (from C_{12} to C_8 or to C_{17}) virtually does not affect the ability of the polymer to form stable monolayers. The limiting area per unit for poly(3-octylthiophene) (**11**) monolayer does not exceed 10 $Å^2$, while that for poly(3-heptadecylthiophene) (**12**) does not exceed 12 $Å^2$ (Fig. 5). The small value of the limiting monolayer area obtained in the latter case is explained [25] by detachment of some fraction of molecules or their units from the surface of the aqueous subphase (incomplete spreading). According to ellipsometry, the layer thickness is 50% larger than that calculated for the monolayer, hence the small value of A_0 can also be due to the formation of a tilted bilayer structure.[25] Figure 5 also shows the compression isotherms for the 3-heptadecylthiophene monomer (**13**). One can see that transition to the monomer, which decreases the intrachain cohesion due to cleavage of the polymer covalent bonds, improves insignificantly the spreading of thiophene and results in a liquid monolayer with low decomposition pressure.



11 **12** **13**

Thus, incorporation of an alkyl chain in the thiophene unit enhances insignificantly the spreading ability of the polymer due to weakening of the cohesion interactions between the thiophene rings. However, the hydrophilicity of the thiophene units remains rather low and does not ensure the formation of a stable monolayer on the surface of water. Incorporation of substituents at positions 3 and 4 of the thiophene ring, for example, of an alkoxy group to give poly(3-octyloxy-4-methylthiophene) (**14**), does not allow a true monolayer to be obtained on the surface of water.[26, 27]



14 **15**

The idea of hydrophilisation of each thiophene ring in polythiophene was implemented by Callender *et al.*,[28] who have synthesised and studied the properties of monolayers of poly(3,4-dibutoxythiophene) (**15**). Polythiophene **15** was synthesised from 3,4-dibromothiophene and sodium butoxide in the presence of copper oxide and platinum iodide with subsequent chemical oxidation of the monomer with iron trichloride.

The compression isotherms of compound **15** at two temperatures are presented in Fig. 6. The monolayer destruction at 11 °C occurs above a surface pressure of 20 mN m^{-1}, which is believed to be due to folding of the monolayer and formation of a bilayer film. Destruction at higher temperatures is observed at lower π. The Langmuir – Blodgett films of polythiophene **15** were obtained at 11 °C and a surface pressure of 12 mN m^{-1}. Under these conditions, changes in π and A were negligibly small within 2 h and the limiting area per residue was 20 Å^2. It was found [29] that the surface of the thiophene chains, whose long axes are arranged at a right angle to the subphase surface and have a dihedral angle of 90°, is 28 Å^2. However, it was shown [18] that a poly(thiophene) molecule, whose chains are parallel to the surface of water and the rings are oriented perpendicularly to this surface, requires a surface of 14.7 Å^2 per residue. In this case, the area per residue equal to 20 Å^2 found for polythiophene **15** should correspond to a polymer with an axis directed parallel to the surface of water and a dihedral angle between repeating units ranging from 0° to 90°. The resulting twisted conformation is formed due to steric interactions between the bulky alkoxy substituents at positions 3 and 4. The absorption spectrum of the 28-layer LB film of polythiophene **15** does not differ from the spectrum of this polymer in the solid state; the absorption intensity in the maximum (the band at 462 nm) increases linearly with an increase in the number of layers ($N \leqslant 30$). Optical spectroscopy was used to analyse the stability of polythiophene **15** LB films stored under various conditions:[28] in the dark, under daylight and under artificial light with a wavelength of > 500 nm. After ageing for 30 days, absorption at 462 nm did not change for the first sample, but it decreased by 35% and 24% for the second and third samples, respectively. The absorption maximum of polythiophene **15** LB films is shifted towards shorter wavelengths relative to the absorption maxima of solid poly(3-alkylthiophenes) (~ 500 nm) [30] and poly(3-butoxy-4-methylthiophene) (545 nm).[26] These data suggest that steric interactions between the two bulky side chains and the polymer chain favour the formation of such a polymer conformation where the thiophene units are turned relative to each other. This decreases the effective conjugation length. X-Ray diffraction data [28] indicate that the bulk polymer **15** is semicrystalline and has a helical conformation, which is apparently preserved in solution (chloroform). Since the polymer chain conformation and the LB film structure determine the electric [27] and nonlinear-optical properties to a considerable extent, structural studies of these systems have to be carried out.

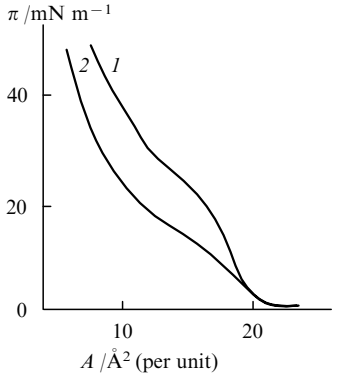
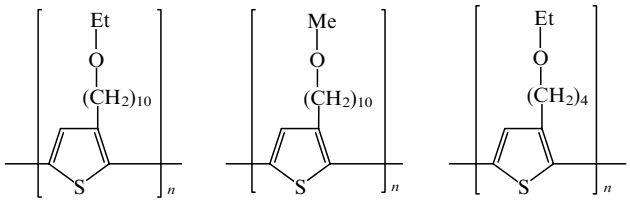


Figure 6. Compression isotherms of monolayers of polythiophene **15** on the surface of water at 11 (*1*) and 26 °C (*2*).[28]

After their failure to obtain stable monolayers and LB films of poly(3-alkylthiophenes), Bolognesi *et al.*[31] synthesised polythiophenes **16** – **18** containing ether groups at position 3.



16 **17** **18**

Figure 7 shows the compression isotherms of monolayers of polythiophenes **16** – **18**. One can see that the curves differ noticeably; the regions of area per residue exceeding 14.7 Å^2 (the minimum area occupied by the thiophene monomer) are the most interesting. The limiting areas per residue are 20, 15.5 and 15.3 Å^2 for the polymers **16** – **18**, respectively. Presumably, in all three cases the oxygen atoms in the monolayers are in contact with the aqueous support, whereas the differences in the areas are explained by different slopes of the hydrocarbon spacers in the side chains. The angle between the adjacent monomeric units should also be taken into account; the area per residue can vary from 28 to 14.7 Å^2 as a function of this angle. The pressures for monolayer collapse differ considerably as well: these are 20.0, 41.0 and 21.5 mN m^{-1} for compounds **16**, **17** and **18**, respectively. The big difference between the collapse surface pressures (π_c) for polythiophenes **16** and **17**, whose side chains differ only in one CH_2 group, is unexpected. This fact was explained [31] by the higher polarity of OMe-substituted polythiophene. However, this would imply that the more polar polymer **18** would form a more stable monolayer. In reality, the opposite phenomenon is observed (see Fig. 7). The viewpoint of Bolognesi *et al.*[31,32] regarding the orientation of polythiophene **17** molecules in the monolayer is also unclear. They consider that the main chain is parallel to the surface of water, the side chain is almost perpendicular to this surface, while the oxygen atom (at the free end of this chain) contacts water. Obviously, the latter two orientations cannot exist simultaneously.

In the case of the polymer **17**, both Y-transfer to a hydrophobic support and Z-transfer to a hydrophilic surface were carried out. In the former case, the transfer ratios were 0.9↑ and 0.8↓ (the arrow indicates the direction of support movement: ↑ means upwards from the subphase, while ↓ means downwards to the subphase) for the first 8 – 10 cycles, while in the latter case they were 1↑ and 0.2 – 0.5↓ for the first 12 – 14 cycles. The transfer ratio decreased as the number of cycles increased. A ten-layer LB film of polythiophene **17** was analysed by optical spectroscopy in combination with a cast film. The difference in positions of the absorption maxima for the LB film (λ_{max} = 472 nm) and for the film obtained from solution (λ_{max} = 460 nm) is explained by a

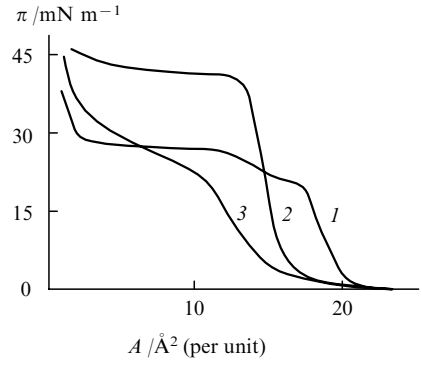
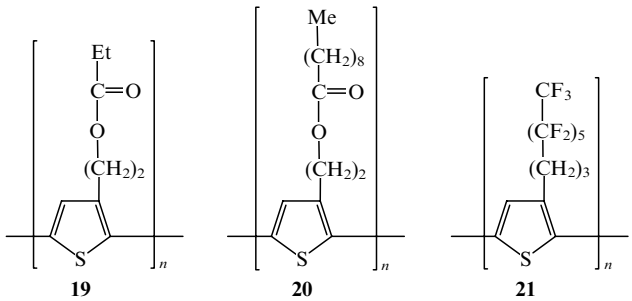


Figure 7. Compression isotherms of monolayers of polythiophenes **16** (*1*), **17** (*2*) and **18** (*3*).[31]

larger conjugation length in the case of the LB film. IR spectroscopy was used to demonstrate the higher planarity of the main polythiophene chain in the LB film. Similar data were also obtained for the polymer **16**.[33] These data differed from those of Callender *et al.*[28] who had also used optical spectroscopy but did not find differences between the spectra of LB films and those of a solution of polythiophene **15**. The discrepancy between the data obtained by both research groups were explained [31] by the absence of a spacer in the side group of the polymer **15** between the thiophene ring and the oxygen atom. The ordered structure of polythiophene **17** in LB films was confirmed by polarisation optical spectroscopy and by electron microscopy.[32] In addition, alternating LB films containing monolayers of **17** and cadmium alkadiynoate were obtained. Polymerisation of the diacetylene was carried out after transferring the monomer onto a solid support.[32] It was shown that polymerisation does not result in destruction of polythiophene, and the spectrum of the Langmuir – Blodgett hetero-film does not show a shift of the exciton band of polydiacetylene, indicating the absence of interactions between the polydiacetylene exciton and the polythiophene macromolecules.

Thus, incorporation of ether groups in the side chain of polythiophene enhances the stability of monolayers in comparison with that of poly(3-alkylthiophenes). However, the problem of orientation of monomeric units both in monolayers and in LB films requires a more thorough analysis.

An increase in the polarity of monomeric units of polythiophene by incorporation of an ester group at position 3 enhances polymer spreading in comparison with that of polyalkylthiophene and polythiophene containing ether groups in the side chains.[24] Figure 8 presents the plots of surface pressure *vs.* the monomeric unit area for poly[3-(2-propanoyloxyethyl)thiophene] (**19**), poly[3-(2-decanoyloxyethyl)thiophene] (**20**) and, for comparison, poly(3-octylthiophene) (**11**). The short polar side chain in compound **19** 'stacks' the thiophene ring parallel to the surface of water: the limiting area per residue in this region is ~ 28 Å^2. Further, the rings are detached from the surface and the increase in pressure is observed in the region of closest packing of vertically arranged thiophene rings. The more complex isotherm shape in the case of polythiophene **20** monolayer is explained by the contribution of the comparatively long hydrocarbon chain arranged so that the polar group in each monomeric unit faces the water surface. The first inflexion on the isotherm results from detachment of these chains from the subphase surface. Although the monolayers of compounds **19** and **20** are stable, Kim *et al.*[24] were unable to transfer them onto solid substrates and to obtain LB films. This problem was solved for mixed monolayers of these polythiophenes with octadecylamine (see below).



19 **20** **21**

The possibility of an increase in the polarity (hydrophilicity) of the side chains of polyalkylthiophenes for enhancement of the stability of monolayers has already been considered. However, the same result can be achieved by means of a considerable increase in the hydrophobicity of the side chain, as was demonstrated by Robitaille *et al.*[34] for poly[3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiophene] (**21**). Monolayers on the surface of water were from a solution of the polymer **21** in octafluorotoluene. The compression isotherm of polythiophene **21** at 9 °C presented in Fig. 9 was obtained after several preliminary 'compression – expansion' cycles in the surface pressure range from 0 to 25 mN m^{-1}. Extrapolation of the curve to $\pi = 0$ gives the limiting area per residue of 34 Å^2, which agrees with the area occupied by a fluorinated fatty acid molecule in the monolayer. The thermochromic properties of polythiophene **21** were studied using its LB films obtained at $\pi = 10$, 14 and 18 mN m^{-1}. Unfortunately, good LB films were not formed under these conditions: the transfer ratio onto silanised glass was $\sim 0.6\uparrow$. Transfer did not occur at all when the support moved to the subphase. Figure 10 shows the temperature dependences of optical absorption in the UV and visible spectral regions for the monolayer and a film obtained from solution on a rotating support. Robitaille *et al.*[34] believe with good reason that comparison of spectra of the two samples makes it possible to understand the nature of the thermochromism of compound **21**. Heating of the samples shifts the absorption maximum at 488 nm to 396 nm. It is believed [35, 36] that this optical effect results from conformational transition of the main polymer chain. It should be noted that the spectra for the two- (monolayer) and three-dimensional (film from solution) states of polythiophene **21** virtually coincide: in both cases, a coplanar structure existing at low temperature is transformed to a non-planar one at high temperature. Since the effects for the two- and three-dimensional systems are identical (Fig. 10 *a* and *b*), it is concluded that this thermally induced conformational transition is determined by the polythiophene chain itself and does not depend on interchain interactions. However, it should be taken into account that this conformational transition is possible only if it is not prohibited by steric hindrance from the substituents at position 3. In the case of polythiophene incorporating rather

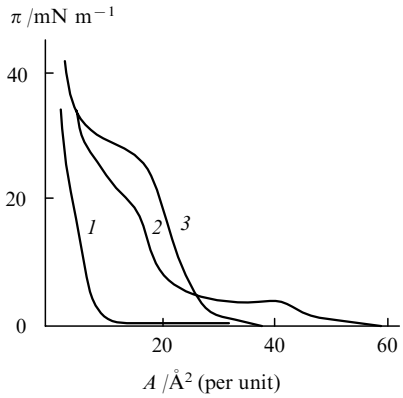


Figure 8. Compression isotherms of monolayers of polythiophenes **11** (*1*), **20** (*2*) and **19** (*3*).[24]

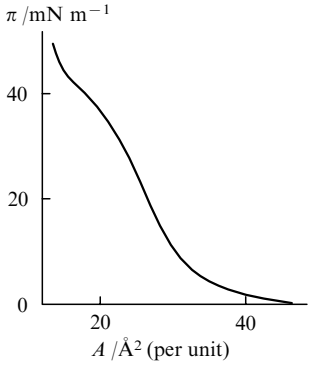


Figure 9. Compression isotherm of fluorinated polythiophene **21** at 9 °C.[34]

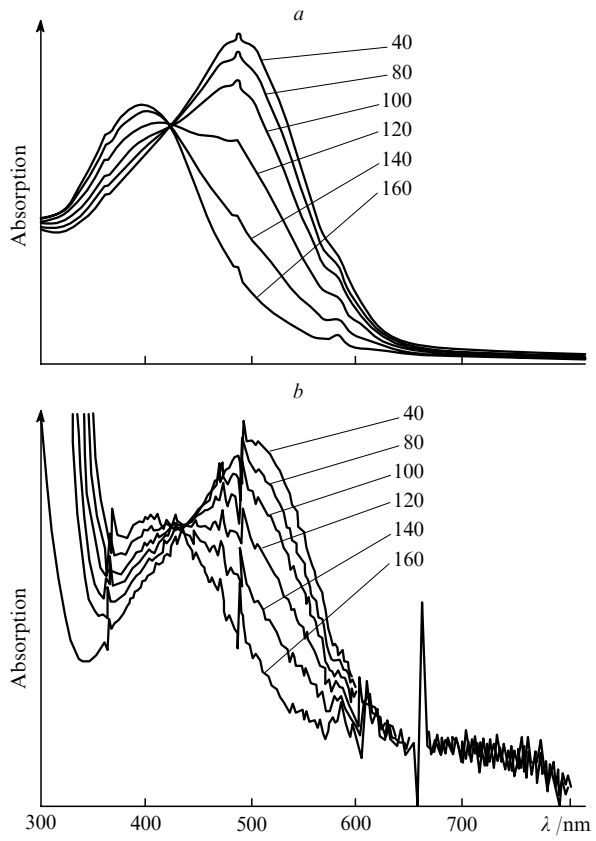
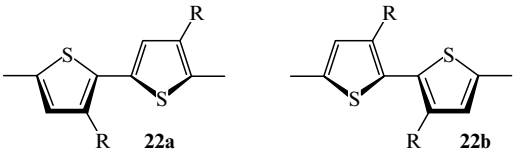


Figure 10. Absorption spectra of a monolayer (*a*) and a coating obtained from solution (*b*) of fluorinated polythiophene **21** at various temperatures.[34]
The numbers at the curves indicate the temperatures (°C).

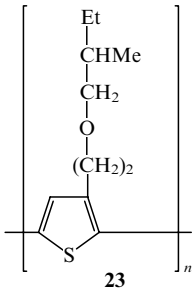
bulky side chains, such a transition is possible only if regioregular regions exist in the polymer ('head-to-tail' diads); however, the existence of such regions was not reported.[34]

The problem of the regioregularity of poly(3-R-thiophenes), including the formation of stable molecular ensembles on liquid and solid supports, has made progress only in recent years after poly(3-R-thiophenes) with regioregularity of up to 100% had been synthesised and their study had begun.[37–44] Two conformations of poly(3-alkylthiophene) are shown below: coplanar ('head-to-tail') (**22a**) and twisted ('head-to-head') (**22b**).



As shown by McCullough *et al.*,[41–43] an increase in the regioregularity of poly(3-alkylthiophene) increases considerably the electric conductivity of the films and results in greater changes in the physical parameters of the polymers than for the samples synthesised with the use of the standard chemical or electrochemical polymer oxidation procedures. Similar conclusions were drawn [39,40] in studies of the photoluminescence of poly(3-hexylthiophene) films with different regioregularity obtained from solutions. Obviously, the use of such an efficient organisation method as the Langmuir – Blodgett technique for obtaining ultra-thin films of structurally uniform poly(3-R-thiophenes) will make it possible to increase their uniformity and improve the parameters of various devices constructed from these films.

Ochiai *et al.*[45] compared the properties of monolayers of regioregular poly(3-{2-[(S)-2-methylbutoxy]ethyl}thiophene) (**23**) containing more than 93% of 'head-to-tail' conformers (**23a**, $M_w = 2.5 \times 10^4$) and polythiophene containing as little as 46% of 'head-to-head' conformers (**23b**, $M_w = 2.05 \times 10^4$).



23

A monolayer of compound **23a** forms a condensed phase with a collapse surface pressure of ~ 18 mN m^{-1} (Fig. 11). The limiting area per residue is 17 Å^2, which corresponds to an almost perpendicular arrangement of thiophene rings with respect to the surface; the head groups of these rings are oriented towards the subphase. A monolayer of compound **23b** has a larger limiting area per residue (19 Å^2), but the low collapse pressure of this monolayer (~ 10 mN m^{-1}) indicates its low stability and random orientation of the molecules. Due to these characteristics of monolayers of **23b**, they do not form LB films. Analysis of the polarised optical spectra in the region of 400 – 650 nm for LB films of the polymer **23a** showed that its molecules are oriented parallel to the surface of the substrate and the chain orientation correlates with the direction of movement of the support when the monolayers are transferred. Comparison of these spectra with those for films deposited from solution showed that in the case of LB films the molecules have a higher degree of orientation and larger conjugation lengths. This increases the lateral conductivity of polythiophene **23a** LB films doped with $NOPF_6$ or $FeCl_3$ to 1 – 5 S cm^{-1}, which is 4 to 5 orders higher than the conductivity of polythiophene **23b** films obtained from solution. In addition, LB films of the polymer **23a** have anisotropy of lateral conductivity and high cubic susceptibility.[45]

Unfortunately, there are as yet few studies of this kind within the Langmuir – Blodgett method, and for individual polythiophenes only the studies cited above are available. Solutions, films obtained from solution, and solid polythiophenes are being studied thoroughly. These systems are not covered in the present review dealing with monolayers and LB films; however, we have to dwell on some general issues of the relationship between the structure, composition and properties of polythiophenes in solutions and in the bulk.

It is known [46] that electrochemical synthesis of poly(3-alkylthiophenes) gives units with substituents at positions 2 and 4, whereas chemical synthesis results in residues with substituents at positions 2 and 5. Both methods give irregular polymers. Naturally , these 'defects' affect the planarity of the main polymer chain

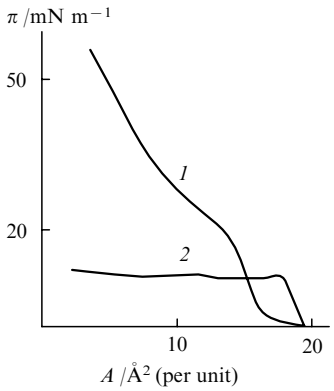


Figure 11. Compression isotherms of monolayers of polythiophenes **23a** (*1*) and **23b** (*2*) at 10 °C.[45]

and hinder both the intrachain and the interchain transport of charge carriers. As a result, poly(3,4-dialkylthiophenes) and poly(3,3′-dihexyl-2,2′-dithiophenes) mostly containing 'head-to-head' conformers have a small conjugation length and low conductivity.[47,48] There are prerequisites for increasing the polymer regularity by polymerisation of long-chain 3-alkylthiophenes.[49,50] However, in this case the polymer contains structural defects as well[48] [C(2)–C(4′) bonds and branchings]. It is believed[51,52] that regular polymers with high conductivities can be obtained from 3,4-disubstituted thiophenes if steric hindrance is removed. This assumption was checked[50] by the synthesis of poly(3-alkoxythiophenes), poly(3-alkoxy-4-methylthiophenes) and poly(3,4-dialkoxythiophenes) by chemical oxidation of monomers with anhydrous $FeCl_3$ (see Refs 48, 53). The effects of the position, size and nature of substituents on the molecular mass, positions of characteristic absorption bands and conductivities of the resulting polymers were determined. It was shown that the absorption band of 3,4-disubstituted polyalkylthiophenes is strongly (by ~ 200 nm) shifted towards the blue region in comparison with the bands of the other polythiophenes synthesised. This implies a non-planar conformation of chains due to strong steric interactions between the substituents and the main chain. As a result, gaps remain between the conjugated chains of the adjacent molecules; these gaps decrease the probability of charge carrier transfer according to the hopping mechanism.[52] Replacement of alkyls by alkoxy groups in poly(3,4-dialkylthiophenes) increases considerably the conjugation length and conductivity of the polymer, which is explained by the smaller van der Waals radius of the oxygen atom (1.4 Å) in comparison with the methylene group radius (2.0 Å). This conclusion can be very important in the synthesis of Langmuir monolayers, since incorporation of a polar group enhances the ability of polythiophenes to spread over an aqueous subphase surface.

Studies on the synthesis of regular polythiophenes with various quantitative and qualitative compositions of substituents and their use for obtaining monolayers and LB films are already under way. For example, works have been published on the synthesis and properties of polythiophenes, polybithiophenes and polyterthiophenes containing such substituents as 3-cyclohexyl, 3-methyl-4-cyclohexyl, 3-alkylphenyl, *etc.*[54–57]

IV. Mixed monolayers and Langmuir – Blodgett films of oligo- and polythiophenes

Analysis of the behaviour of monolayers and LB films of simple oligo- and polythiophenes showed that the formation of stable films on the surface of water requires adjustment of the hydrophilic-lipophilic balance of thiophenes towards enhancement of the hydrophilicity of the head group. In addition, a side group, most commonly an alkoxy group, is to be introduced into each thiophene ring of the main chain (in most cases, at position 3) in order to weaken the interchain interactions responsible for aggregation of macromolecules on the surface of water and incomplete spreading of the compound to form a monolayer. An easier method to obtain stable monolayers containing polythiophenes involves formation of mixed monolayers with an amphiphilic compound which forms stable monolayers with high collapse pressure. The problem of the role of intra- and interchain charge transfer is solved using mixed monolayers of conjugated polymers with compounds which are inert with respect to electric conductivity (fatty acids, alcohols, polymers). Obviously, incorporation of an inert component should not hinder the interchain charge transfer in the case of mixed films.

A five-membered oligomer of thiophene **1** ($n = 3$, S_5) was mixed with stearic acid[29] or eicosanoic acid[58] and placed on the surface of aqueous solutions containing $CdCl_2$. Compression isotherms obtained for monolayers of mixtures with different component ratios were used to determine the limiting area per molecule of oligothiophene S_5, which was 26 Å^2 for mixtures of S_5 with stearic acid[29] and 19 Å^2 for mixtures of S_5 with eicosanoic acid.[58] Such a large difference was explained by the higher pH used in the former study[29] and better correspondence between the lengths of the molecules of S_5 and cadmium stearate (25.8 Å) than of S_5 and cadmium eicosanoate (28 Å). According to calculations,[29] the area of an S_5 molecule arranged at a right angle to the film surface and having a dihedral angle of 90° is 28 Å^2. Therefore, the area per S_5 molecule equal to 26 Å^2 should correspond to vertical orientation of oligothiophene with the dihedral angle ranging between 20° and 50°.

Figure 12 shows the dependence of the specific electric conductivity of iodine-doped LB films obtained from a mixture of S_5 and stearic acid (the content of S_5 was 30 mol.%) on the number of layers (N) in a Y type film.[29] One can see that for $N \leqslant 7$, the conductivity increases rapidly and reaches a steady-state value of

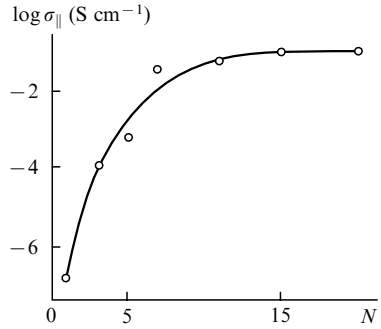


Figure 12. Dependence of the lateral conductivity on the number of layers in an LB film obtained from a mixture of oligothiophene **1** (S_5) (30 mol.%) and stearic acid.[29]

0.1 S cm^{-1} at $N > 15$. The dependences of the lateral conductivity on the mole fraction of S_5 in the mixture for 1-, 3- and 11-layer, iodine-doped LB films are presented in Fig. 13. Two regions are observed in the curves. For the 11-layer LB film, the conductivity reaches a plateau at a mole fraction $[S_5] \geqslant 0.35$. The limiting conductivity (0.2 S cm^{-1}) corresponds to $\sigma_\parallel$ for iodine-doped bulk polythiophene (0.01 – 0.1 S cm^{-1})[59] and exceeds the $\sigma_\parallel$ for the spray-deposited, iodine-doped S_5 film. The lateral conductivity of non-doped LB films does not exceed 10^{-9} S cm^{-1}, while the transverse conductivity $\sigma_\perp$ is lower than 10^{-12} S cm^{-1}. The maximum conductivity can be reached by doping for a period of two days. The doping process is partially reversible: for the 21-layer LB film obtained from a mixture of S_5 with stearic acid (1 : 1), $\sigma_\parallel$ and $\sigma_\perp$ were 3.0×10^{-3} and 1.5×10^{-7} S cm^{-1}, respectively, after removal of iodine.

Since neither the oligothiophene chain length nor the film ordering affect noticeably the electric conductivity of oligomers

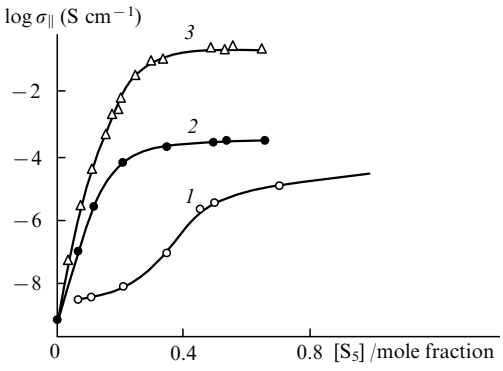


Figure 13. Dependence of the lateral conductivity of LB films consisting of monolayers of oligothiophene **1** (S_5) and stearic acid on the mole fraction of S_5 for an LB film containing 1 (*1*), 3 (*2*) and 11 layers (*3*).[29]

doped with iodine,[29] it was concluded that the electric conductivity of polymers and oligomer ensembles is determined by the intermolecular transfer of charge carriers.

There are many more studies of mixed monolayers and LB films containing polythiophenes than of those dealing with monolayers of oligothiophenes and films of individual compounds. It is believed[60] that pure poly(3-alkylthiophenes) are unsuitable for obtaining organised ensembles for at least two reasons. First, they do not form true monolayers; when they spread over the surface of water, they form islets visible by naked eye. The same situation is observed for poly(3-alkylthiophenes) containing up to 18 carbon atoms in the side chain. Second, monolayers can be transferred onto solid supports only by the horizontal method. The films obtained in this manner have low degree of organisation. As in the case of oligothiophenes, these drawbacks can usually be overcome by using fatty acids such as stearic and eicosanoic acids.[61–65]

Figure 14 shows the $\pi - A$ plots for mixed monolayers with various compositions obtained from mixtures of poly(3-hexylthiophene) and stearic acid.[60] It is evident that the mixture containing up to 80 mol.% of the polymer (with respect to the repeating thiophene unit) forms a stable condensed monolayer. The phase transition in this monolayer is observed at high surface pressures (25 mN m^{-1}). For all component ratios, π increases with a decrease in the area until the transition region is reached where the surface pressure remains constant. A new abrupt increase in π starts at monolayer areas close to A for a monolayer of pure stearic acid. Obviously, the plateau corresponds to displacement of the polymer molecules from the liquid surface and formation of a bilayer film. This picture is observed for all alkyl-substituted polythiophenes except for poly(3-octadecylthiophene) in which strong interactions of the alkyl chains with the chains of similar length of stearic acid prevent polymer displacement from the interface.

Let us consider the properties of LB films obtained from these mixtures. The LB film thicknesses after one passage of the support through a mixed polythiophene – acid (2 : 1) monolayer at transfer pressures below (20 mN m^{-1}) and above (28 mN m^{-1}) the phase transition (plateau) were 32 and 44 Å, respectively (see Fig. 14). According to the optical spectroscopy data, the bilayer structure formed on the surface of water at high π is transferred onto the solid support. However, more precise X-ray diffraction data showed that the bilayer thickness in LB films correlates with the size of two stearic acid molecules and does not depend on the transfer pressure. The formation of high-quality LB films from a mixture of poly(3-hexylthiophene) with stearic acid was evidenced by linear dependences of the absorption intensity at the maximum of the characteristic absorption band of polythiophene on the

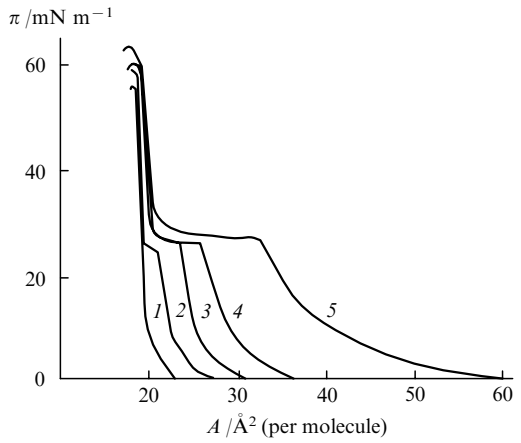


Figure 14. $\pi - A$ Dependences for mixed monolayers of poly(3-hexylthiophene) and stearic acid for the molar component ratios: 0 : 1 (*1*); 1 : 2 (*2*); 1 : 1 (*3*); 2 : 1 (*4*) and 5 : 1 (*5*).[60]

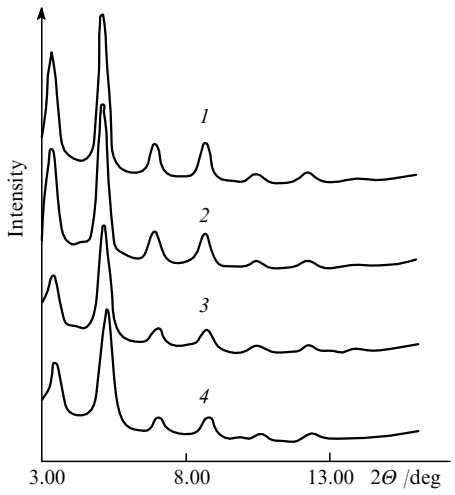


Figure 15. X-Ray diffraction diagrams for LB films consisting of mixed monolayers of poly(3-hexylthiophene) and stearic acid for the molar component ratios: 1 : 2 (*1*); 1 : 1 (*2*); 2 : 1 (*3*) and 5 : 1 (*4*).[60]

number of layers for various component ratios and surface transfer pressures and by a linear relationship between the inverse capacity of LB films and the number of layers. The layered structure of LB films was confirmed by X-ray diffraction (Fig. 15). The X-ray diffractogram displays distinct Bragg peaks with an interlayer distance of 50 Å, which corresponds to a bilayer of stearic acid. Near-edge X-ray absorption fine structure analysis showed a high degree of organisation of stearic acid hydrocarbon chains in the bilayers and an irregular orientation of poly(3-hexylthiophene) chains. A model of a mixed LB film structure was built on the basis of the experimental data (Fig. 16).

The effect of the content of poly(3-octylthiophene) in a mixture with eicosanoic acid on the properties of monolayers and LB films was studied.[65] No plateau was found on the compression isotherms of monolayers (the mixture containing 60% of the polymer was an exception). As in other studies, an increase in the polymer fraction in the mixture resulted in an increase in the monolayer limiting area. The high stability of mixed monolayers [unlike the monolayers of pure poly(3-octylthiophene)] and the high surface collapse pressure (> 50 mN m^{-1}) made it possible to form a 45-layer LB film at a

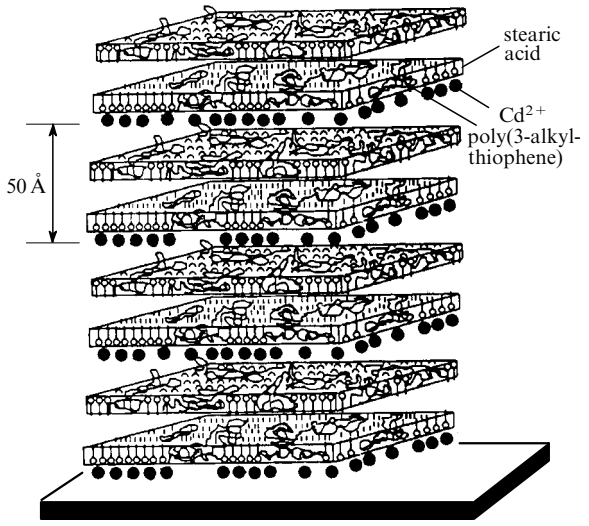


Figure 16. A model of the structure of an LB film obtained from a mixture of poly(3-hexylthiophene) and stearic acid.[60]

transfer ratio close to 1. Despite the instability of pure poly(3-octylthiophene) monolayers, the respective LB films were obtained and their thicknesses were determined by ellipsometry. The thickness of one layer in an LB film was 40 Å, which is 3 Å thicker than that of one monolayer in the LB film obtained from a mixture of eicosanoic acid and poly(3-octylthiophene) measured by the same method. These data were not discussed, but it is easy to understand the origin of the larger thickness of the pure polythiophene LB film if its 'monolayers' were transferred at area per unit parameters insignificantly in excess of 5 Å^2. It should be noted that the thickness of one LB film layer of pure poly(3-octylthiophene) and its mixtures with eicosanoic acid specified above is considerably larger than the thickness of a densely packed monolayer of eicosanoic acid. In addition, ellipsometry, unlike X-ray diffraction, does not allow determination of the structure spacing parameters and hence does not provide data on the film layered structure. Such data were reported.[60,66] It was found for mixed LB films of stearic acid with poly(3-hexylthiophene) in the ratios from 2 : 1 to 1 : 5 that the structure spacing corresponded to the thickness of a stearic acid bilayer.[60] It was also found for LB films obtained from binary mixtures (1 : 10 and 1 : 3) of poly(3-heptylthiophene), poly(3-decylthiophene) or poly(3-undecylthiophene) with cadmium eicosanoate that the structure spacing of all three systems corresponds to the thickness of a cadmium eicosanoate bilayer (55.2 Å).[66] Two reflections were observed for rather high contents of poly(3-decylthiophene) in a mixture with cadmium eicosanoate (3 : 1); these reflections corresponded to interlayer distances of ~ 70 and ~ 50 Å. This result and the broadening of the diffraction bands indicated a decrease in the system ordering. Despite the high content of behenic acid in a mixed monolayer with poly(3-hexadecylthiophene) (5 : 1 w/w) and its high stability (π_c = 60 mN m^{-1} and A_0 = 13.7 Å^2 per unit), only a Z-type LB film (20 layers) could be obtained.[67] It was found in a study of these films by attenuated total internal reflection IR spectroscopy and reflection at grazing light angles that the LB film obtained from a mixture has a less organised structure than the LB film of pure behenic acid.

Mixed monolayers of poly(3-octylthiophene) and unsaturated oleic acid having the same hydrocarbon chain length as stearic acid were studied.[68] It was shown that an increase in the content of polythiophene in the mixture from 10% to 90% decreased the mean molecular area of the monolayer upon its destruction from 42 to 5 Å^2. Let us remind that in the case of saturated acids, the monolayer area generally increases with an increase in the polymer fraction.[60,69] Exposure of the solution used for the formation of mixed monolayers of oleic acid and poly(3-octylthiophene) to daylight shifted the dependence of the monolayer area on the polymer content towards larger areas. The shoulder at 590 nm found[68] in the absorption spectra of LB films composed of mixed monolayers is explained by the formation of a charge-transfer complex between oleic acid and the thiophene rings.

The study of mixed monolayers of poly(3-butylthiophene) and stearic acid,[70] like yet another study[65] of the poly(3-octylthiophene)–eicosanoic acid system, did not show a plateau on the compression isotherms for the polymers with molecular masses differing by an order of magnitude (2.5×10^5 and 1.5×10^4). For these systems, as for the majority of other mixtures of fatty acids with polythiophenes, the area per monomer unit in a monolayer increases with an increase in the polymer content in the mixture.[65] The main differences in the shape of the compression isotherms for polythiophene samples with different molecular masses were observed in the region of destruction of mixed monolayers, *i.e.* in the transition from a two-dimensional to a three-dimensional state of the material. The surface potential of monolayers is 'insensitive' to these differences and to the obvious differences of the aggregation states of polymer monolayers with significantly different molecular masses. In both cases (as for the majority of monolayers of low- and high-molecular-mass compounds), the surface potential starts to increase at monolayer areas considerably exceeding those where the increase in the surface pressure starts. The transfer of mixed monolayers onto a glass surface by the vertical method was studied in detail;[70] it was found that the transfer ratio is close to unity and that the resulting LB films of the Y type have homogeneous structures.

It was noted above that important information on the properties of conjugated systems can be obtained from absorption spectra of LB films and their comparison with the spectra of polymers in solutions. High quality LB films of the Y type with various ratios of stearic acid and poly(3-hexylthiophene) were described.[60] Differences between the absorption spectra of LB films of individual polythiophenes **16** and **17** and their films obtained from solution were observed;[31–33] however, no differences were found between similar spectra of LB films obtained from a mixture with stearic acid and that of a film obtained from a solution of pure poly(3-hexylthiophene).[60,69,70]

The position of the $\pi-\pi^*$-transition maximum in the absorption spectra of LB films consisting of mixed monolayers of poly(3-alkylthiophenes) and cadmium eicosanoate depends on the length of the polymer alkyl chain.[66] For example, for LB films of poly(3-decylthiophene) and poly(3-undecylthiophene), the absorption maximum of a 1 : 3 polymer : salt mixture was observed at 520 and 515 nm, respectively, whereas in the case of a film obtained from solution, the absorption maxima were at 477 and 500 nm. For poly(3-heptylthiophene), no differences between the absorption spectra of mixed LB films and a film formed from solution were found. These data are believed[66] to be consistent with other data.[60,71] It was therefore concluded that the conjugation length in poly(3-decylthiophene) and poly(3-undecylthiophene) is larger in LB films than in films formed from solution. This effect was explained by interactions between the hydrocarbon chains of the acid and poly(3-alkylthiophenes). For poly(3-heptylthiophene), no increase in the conjugation length in LB films was observed.

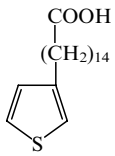
The absorption spectra of LB films containing poly(3-octylthiophene) and eicosanoic acid displayed a red shift of the absorption band maximum by 60 nm in comparison with the position of the absorption band maximum of a solution of the polymer in chloroform.[65] As in yet another study,[36] this effect was explained by conformational reorganisation of the chain in LB films. Ageing of the film shifted this absorption band towards the short-wave region. Doping of LB films was carried out in $SbCl_5$ or iodine vapour. As a result, the LB film colour changed from red to blue, while the conductivity increased from 2×10^{-9} to 2×10^{-5} S cm^{-1} for iodine and to 1×10^{-4} S cm^{-1} for $SbCl_5$.[65]

The conductivity of a mixed 34-layer LB film doped with nitrosyl hexafluorophosphate depends on the component ratio.[60] An increase in the poly(3-hexylthiophene) content in a mixture with stearic acid from 1 : 2 to 5 : 1 increases the electrical conductivity from 0.02 to 2.0 S cm^{-1}. Similar results were obtained[72] for LB films consisting of binary mixed monolayers (2 : 1) of stearic acid with poly(3-butylthiophene), poly(3-octylthiophene) or poly(3-octadecylthiophene); the maximum electric conductivity was 5.0 S cm^{-1}. Doping also results in significant changes in the absorption spectra of mixed LB films. The intensity of the strong absorption band corresponding to $\pi-\pi^*$-transition of the conjugated main chain (λ_{max} = 500 nm) decreases considerably and two new bands appear at 800 and 2200 nm, which correspond to transitions between the valence band and the new bipolar charged states that appear due to doping.[73]

Attempts to incorporate ions in mixed LB films consisting of poly(3-octylthiophene) with stearic acid (1.4 : 1) were made in order to increase the conductivity of these films.[69] However, even small contents of *e.g.*, N^+ (5×10^{14} ions per cm^2) violated the LB film layer structure, apparently due to destruction of stearic acid. The conductivity increased to only 10^{-3} S cm^{-1} with increase in the N^+ content by 2 orders of magnitude and resulted from formation of a conducting form of carbon. This not only destroyed completely the layer structure of the film but also destroyed the conjugated polymer structure (optical spectroscopy data).

Mixed monolayers and LB films of poly(3-hexylthiophene) or poly(3-dodecylthiophene) with poly(isobutyl methacrylate) were studied.[71] Taking account of the deviation from linearity of the relationship between the monolayer limiting area and composition, it was concluded in this study that polyalkylthiophenes and poly(isobutyl methacrylate) are compatible. Comparison of the optical spectra of mixed LB films with those of films with the same component ratio cast from solution showed that the conjugation efficiency for LB films containing poly(3-dodecylthiophene) is higher than for cast films but it is lower for films containing poly(3-hexylthiophene). The aggregation states of macromolecules are also different for these two film types. The conductivity of mixed LB films doped with sulfuric acid ranged from 0.05 to 0.1 S cm^{-1}; doping changed the LB film colour from red to blue.

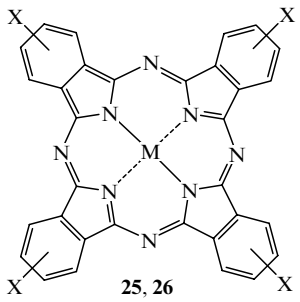
Polymerisation of thiophenes can occur in organised planar systems, resulting in the formation of anisotropic macromolecules.[74] In view of this, the properties of pure thiophene **24** and its mixtures with viologen were studied.[75]



24

It was shown by X-ray photoelectron spectroscopy with angular resolution [76–78] that an LB film of compound **24** has a layered structure (bilayers of the Y type) with a distance of 4.6 nm between the thiophene sublayers. In mixed monolayers and in LB films containing thiophene **24**, phase separation does not occur due to interactions between the positive charges of viologen and the deprotonated carboxyls of thiophene resulting in donor-acceptor diads.

In addition to mixed monolayers and LB films of polythiophenes with insulating molecules (mostly, fatty acids), of significant interest are thin planar systems consisting of mixtures of a conducting polythiophene with a conducting compound manifesting a surfactant property in an aqueous medium. Rikukawa *et al.*[79] used mixed monolayers of poly(3-hexylthiophene) with nickel (**25**) and iron (**26**) tetra-*tert*-butylphthalocyanines.



25, **26**

M = Ni (**25**), Fe (**26**); X = Bu^t.

It is considered [80, 81] that, along with unique electrical properties, phthalocyanines have an important advantage of higher stability of their monolayers in comparison with the stability of monolayers of fatty acids. The behaviour of pure phthalocyanine monolayers is essentially different: the limiting area of a phthalocyanine **26** monolayer is 75 and that of phthalocyanine **25** monolayer is only 34 $Å^2$ per molecule. In the former case, the molecular planes are oriented perpendicularly to the surface of water, and in the latter case the monolayer consists of aggregates whose thickness exceeds the size of one molecule. Incorporation of polythiophene expands slightly the monolayer of compound **25** and increases considerably the area of the monolayer of compound **26**. Thus, in the latter case the compatibility of monolayer components was higher than in the former, and displacement of polythiophene molecules occurred with much greater difficulty.

The structural organisation of mixed monolayers and films on a solid substrate and the character of interactions between the components were determined more accurately by comparison of the optical spectra of two mixed LB films with the spectra of phthalocyanines in solution and with the spectra of mixed LB films of phthalocyanines with stearic acid. It was found that the sulfur atoms of the thiophene rings tend to coordinate with the iron atoms of phthalocyanine. This limits the possibility of formation of phthalocyanine dimers and trimers and increases the extent of molecular mixing. For mixed LB films of compound **25** with polythiophene (as with stearic acid), the interactions between the molecules are not so strong and aggregation of molecules of compound **25** is much stronger than that in mixed LB films containing compound **26**. Interesting results of structural studies of mixed films carried out by small-angle X-ray scattering and by optical spectroscopy were reported. In mixed LB films of phthalocyanine **25** with polythiophene, as in the LB films of pure compounds **25** and **26**, the majority of phthalocyanine molecules form one-dimensional linear structures in which the ring planes are oriented perpendicularly to the substrate surfaces. In mixed films of phthalocyanine **26** and polythiophene, the phthalocyanine molecules exist mainly as monomers and have random organisation because of interaction with the thiophene units. The conjugated polymer chains in both mixed films are oriented parallel to the film surface, while the side chains have no preferential orientation. It should be noted that irreversibility of thermochromic properties was reported only for mixed LB films of poly(3-hexylthiophene) with phthalocyanine **26**:[79] heating from 25 to 120 °C changed the colour of the film from dark brown to green. The absorption spectrum of the film changed correspondingly. It should be noted that mixed films with the same component ratio cast from solution on a solid substrate did not display thermochromic properties. Doping of mixed LB films was carried out in iodine and $SbCl_5$ vapours.[79] As a result, electrical conductivity increased in comparison with the electrical conductivity of the LB films of pure phthalocyanines (10^{-5}–10^{-6} S cm^{-1}) by several orders and reached 10^{-1}–10^{-2} S cm^{-1}. Unlike LB films doped with iodine, the films doped with $SbCl_5$ were stable in vacuo and in an atmosphere of nitrogen. According to optical spectroscopic data, both components of the mixed film underwent doping. Figure 17 shows the dependences of the lateral conductivity of mixed LB films on the content of polythiophene components. It is evident that the maximum conductivity is reached at 80 mol.% of the polymer in the mixture; the conductivity of the system with phthalocyanine **26** is by an order of magnitude higher than that for the systems with phthalocyanine **25**. This effect is explained by coordination between the molecules of polythiophene and iron phthalocyanine.

Of considerable interest are the alternating Langmuir – Blodgett heterofilms consisting of materials with different conductivity band widths. These films are convenient models of quantum wells in organic systems.[82, 83] In addition, these alternating systems can be used for studies of energy transfer in

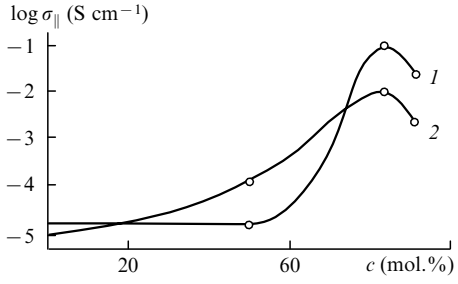


Figure 17. Dependence of the lateral conductivity of $SbCl_5$-doped Langmuir – Blodgett films consisting of mixed monolayers of poly(3-hexylthiophene) and iron (*1*) and nickel (*2*) phthalocyanines on the polymer content (*c*).[79]

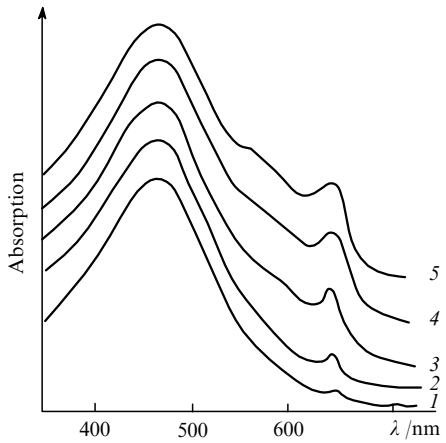


Figure 18. Absorption spectra of an alternating Langmuir – Blodgett film obtained from a mixture of polythiophene **17** and alkadiynoic acid at different irradiation times (light with the wavelength of 254 nm).[32]
Time /min: (*1*) 0.25; (*2*) 2; (*3*) 12; (*4*) 24; (*5*) 56.

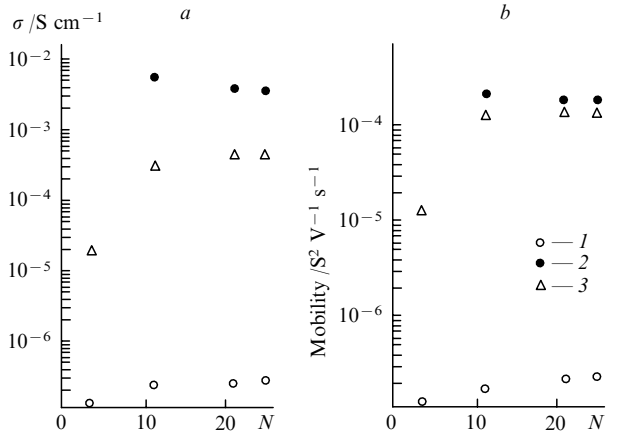


Figure 19. Dependences of specific electric conductivity (*a*) and charge mobility in electric field (*b*) for LB films consisting of mixed layers (5 : 1) of poly(3-hexylthiophene) and 3-octadecanoylpyrrole on the number of layers.[62]
Film: (*1*) non-doped; (*2*) doped with $NOPF_6$; (*3*) dedoped.

polymeric materials. For this purpose, Bolognesi *et al.*[32] chose alternating mixed LB films consisting of poly(3-methoxydecylthiophene) **17** and cadmium salt of the alkadiynoic acid $H(CH_2)_{12}C{\equiv}CC{\equiv}C(CH_2)_8COOH$. UV irradiation of the LB films formed from a polymer: monomer mixture at a wave length of 254 nm gave a film that contained alternating layers of two conjugated polymers. Figure 18 shows the absorption spectrum of a Langmuir – Blodgett heterofilm for various irradiation times determining the degree of polymerisation of diacetylenic acid. The band at 640 nm corresponds to exciton absorption of the extended polydiacetylenic chain. The band at 540 nm overlapping with the neighbouring bands originates from absorption of short polydiacetylenic chains.[84] It should be noted that irradiation of the Langmuir – Blodgett heterofilm does not shift the polythiophene absorption band at 505 nm nor decreases its intensity. On the other hand, laser irradiation of the original heterofilm near the polythiophene absorption (488 nm; light with this wavelength does not cause polymerisation of pure diacetylenic acid or its salt) results not only in polymerisation of the amphiphilic diacetylene but also in a shift of the maximum of the polythiophene absorption band to higher energies and in a decrease in its intensity. This result suggests photooxidation of the polythiophene component of the hetero structure and its subsequent sensitising effect on the photopolymerisation of the diacetylene. The identity of the absorption spectra of Langmuir – Blodgett homo- and heterofilms containing polydiacetylene indicates the one-dimensional exciton nature in the structures of both films, *i.e.* the absence of interactions between the polydiacetylene exciton and the polythiophene macromolecules.[32]

Mixed monolayers of poly(3-hexylthiophene) and pentacosa-10,12-diynoic acid were studied by Tsumura *et al.*[85] Stable monolayers were obtained for various component ratios; after transferring them onto a solid substrate by the vertical method they were polymerised by exposure to light. It was found that polythiophene does not affect the polymerisation of the diacetylenic acid and the LB film has a layered structure with oriented molecules of both components; the area per molecule in the mixed monolayer and the structure spacing in the LB film indicate the formation of bilayer films.[85] In this LB film variant, the bilayer consists of identical mixed monolayers rather than of alternating monolayers of different polymers (as in the previous case).

A detailed study of the effect of thickness, temperature and electric field on the conductivity mechanism in LB films consisting of mixed (5 : 1) monolayers of poly(3-hexylthiophene) and 3-decanoylpyrrole was carried out.[62] The dependence of the lateral conductivity and charge mobility in external electric field for an non-doped LB films, an LB film doped with $NOPF_6$ and a dedoped LB film (a sample which was allowed to relax after doping to a certain high conductivity) on the number of layers is presented in Fig. 19. It is evident that doping increases the conductivity by 5 orders of magnitude, while the mobility is increased by 4 orders. In view of this, a conclusion on the primary role of charge mobility in the LB film conductivity was drawn.[62] The thickness of LB films has but an insignificant effect on these parameters, except for the region between the 3- and 11-layer LB films. The decrease in conductivity upon keeping the samples in air (preparation of the dedoped system) is due to the loss of activity of the PF_6^- anions because of their reaction with moisture. Obviously, this affects the thinner film most strongly (see Fig. 19). It was shown in the same study that the dependence of conductivity (and charge mobility) on temperature for the non-doped film has the form $\log\sigma \sim T^{-1/4}$. This means that the hopping mechanism is the main mechanism of conductivity.[86] Based on this conclusion and on the experimental dependences of conductivity on external electric field, the mean hopping length and energy were calculated as 230 Å and 0.41 eV, respectively, using the Mott equation.[87]

In the case of doped and dedoped samples, the temperature dependence of conductivity had the form $\log\sigma \sim T^{-1/4}$ (Fig. 20). Extrapolation of the straight line obtained for the doped LB films to room temperature gave a conductivity of 0.1 S cm^{-1}. After dedoping, the plot slope and hence the activation energy changed, but the dependences still remained linear. Similar relationships are observed in the case of metal and metal-ceramic systems consisting of grains;[88,89] in view of this, some possible mechanisms describing the conductivity in these systems were considered.[62] Based on comparative analysis, the conclusion was drawn that the tunnel mechanism with charge transfer operates in poly(3-alkylthiophene) films doped with $NOPF_6$ (see Ref. 90). It was established on the basis of these concepts that dedoping results in an increase in the size of conducting grains (domains) in LB films from 30 to 50 Å. The conducting domains are formed by the main conjugated polymer chains separated by the side alkyl groups. Interesting data on changes in the conductivity mechanism were obtained for 11-layer LB film samples exposed to external electric fields with field strengths up to 0.5 MV cm^{-1}. Transition to the Fowler – Nordheim tunnelling mechanism was observed in this case.[91,92]

Analysis of the properties of monolayers and LB films of individual regioregular polythiophenes synthesised in recent years showed the advantages of these structurally homogeneous polymers assembled in organised planar ensembles over the systems

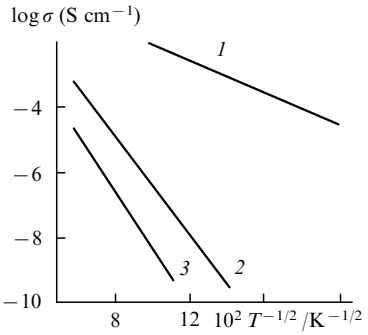


Figure 20. Temperature dependence of specific electric conductivity of a 25-layer LB film consisting of mixed (5 : 1) monolayers of poly(3-hexylthiophene) and 3-octadecanoylpyrrole.
Film: (*1*) non-doped; (*2*) moderately doped with $NOPF_6$; (*3*) dedoped.

containing poly(3-R-thiophenes) with random orientation of substituents.

The effect of the structural homogeneity of the polymer chain on the properties of monolayers and LB films also manifests itself in the case of mixed monolayers.[93] This is evident if one compares the compression isotherms of mixed monolayers of stearic acid with regioregular poly(3-hexylthiophene) containing up to 100% of 'head-to-tail' diads presented in Fig. 21 with the compression isotherms of a mixture of stearic acid with poly(3-hexylthiophene) having a random distribution of the chain substituents (see Fig. 14). Both monolayers consist of two phases, but the larger area and the smoother transitions between the phase states in the range of 20 – 30 mN m^{-1} for the former monolayer (see Fig. 21) suggest the better compatibility of stearic acid with the regular polythiophene. A similar trend was observed [94] in a study of the effect of the chain length of the alkyl substituent in polythiophene on the behaviour of monolayers and LB films obtained from its mixture with stearic acid. Smoothing of compression isotherms in the phase change region observed for the mixture of fatty acid with poly(3-hexylthiophene) is explained by better compatibility in this system than in the system with shorter alkyl substituents in polythiophene.

The mixed monolayers of stearic acid with regioregular poly(3-hexylthiophene) were transferred by the horizontal method at a surface pressure of 20 mN m^{-1} to give the Y type LB films (20 layers) on a hydrophobised glass plate surface.[93] It was shown by X-ray diffraction for LB films containing 2 : 1 polythiophene and stearic acid in monolayers that the film has a distinct layered structure with an interlayer distance of 17 Å. The same structure spacing found previously for poly(3-hexylthiophene) films cast from solution [42, 95] corresponds to the distance between the polymer chains stacked parallel to the substrate surface. However, the interlayer distance determined by X-ray diffraction for LB films composed of mixed (1 : 2) monolayers of stearic acid and irregular poly(3-hexylthiophene) corresponded to a bilayer of cadmium stearate, *i.e.*, 50 Å.[96] Figure 16 illustrates the structure of such an LB film. No similar scheme for LB films consisting of stearic acid and regular poly(3-hexylthiophene) has been reported in the literature; however, it can be expected that the stearic acid molecules in this system either form a tilted phase or are distributed along the polythiophene chains.

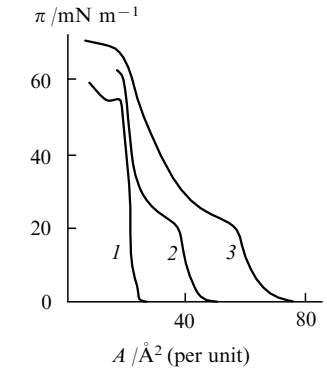


Figure 21. Compression isotherms of monolayers of regioregular poly(3-hexylthiophene) and stearic acid with component molar ratios of 0 : 1 (*1*); 2 : 1 (*2*); 5 : 1 (*3*).[93]

Rikukawa *et al.*[93] compared the UV and visible absorption spectra for 2 : 1 mixtures of regioregular and irregular poly(3-hexylthiophene) and stearic acid. According to the spectra presented in Fig. 22, the π – π*-transition energy of the mixture with the regular polymer is lower than that in the system with irregular polythiophene. This implies that the molecules of the former polythiophene in LB films have a more stretched structure and have a larger conjugation length than the molecule of the latter polythiophene. The lateral conductivity of LB films of mixed (5 : 1) monolayers of regioregular poly(3-hexylthiophene) with stearic acid doped with $NOPF_6$ was 50 – 100 S cm^{-1}, which is almost 1000 times higher than the lateral conductivity of a similar system containing irregular poly(3-hexylthiophene). It should be noted that the conductivity of LB films obtained from a mixture of regioregular poly(3-hexylthiophene) and stearic acid is several tens times higher than the conductivity of LB films obtained from the pure regioregular compound.[45]

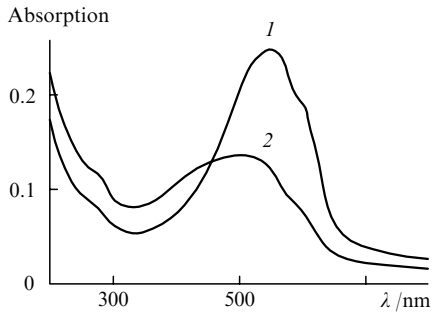


Figure 22. Absorption spectra of a 20-layer LB film consisting of mixed (2 : 1) monolayers of regioregular (*1*) and irregular (*2*) poly(3-hexylthiophene) and stearic acid.[93]

Thus, the regioregularity of polythiophene favours an increase in compatibility of the polymer with stearic acid and results in a sharp increase in electric conductivity of thin films consisting of these components. These features of polythiophene can intensify the development of molecular devices. In addition, comparison of systems containing polythiophenes with different degrees of regularity enables deeper insight into the relationship between the structure and properties of conducting polymers.

V. Prospects for the application of polythiophene Langmuir – Blodgett films in molecular devices

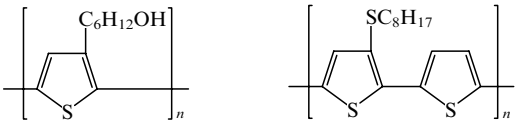
It has been noted in many publications that LB films of polythiophenes and their mixtures with other substances can be used for practical purposes, nevertheless only a few works describing molecular devices based on these compounds are available.

The first study with mixed monolayers of oligothiophene **1** (S_5) with eicosanoic acid in a Langmuir – Blodgett heterofilm (alternating mixed monolayers and pure eicosanoic acid monolayers) was carried out as early as in 1974 [58] (see footnote ‡). A cell was designed for photocurrent measurements, in which the LB film contained a mixed monolayer with oligothiophene S_5 located

‡ This was the first publication of Kuhn and his colleagues who laid the foundation of rapid development of studies in molecular design combined with the Langmuir – Blodgett technique.

close to one of the electrodes (aluminium or mercury) or at a certain distance set by the number of spacer monolayers of pure eicosanoic acid. By measuring the dependences of photocurrent on the applied voltage, temperature, and the arrangement of the conducting and insulating layers, the photophysical parameters of the device and the mechanism of generation of thermo- and photocurrent were determined. The authors suggested the main directions in the design of photoelectric devices. However, to date, scientific literature contains no information on the development of these kinds of devices based on polythiophene LB films. Nevertheless, metal – insulator – semiconductor transistors [97] and light-emitting devices [39, 40, 55, 56, 98] suitable for inexpensive flat colour displays and adjustable lasers from oligo- or polythiophene films deposited from solution or spray-deposited on electrodes are being designed.

Ng *et al.*[99] used LB films of mixed monolayers of poly [3-(6-hydroxyhexyl)thiophene] (**27**) or poly(3-octylthio-2,2′-bithiophene) (**28**) and octadecanol as a sensor for heavy metal ions. A quartz crystal microbalance was used as the recording device. The high quality of the LB films obtained (up to 40 monolayers) was confirmed by the facts that the change in frequency of the quartz resonator depended linearly on the number of LB film layers and that the transfer ratio of monolayers was equal to unity.



27 **28**

Figure 23 shows the dependence of adsorption of metal ions on a 10-layer LB film from mixed (3 : 1) polythiophene **27** : octadecanol monolayers deposited on the quartz resonator on the time of LB film exposure to 20 ppm solutions of ions at neutral pH and 25 °C. Similar results were obtained for mixed (1 : 3) polythiophene **28** : octadecanol LB films. One can see in the figure that the LB films of pure octadecanol does not adsorb metal ions under the same conditions. Complexing of metal ions with the polythiophene sulfur atoms is the driving force of adsorption. The selectivity in the series of ions $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+}$ correlates with the ionisation potentials and ionic sizes in the Irving – Williams series. The higher adsorption of Ag^+ and Hg^{2+} in comparison with the other ions is explained by the high affinity of these ions to the sulfur atom. An important feature of the sensor is its reversibility: complete regeneration of the sensor upon exposure of the resonator with LB films in 1 mM ethylenediaminetetraacetic acid solution occurred in 5 min. An increase in the number of layers in the LB film increased the absolute value of the change in the quartz resonator frequency Δf (the mass of the absorbed ions increases). This result indicates that the diffusion of ions in LB films does occur. However, for example, the 40-layer LB film was unstable and delaminated from the substrate after 7 – 10 measurements, whereas the 20-layer LB film withstood 50 measurements.

The concentration dependences of Δf for Ag^+ and Hg^{2+} ions are shown in Fig. 24. It is evident that a linear dependence is preserved up to the 100 ppm concentration. At higher concentrations, the frequency is unchanged because of saturation of the LB film with ions.

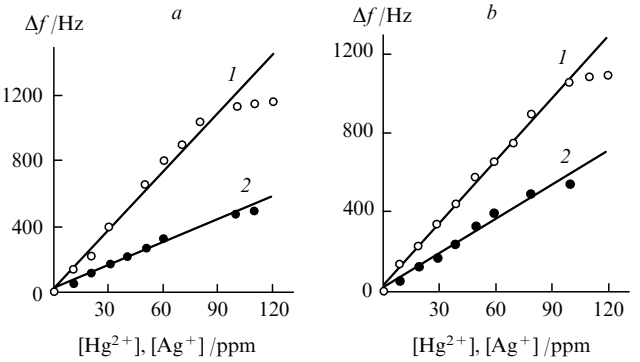


Figure 24. Concentration dependences of changes in the frequency of a quartz resonator with a 20-layer mixed LB film after exposure to a solution containing Hg^{2+} (*1*) and Ag^+ (*2*).
Film: (*a*) polythiophene **27** : octadecanol (3 : 1); (*b*) polythiophene **28** : octadecanol (1 : 3).[99]

The time dependence (Fig. 25) shows the lower detection limit of Hg^{2+} ions by the 20-layer LB film. Adsorption where Δf exceeds the 'noise' (30 Hz) by a factor of three is chosen as the criterion. Each addition of Hg^{2+} ions with a concentration of 0.1 ppm to the solution where the resonator with the LB film is located produces a sharp change in the resonator frequency. The three changes in frequency shown in Fig. 25 corresponded to changes in the Hg^{2+} mass by 45, 38 and 36 ng. It was noted [99] that the sensor sensitivity can be increased at least twofold. The sensor selectivity was tested for the 5 ppm concentration of the Hg^{2+} ions. It was found that such cations as Na^+, K^+, Ca^{2+}, Pb^{2+}, Cr^{2+}, Co^{2+} and Ni^{2+} (but not Ag^+ and Cu^{2+}) interfere with the determination of Hg^{2+} if their concentrations in solution were twice as high as that of mercury. The same concentrations of anions such as CO_3^{2-}, ClO_4^-, SO_4^{2-}, PO_4^{3-} and Cl^- do not affect the

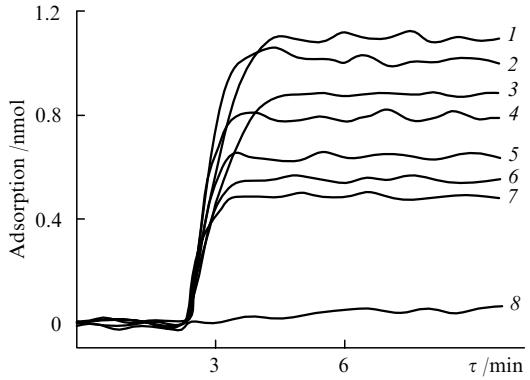


Figure 23. Dependence of the adsorption of metal ions on a 10-layer LB film consisting of mixed (3 : 1) polythiophene **27** : octadecanol monolayers on the time of exposure to solutions containing ions: Ag^+ (*1*); Cu^{2+} (*2*); Hg^{2+} (*3*); Ni^{2+} (*4*); Co^{2+} (*5*); Zn^{2+} (*6*); Fe^{2+} (*7*); Cu^{2+} + octadecanol LB film (*8*). The concentrations of the ions are 20 ppm (see Ref. 99).

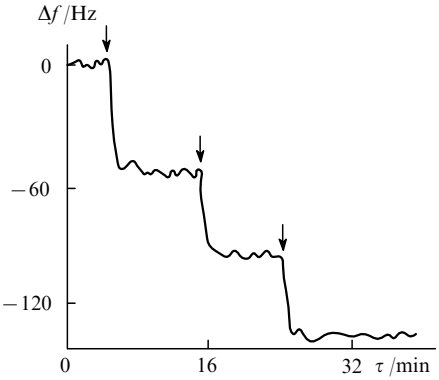


Figure 25. Dependence of the frequency of a quartz resonator with a 20-layer LB film consisting of mixed (3 : 1) polythiophene **27** : octadecanol monolayers on time of exposure in a solution containing Hg^{2+}. The arrows indicate the instants of addition of Hg^{2+} ions with a concentration of 0.1 ppm (see Ref. 99).

determination of Hg^{2+}, but anions such as Br^-, I^-, CrO_4^- and CNS^- form stable complexes with mercury. Thus, although the sensitivity and selectivity for many cations and anions are high, the problem of selectivity remains unsolved for a number of anions.

Mixed (1 : 1) binary monolayers of polythiophenes **11**, **19** and **20** and octadecylamine were studied with the purpose of obtaining a sensor for NO_2.[24] The compression isotherms for the mixtures have the same character as those of the pure compounds but with lower compressibility and a considerably smaller difference in the monolayer areas; the $\pi - A$ plot for polythiophene **11** is shifted to larger areas: the limiting monolayer area per thiophene unit increased from 9 to 20 Å^2. Figure 26 shows the dependences of quartz resonator frequency on the exposure time of a 14-layer LB film composed of mixed binary monolayers of polythiophenes **11**, **19** and **20** and octadecylamine in NO_2 (550 ppm). The differences in sensitivity of films containing the three polythiophenes cannot be caused by differences in the initial mass of the deposited substance as the monolayer areas corresponding to the surface pressure used for their transfer (30 mN m^{-1}) differed insignificantly. Taking into account the identity of the head groups of these compounds, one can state that the observed differences in sensitivity are caused by the side chains. Unfortunately, the sensor reversibility was low: treatment of the films in vacuo at 40 °C for one hour changed the frequency by no more than 10% (see Fig. 26).[24] NO_2 can be determined using a reported principle[100] for a gas sensor (for NO_2, H_2S, NH_3 and others) in which a thin film (not LB film) of electropolymerised polythiophene is used as the working element. Changes in electrical resistance of this sensor upon exposure to NO_2 (an electron acceptor) occur due to chemical doping, whereas in the case of electron-donating gases (for example, H_2S), the resistance changes due to a decrease in the number of charge carriers in the polythiophene film.

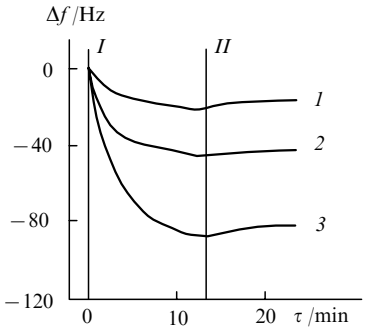


Figure 26. Dependence of frequency change on the time of exposure of a 14-layer LB film consisting of mixed (1 : 1) polythiophene : octadecylamine monolayers in NO_2 (550 ppm).[24]
Polythiophene: (*1*) **20**; (*2*) **19**; (*3*) **11**. The vertical lines indicate the times of turning on (*I*) and off (*II*) the NO_2 generator.

VI. Conclusion

The above analysis of the properties of conducting polythiophenes in monolayers and LB films shows that these objects are of significant interest for theoretical study and for practical application. The solubility of polythiophenes in ordinary solvents and formation of rather stable monolayers in one-component systems and definitely stable layers in multicomponent systems (in mixtures with inert and reactive amphiphilic compounds) and their resistance against moisture and oxygen in the initial and doped states make these polymers superior to the known conjugated polymers (for example, polydiacetylene, polypyrrole, *etc*.). Incorporation of substituents at positions 3 or 3 and 4 of the thiophene monomer, control of the chain length and polarity of the substituents and the regularity of their arrangement along the polymer chain make it possible to control the structural, physicochemical and electrophysical characteristics of polythiophenes in organised planar systems. This primarily corresponds to the control of the effective conjugation length of the polythiophene main chain and to the synthesis of uniformly oriented chains separated by distances which provide charge transfer between the adjacent macromolecules. In certain cases, creation of mixed monolayers of polythiophenes with surfactants (fatty acids, alcohols, amines, *etc*.) increases the stability of monolayers, ensures their transfer onto solid substrates and formation of high-quality multilayer LB films. In these cases, the conducting characteristics of polythiophene films are not inferior to those of similar systems containing pure polythiophenes. The use of dopants allows one to reach the electrical conductivity of substituted polythiophenes in the range from 500 to 1000 S cm^{-1}. The practically important properties of polythiophenes also include the photo- and electrochromic properties as well as the ability to form complexes with metals and gases. These properties enable the use of polythiophenes for creating thin-film light-emitting devices, sensors, *etc*. The Langmuir – Blodgett method has good prospects in this respect as it provides organised ultra-thin films with larger conjugation lengths than those of the films formed from solutions, and hence higher functional capabilities of molecular devices.

Based on the analysis carried out above, we can suggest the directions and priorities in the study of these systems. First, it is necessary to synthesise novel polythiophenes with functional substituents which are regularly distributed along the chain but are not included in each thiophene unit. These substituents can be represented, for example, by azo compounds which can undergo photoisomerisation disturbing the macromolecule conformation, which, in turn, should switch the conjugation length and hence change the conductivity and the chromatic characteristics of the systems. Second, more detailed studies of the structure of monolayers on the surface of water with the use of such methods as optical spectroscopy, Brewster angle microscopy and synchrotron X-ray reflectometery should be carried out. Third, the problem of monolayer stability requires a detailed study. In this connection, studies of the relaxation properties of two-dimensional systems would be rather useful. Fourth, it is necessary to study more intensely the structures of LB films comprising both individual and mixed monolayers. In the latter case, it would be desirable to obtain a consistent model of the distribution of film components in the layers. And, fifth, much greater attention should be given to the development of molecular devices based on LB films consisting of polythiophenes.

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