Colloid Polym Sci 276:1078–1087 (1998)

ORIGINAL CONTRIBUTION

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Influence of molecular weight on stepwise collapse of Langmuir monolayers of cyclolinear polyorganosiloxanes

Received: 2 March 1998
Accepted: 20 July 1998

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Abstract The series of hexacyclolinear polyorganosiloxanes containing methyl and phenyl side groups, which differ by molecular weight and tacticity, were analyzed for the dependence of surface pressure on surface area per monomer unit. The effects of temperature and the nature of substrate were also investigated. All the polymers investigated are capable of forming Langmuir monolayers on the surfaces of liquid substrates. Being under compression, the monolayers of these polymers are able to form discrete multilayers. This property is closely related to the existence of thermodynamically stable mesophase in cyclolinear polyorganosiloxanes. It has been established that formation of the multilayers in these polymers is quite sensitive to the molecular weight of the polymer. This effect is explained by a change in the value of the shear module of the polymer with molecular weight.

Key words Cyclolinear polyorganosiloxanes – mesophase – Langmuir films – discrete multilayers – molecular weight

Introduction

Molecular weight (degree of polymerization) is one of the fundamental characteristics of polymers and it can have a strong influence on their properties. Summarized in [1], the results of many investigations show that the surface pressure – surface area isotherms are independent of MW in the range ($\pi > 0.5$ mN/m). However, in some cases a certain dependence of π–A isotherms on degree of polymerization was observed. For example, an increase in dense area per monomer unit by a factor of 1.5 with increase in MW from 2.5×10^4 to 10^6 has been found in monolayers of polymethylmetacrylate [2]. A decrease in equilibrium spreading pressure has been observed for fractions of polyethyleneoxide with $MW < 10^5$ g/mol [3]. Significant influence of MW on the surface pressure of plateau, and value of $\Delta\pi$ corresponding to the second step, has been observed for fractions of cyclic PDMS in [4]. Both of these values decrease with increase in MW. An influence of MW on the π–A isotherms of linear PDMS in the plateau region is absent. However, the authors do not give considerable explanations of these phenomena.

PDMS spreads on water surface forming a monolayer. The collapse of the PDMS monolayer under compression occurs in two stages. According to the widely accepted point of view the second step in the π–A isotherm of PDMS is connected with transition from extended chain to helical conformation with axes of helices parallel to the water surface [5, 6]. However, Granick et al. [4] have observed, for cyclic PDMS, the same profile of the π–A isotherm with two steps, which is typical of linear PDMS. This finding allowed to suggest the analogous deformation mechanism, though collapse through formation of helices in the case of small cycles, containing only 20 silicon atoms, is unlikely. Recent investigations of PDMS monolayer collapse by fluorescent microscopy and external IR-scattering [7] showed that in the region of high surface concentrations, oxygens are mainly excluded from contact with water, which may correspond to a formation of helices. Brewster angle microscopy [8], capillary waves method, Brewster angle ellipsometry [9], small-angle neutron scattering [10] have pointed out the presence of significant surface inhomogeneity, which is consistent with phase transition. However, a polymer configuration was not confirmed. PDMS oligomers with short chains and also oligomers with chains, having end groups strongly interacting with water (for example, aminogroups), could be compressed with formation of close packed structures with areas per molecule corresponding to chains in the extended *cis-trans* conformation [11]. Long chains and chains with end groups weakly connected to the water show areas corresponding to the helical conformation of macromolecules.

Collapse of monolayers through formation of multilayer structures is characteristic of several low molecular weight substances, capable of forming a smectic mesophase. For example, consecutive formation of multilayers has been found in ferroelectric liquid crystals [12, 13]. Transformation of a monolayer into a stable trilayer consisting of a monolayer and an interdigitated bilayer has been observed in thermotropic liquid crystalline 4′-*n*-octyl-4-cyanobiphenyl [14] and in triblock organosiloxane smectogens [15]. Multilayer formation in these papers was treated as first-order thermodynamic phase transition and associated with a trend of these substances to form smectic layers in bulk.

Formation of multilayers on the liquid surface is also known for some polymers. A stable trilayer, which could be easily transferred onto solid substrates, has been found in polyelectrolytes at the air–water interface [16]. Formation of multilayers with strong hysteresis of the surface pressure of monolayer collapse has been observed for liquid-crystalline side-chain polymers [17]. Formation of additional layers, consisting of polymer molecules in α-helical conformation, occurs in polypeptides [18]. Several structural transitions, taking place consecutively during compression, have been observed in the π–A isotherms of phthalocyaninato-polysiloxanes [19, 20].

A novel mechanism of monolayer collapse has been found recently in cyclolinear polyorganosiloxanes (CLPOS) [21]. It has been pointed out that most of CLPOS are capable of forming a stable monolayer on a water surface, whose collapse under compression occurs through consecutive formation of bilayer, trilayer, tetralayer and so on (up to seven layers). Influence of flexible spacer between organosiloxane cycles, cycle size, nature of substituents was investigated [22, 23]. Process of multilayer growth has been visualized by means of scanning force microscopy [24]. Formation of multilayers in these polymers is closely related with their ability to form stable mesophase, despite the absence of mesogenic groups in the macromolecule. The mesophase state in CLPOS is quite sensitive to the change in MW of the polymer [25]. The aim of this work is to clarify the influence of the MW on the surface properties of CLPOS.

Experimental

Samples

Poly[oxy(4,4,6,6,10,10,12,12-octamethyl-2,8-diphenylcyclohexasiloxy-2,8-diyl)] (PMPhCS-6) with different molecular weights and tacticities have been synthesized according to a method described in detail in [26]. Fractions PMPhCS-61-PMPhCS-67 were prepared by fractionation of the sample PMPhCS-6a. Transtactic sample PMPhCS-6t is also a fraction, but obtained from another fractionation. A general chemical structure of PMPhCS-6 is given in the inset of Fig. 1. Characteristic viscosities $[\eta]$, weight-average molecular weights M_w, weight average degrees of polymerization $\bar{x}_w$, melting T_m, and isotropization T_i temperatures of the polymers investigated are summarized in Table 1.

All the samples show a mesophase up to high temperatures. In these samples mesomorphic state is present even at low values of degree of polymerization in contrast to linear PDES and PDPS. Isotropization temperatures of fractions show significant broadening of the temperature range of the mesophase state existence with increase in MW. On the contrary, melting temperatures of the fractionated samples are virtually independent of MW ($45 \pm 5\,^{\circ}$C) and exceed T_m of the non-fractionated sample of 35 °C.

Methods

The surface pressure–surface area isotherms were measured by means of the conventional Langmuir trough (FW1, Lauda). The surface pressure was determined by the Langmuir method. The polymer solution was placed on the surface of the substrate by a microsyringe. Concentrations

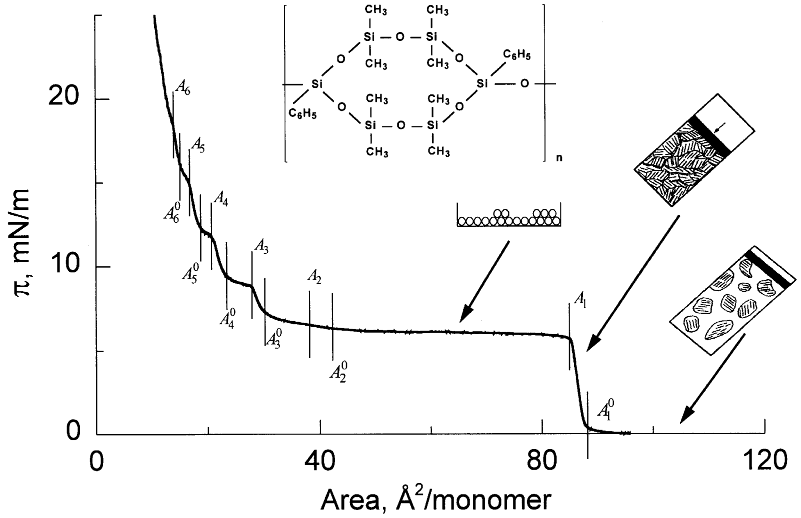

Fig. 1 Dependence of the surface pressure of PMPhCS-6a on the area per monomer unit on water at 23 °C. Structure of the monomer unit is given in the inset

Table 1 Characterization of the investigated cyclolinear polyorganosiloxanes[a)]

Sample	[η] [dl/g]	M_w	$\bar{x}_w$	T_m[°C]	T_i [°C]
PMPhCS-6a	0.5	75000	136	11	403
PMPhCS-61	0.06	8900	16	51	350
PMPhCS-62	0.13	18100	33	49	407
PMPhCS-63	0.14	19200	35	47	408
PMPhCS-64	0.20	28500	52	45	410
PMPhCS-65	0.23	33000	60	43	413
PMPhCS-66	0.33	49000	90	42	421
PMPhCS-67	0.55	85000	154	41	432
PMPhCS-6t	0.05	8100	15	145	425

[a)] All the polymers investigated are mainly atactic in the presence of up to 40% transequences, with exclusion of PMPhCS-6t, which is 100% transtactic.

of solutions were 0.05–0.5 mg/ml, aliquots were 50–500 μl. Toluene (nanograde, Mallinckrodt Inc.) and chloroform (spectroscopic grade, Merck) were used as solvents. π–A isotherms for both solvents were identical. To avoid contamination, the trough was cleaned with ethanol and water prior to experiments. Demineralized water and a mixture of glycerin (for analysis, Fluka) with water in the volume ratio 50 : 50 were used as substrates. The tests performed with water additionally purified by Milli-Q system, Millipore Corporation, have not shown any differences in isotherms. A blank experiment by addition of pure solvent to the water surface has also been done. The temperature was stabilized with an accuracy of ± 0.2 grad. The accuracy of surface pressure measurement was 0.1 mN/m. Compression velocity was 5 Å^2/(monomer × min).

Temperatures of phase transitions were obtained from the dependence of transmittance of polarized light through a preliminary quenched sample on temperature. To prevent the thermo-oxidative destruction, heating was conducted in nitrogen atmosphere with a rate of 10 grad/min.

Monolayers of PMPhCS-6a have been successfully transferred onto a solid substrate. Mica freshly cleaved by an adhesive tape was used as substrate. The transfer has been carried out by vertical dipping at a constant surface pressure. Dipping velocity was 1 mm/min. Transfer ratio was 0.9. The contact AFM mode images have been obtained in the constant force mode by means of a commercial microscope Nanoscope III (Digital Instruments).

Results

General characterization of the surface pressure–surface area isotherms

The polymer solution forms a monomolecular Langmuir film after deposition on the surface of the liquid substrate and evaporation of the solvent. Surface pressure plotted against the surface area per monomer unit at 23 °C for PMPhCS-6a on water is given in Fig. 1. During compression until point A_1^0(88 Å^2 per monomer unit) the surface pressure is close to zero. This point corresponds to the formation of a dense monolayer. Further compression of the monolayer is accompanied by a linear increase in the surface pressure. When pressure reaches a value of 6 mN/m, (A_1, 85 Å^2 per monomer unit), collapse of the monolayer occurs. After this point there is a plateau in the surface pressure. It should be mentioned that the linear increase in the surface pressure on compression of the monolayer with two sharp bends (A_1^0 and A_1) is also typical of other CLPOSs [22]. However, it is fundamentally different from a smooth S-shaped increase in the surface pressure with one inflection point in the case of PDMS. Several sharp steps in the surface pressure at areas per monomer unit related to the area of the first step as 1:0.45:0.33:0.25:0.2:0.16 occur on following compression. The beginning of increase in the surface pressure of each step, as in the case of the monolayer (A_n^0, where $n = 2, 3, 4, 5, 6$), corresponds to a fully filled n-layer. Deformation of a homogeneous layer with thickness n occurs on further compression until the inflection point (A_n). Each point A_n corresponds to the beginning of the formation of the $n + 1$-layer. Thus, segments $A_nA_{n+1}^0$ correspond to gradual transition from n to $n + 1$-layers, segments $A_n^0A_n$ correspond to the existence and deformation of the dense n-layer. Transition from bilayer to trilayer on the π–A isotherm at 23 °C is not pronounced markedly. However, a sharp step of 0.9 mN/m at area ratio 1:0.49 is observed at 10 °C. The height of the surface pressure step, which occurs on formation of each next layer, increases slightly with each layer. Data on surface pressure step heights ($\Delta\pi_n$) and corresponding areas per monomer unit or PMPhCS-6a at 23 °C are summarized in Table 2.

The surface pressure of the first plateau is independent of the compression velocity. A slight increase in $\Delta\pi$ with increase in the compression velocity is observed for other steps in the surface pressure. The shape of π–A isotherm changes, steps become less sharp. However, the areas per monomer unit of steps stay unchanged.

Stability and reversibility of π–A isotherms at 23 °C have been investigated in the following experimental procedure. Consecutive compressions of the surface layer were alternated with pauses for relaxation of the surface pressure. During these pauses the area per monomer unit was kept constant. When compression was stopped, the surface pressure began to fall down. The higher was its value, the faster it reduced (Fig. 2). A two-hour delay was enough to reach equilibrium for the areas exceeding 30 Å^2 per monomer unit, however, it was not enough for smaller areas. The curve plotted through points, corresponding to the value of the surface pressure after a 2 h relaxation, has no steps, which are characteristic of compression is continuous mode. On expansion of the system consisting of no more than six layers, the surface pressure fell down immediately to the value a little lower than the pressure of the first step. The isotherm was fully reproducible on the next compression. The surface pressure descended during pauses in the course of compression and raised during pauses in the course of expansion. In both cases its value aspires to a common limit equilibrium pressure of approximately 5.5 mN/m. The collapse became irreversible, if compression was continued until formation of the surface film with thickness of more than six layers. On expansion of such a film π fell down to zero value immediately.

Monolayer transferred onto the solid substrate

Figure 3 shows the AFM-image obtained in the contact mode for the dense monolayer of PMPhCS-6a, which was transferred onto mica from the point A_1. The transferred monolayer is quite uniform. The following procedure was

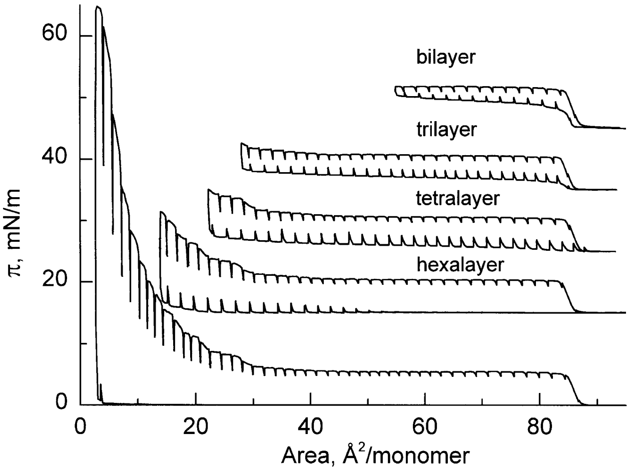

Fig. 2 Compression–expansion cycles of PMPhCS-6a until different degrees of compression with periodic pauses for relaxation of the surface pressure (duration of pauses 20 min) at 23 °C. The curves are shifted in π only for clearity

Table 2 Characteristics of π–A isotherm of PMPhCS-6a on water at 23 °C

n (Step number)	A_n^0 [Å^2/monomer]	A_n [Å^2/monomer]	$\Delta\pi_n$ [mN/m]	A_n/A_1
1	88	85	6.0	1
2	43	38	0.5	0.45
3	30	28	2.3	0.33
4	23	21	2.8	0.25
5	18	17	3.2	0.20
6	15	14	3.5	0.16

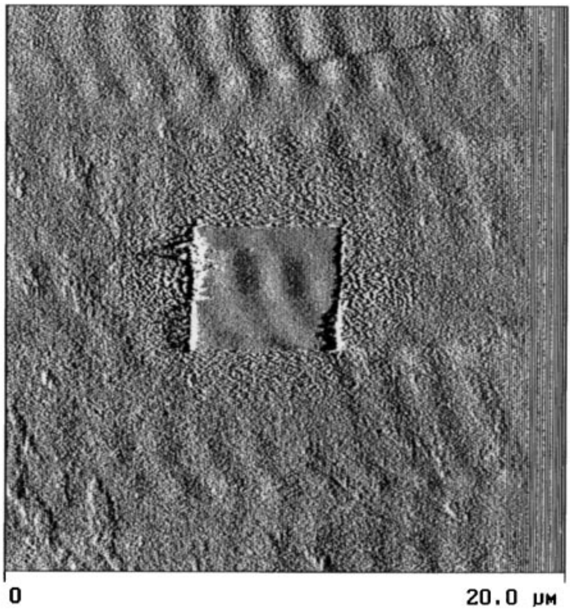

Fig. 3 Contact mode AFM image of the dense monolayer of PMPhCS-6a transferred onto mica from point A_1

used to measure the monolayer thickness. At first, the square area of $5 \times 5\ \mu m^2$ has been scanned with a high normal force applied. As a result, the polymer monolayer has been removed from the mica surface on this area. Afterwards, the large area of $20 \times 20\ \mu m^2$ has been scanned. Finally, on the image presented one could observe that the whole area of the substrate is covered with the uniform monolayer of the polymer except for the square hole $5 \times 5\ \mu m^2$ in the middle of the image. The thickness of the monolayer of PMPhCS-6a measured from this image was 12 ± 1 Å.

Influence of the molecular weight

The π–A isotherms for the various fractions at 23 °C are presented in Fig. 4. Isotherms for all the fractions except for the lowest molecular weight (PMPhCS-61) demonstrate the same qualitative pattern typical of the non-fractionated sample. A_1 and $\Delta\pi_1$ are independent of the polymer's MW and equal to the correponding values typical of a non-fractionated sample. Thus, the interaction of a polymer monolayer with the water surface is independent of molecular weight and molecular weight distribution of the polymer. On the contrary, the elastic deformation of a monolayer depends strongly on MW. It is expressed as different inclination of $\pi(A)$ in the region of linear increase in the surface pressure (Fig. 5a). The compressibility of the monolayer $-(1/A)(\partial A/\partial\pi)$ decreases with increase in MW. Molecular weight also noticeably influences the process of multilayer formation. The plateaus, corresponding to the formation of each following layer for all the high molecular weight fractions, are much more distinct, bends are better expressed than for the

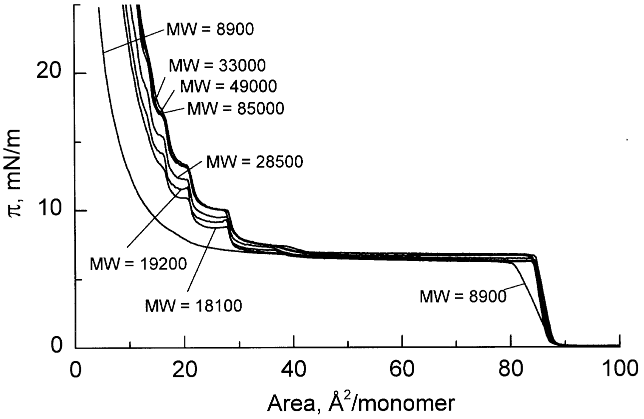

Fig. 4 π–A isotherms of PMPhCS-6 fractions on water at 23 °C

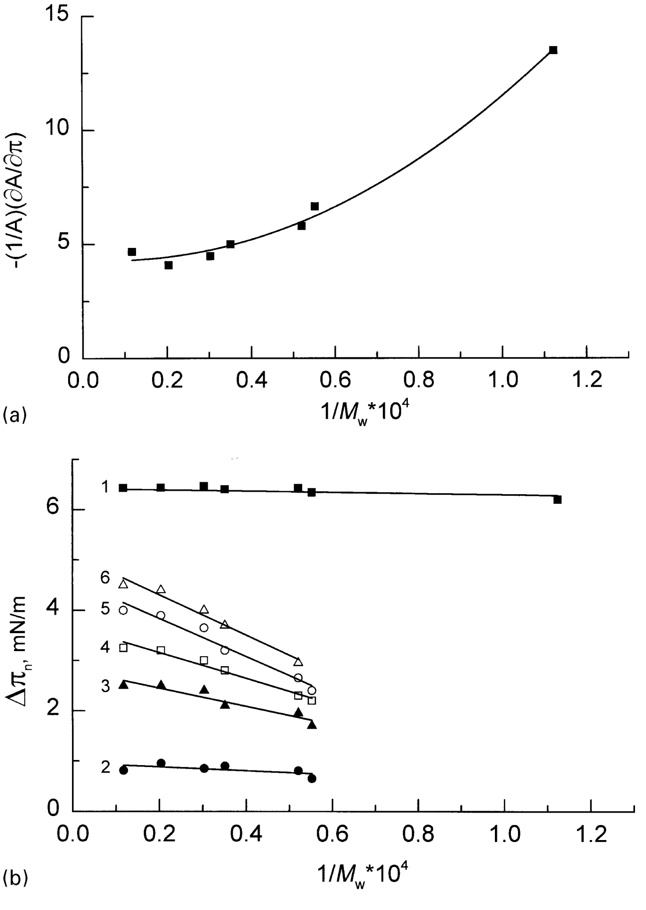

Fig. 5 Monolayer compressibility $-(1/A)(\partial A/\partial\pi)$ (a), height of the surface pressure step $\Delta\pi_n$, $n = 1, 2, 3, 4, 5, 6$ (b) of fractions versus 1/MW at 23 °C

non-fractionated sample. The areas per monomer unit, corresponding to the formation of the next layer, is unchanged, whereas the value of the surface pressure step after a change from the formation of the *n*-layer to $n + 1$ increases with MW. The step heights $\Delta\pi_n$ plotted against 1/MW at 23 °C are shown in Fig. 5b. An increase in the degree of polymerization twice from 33 to 60 is followed by an increase in step height by a factor of 1.4–1.5. This value is virtually independent of MW for fractions with the degree of polymerization higher than 60. Such a dependence of the surface pressure step on the degree of polymerization is opposite to the one observed in [4]. In this paper, a decrease in the plateau height and the surface pressure of the second step with the increase in molecular dimensions for cyclic PDMS is reported.

Compression of the monolayer of PMPhCS-61 is accompanied by an almost linear increase in the surface pressure within the areas 88–81 Å^2 per monomer unit with a following plateau. There is no distinct steps on the π–A isotherm of PMPhCS-61 on further compression. However, similar behavior of the surface pressure at high compressions, which is typical for all other samples of CLPOS, allows us to suggest a similar mechanism of the monolayer collapse. The surface pressure steps on the PMPhCS-61 isotherm could be non-distinguishable because of their small values.

Influence of temperature

π–A isotherms of PMPhCS-6a in the temperature interval from 10 °C to 55 °C are shown in Fig. 6. The shape of the π–A isotherm varies significantly with the temperature changes. All the steps in the surface pressure at the lower temperature are more sharply edged. The isotherm at 10 °C has a distinct second step of 0.9 mN/m, corresponding to the beginning of the formation of a trilayer from a bilayer, which is not well pronounced at 23 °C. π–A isotherms are going to be more smooth with the increase in temperature. The sharp steps, corresponding to the formation of each following layer, disappear. The monolayer compressibility $-(1/A)(\partial A/\partial\pi)$ in the region of its elastic deformation versus temperature is presented in Fig. 7a. The heights of the second and following steps decrease linearly with temperature (Fig. 7b). The slope $(\partial\pi/\partial T)$ is negative. For all the steps except for the first one it gives -0.0025 ± 0.007 mN/(m × K). $\pi(T)$ of the first step changes also linearly within the temperature interval 15–40 °C with $(\partial\pi/\partial T) = -0.072$ mN/(m × K). The negative $(\partial\pi/\partial T)$ is a characteristic property of many polymers (for example, PDMS [4], phthalocyaninatopolysiloxanes [19]). The dense area per monomer unit is also a function of temperature. The area A_1^0, obtained by extrapolation of the surface pressure in the region of its linear increase down to $\pi = 0$, is plotted against the temperature in Fig. 7c. This value increases significantly with the increase in temperature.

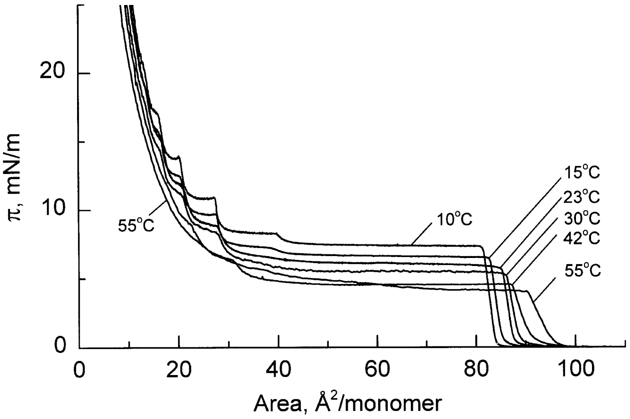

Fig. 6 π–A isotherms of PMPhCS-6a on water at different temperatures

Influence of the nature of substrate

Investigation of π–A isotherms has been carried out using two substrates: water and an equal mixture of glycerin and water. PMPhCS-6a forms a stable monolayer on the surface of the glycerin–water mixture (this polymer is able to spread on the surface of pure glycerin, but the shape and absolute characteristics of the isotherm are badly reproducible). The π–A isotherm of the polymer on the glycerin–water mixture at 23 °C (Fig. 8A) qualitatively reproduces corresponding isotherms obtained on the pure water. However, the surface pressure, which is necessary to remove the polymer from the surface of the substrate, in the case of glycerin-water mixture, exceeds that of pure water by a factor of 1.6 and gives 9.5 mN/m. This value is expressed by the following relation:

$$\pi = \sigma_{\text{substrate/air}} - \sigma_{\text{substrate/polymer}} - \sigma_{\text{polymer/air}} .$$

The surface tension $\sigma_{\text{glycerine–water/air}}$ is lower than $\sigma_{\text{water/air}}$. (at 18 °C, for mixture glycerin–water 50:50 this value is 70 mN/m, whereas for pure water it is 73.05 mN/m [27]). Thus,

$$\sigma_{\text{glycerin–water/polymer}} < \sigma_{\text{water/polymer}} .$$

This is likely caused by the presence of an additional specific interaction of polymer, containing both polar Si–O fragments, and non-polar hydrocarbon side groups, with glycerin.

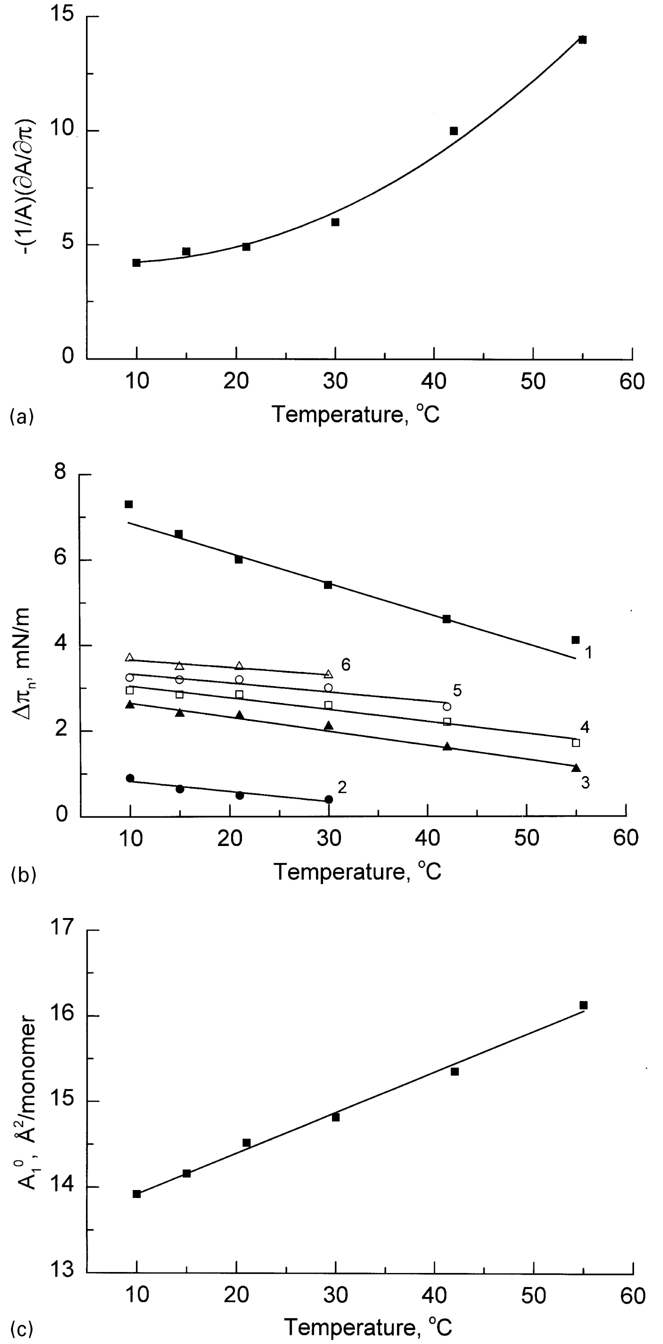

Fig. 7 Monolayer compressibility (a), height of the surface pressure step (b), area per monomer unit of the dense monolayer (c) of PMPhCS-6a versus temperature

Influence of molecular structure

PMPhCS-6t fraction is 100% transtactic, whereas all other polymers investigated are mainly atactic, containing up to 40% of trans-sequences. The π–A isotherm of PMPhCS-6t is shown in Fig. 8B. The values of A_1 and $\Delta\pi_1$ (Table 3) for this fraction and PMPhCS-6a are similar. However, with the increase in the thickness of the surface layer, some differences occur. Steps $\Delta\pi_2$ and $\Delta\pi_3$ of PMPhCS-6t, exceed those for PMPhCS-6a. The areas ratio stays unchanged. If compression of PMPhCS-6t is stopped below the formation of the three layers, the isotherm is fully reproducible at the successive compressions (Fig. 9). However, after compression above these values the steps are not observed at all. The surface pressure increases almost vertical. The system loses its ability to return to the initial state.

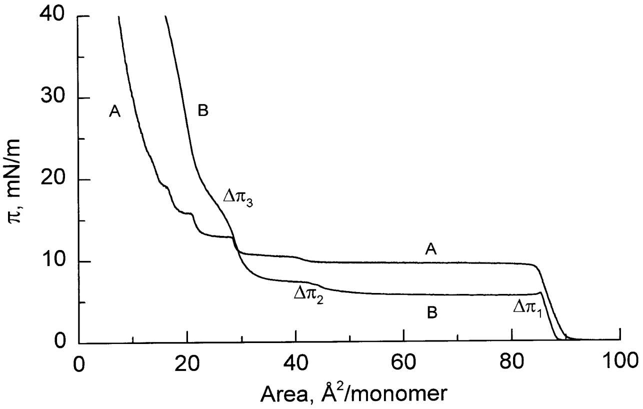

Fig. 8 π–A isotherm of PMPhCS-6a on the mixture glycerin/water 50/50 (A) and π–A isotherm of PMPhCS-6t on water (B) at 23 °C

Discussion

The results obtained can be interpreted as follows. CLPOS form a monomolecular film on the surface of the liquid substrate after spreading and evaporation of a solvent. It is supposed that polymer macromolecules lie on the surface of the substrate in such a way, that siloxane fragments adjoin to the water surface, and hydrocarbon side groups are directed towards the air phase. Following [22] we suggest, the polymer forms a condensed monolayer, consisting of macromolecules in the extended chain conformations (solid island-like phase). Moreover, the macromolecules in each island are parallel to each other. However, the orientation of macromolecules in different islands could be different (Fig. 1). This behavior is a direct consequence of the mesomorphic nature of CLPOS. The regions of the free subphase surface or those of the subphase surface with the low concentration of polymer macromolecules coexist with the regions covered by the dense monolayer of the polymer. It is supposed that mutual approaching of the isolated polymer domains occurs during the initial stage of compression. This process is not

Table 3 Characteristics of π–A isotherm of PMPhCS-6t on water at 23 °C

n (Step number)	A_n^0 [Å^2/monomer]	A_n [Å^2/monomer]	$\Delta\pi_n$ [mN/m]	A_n/A_1
1	88	85	5.6	1
2	48	43	1.6	0.51
3	31	28	7.4	0.33

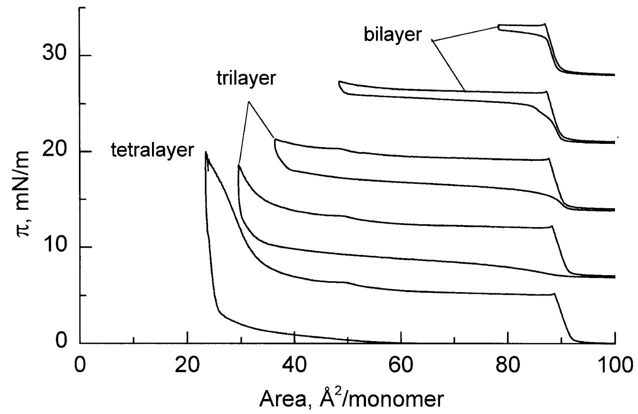

Fig. 9 Compression–expansion cycles of PMPhCS-6t until different degrees of compression on water at 23 °C

accompanied by a change in the surface pressure and continues until point A_1^0, where the whole system consists of the dense monolayer. Linear elastic deformation of the dense monolayer occurs following compression ($A_1^0A_1$). This behavior is fundamentally different from that observed in PDMS. Compression of the PDMS monolayer is accompanied by a smooth S-shaped increase in the surface pressure with one inflection point. The polymer chains of PDMS are disordered and highly compressible. A process of chain condensation occurs, and simultaneously water is displaced from the gaps between molecules. The inflection point of the π–A isotherm of PDMS corresponds to the formation of the dense monolayer. The true monolayer destruction (all polar groups are fixed on the water surface) occurs after this point [28]. On the contrary, the dense monolayer of CLPOS (A_1^0) consists of preliminary oriented mesophase domains. During compression elastic deformation of the homogeneous solid-like layer occurs. It is accompanied by a linear increase in the surface pressure with two sharp bends. The surface pressure becomes constant in point A_1. This corresponds to the beginning of removing of polymer macromolecules from the water surface and pushing them out over the dense monolayer.

The area, corresponding to the dense monolayer of organosiloxane rings laying flat on the water surface, has been calculated in [24] to be 127 Å^2 per monomer unit for another hexacyclolinear polyorganosiloxane. It differs from the polymer investigated by two methyl substituents instead of two phenyl ones at silsesquioxane silicon atoms. The surface pressure of the first plateau for this polymer was 8.9 mN/m. The monolayer thickness in this case was 7.5 Å, instead of 12 Å for PMPhCS-6a. It is possible to suggest that in the polymer investigated, siloxane rings in the dense monolayer are not lying flat on the water surface, because of spatial difficulties caused by the presence of bulky phenyl groups. Therefore, compression of the PMPhCS-6a film is accompanied by the smaller values of the dense monolayer area and force needed to remove polymer molecules from the water surface.

Several steps in the surface pressure, corresponding to the gradual formation of multilayers, are observed in the π–A isotherm on further compression. Each surface pressure step corresponds to the increase in thickness of the polymer layer by one. The gradual formation of multilayers can continue until the formation of sixth layer. On expansion of the system, consisting of six or less layers of PMPhCS-6a, the surface pressure falls down to the value close to the pressure of the first step immediately. The uniform multilayer is destroyed. It is supposed, that during the breakage, islands of the initial multilayer occur, while the gaps between the islands are filled with monolayer. Following expansion, the islands are gradually transformed to a monolayer and, finally, the system returns to the initial state identical to the one after spreading of the polymer on the water surface. However, reversibility of the isotherm disappears if compression has been done until the formation of the layer with higher thickness. On expansion of such a system the surface pressure falls down to a zero value immediately. The polymer will not spread back with the formation of a monolayer. This is probably due to formation of the three-dimensional phase, which remains even after expansion (at least during experimentally observable time interval).

Reversibility of π–A isotherm disappears also in the case of PMPhCS-6t. However, this phenomenon seems to have another nature. It is known that crystallizable polymer cannot crystallize being spread as a monolayer. Crystallization means formation of 3D ordering, and it can not occur in a 2D monolayer. Thus, transtactic PMPhCS-6t with $T_m = 145\,^\circ$C, spread from a solution as a monolayer on the water surface, at 23 °C exists in the mesomorphic state, similar to PMPhCS-6a. Consequently, the initial part of the π–A isotherm of PMPhCS-6t coincides with the one of PMPhCS-6a. Noticeable differences arise with the increase in the layer thickness. When the thickness of the layer of PMPhCS-6t reaches the thickness of four molecules, a sudden increase in the surface pressure and the loss of the multistep character and the isotherm reversibility occur. It is caused by crystallization of the polymer.

The equilibrium surface pressure for PMPhCS-6a is equal to ~5.5 mN/m, that is a little lower than the surface pressure of the first step. The surface pressure falls down to this value during pauses in the course of compression and rises to the same value during pauses in the course of expansion. Hence, this is the pressure necessary to remove the polymer from the water surface. It arises from an increase in area of the free water surface at the expense of decrease in the area of the water surface covered by the polymer layer. This process requires a certain force, determined by the difference in the free surface energies of the pure water and water with the polymer layer, and is independent of the MW of the polymer.

The analysis of the dependence of the equilibrium surface pressure on temperature allows to separate the enthalpic and entropic contributions. According to Harkins [29], change in the thermodynamic functions of a monolayer is expressed as follows:

$$\left(\frac{\partial G}{\partial a}\right)_{T,A} = -\pi;\quad \left(\frac{\partial S}{\partial a}\right)_{T,A} = \left(\frac{\partial \pi}{\partial T}\right)_{a,A},$$

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

where G is the surface Gibbs free energy, S the surface entropy, H the surface enthalpy, a the film area, A the total area of the film and free water surface and T the absolute temperature.

The differential surface entropy and enthalpy of PMPhCS-6a for the transition from monolayer to bilayer at the air/water interface, were calculated with the help of Eq. (1). They are plotted against the area per monomer unit at 23 °C in Fig. 10. In the dilute region the thermodynamic functions are constant. The differential surface entropy and enthalpy are positive on compression of the monolayer between points A_1^0 and A_1. It corresponds to a decrease in the surface entropy and enthalpy in this region as a result of hardening of the monolayer in the course of elastic deformation. Another possibility is a change in ordering of the water molecules adjoining the surface of the polymer layer. The change in sign of the differential surface thermodynamic functions on compression beyond the point A_1 expresses the arising of an additional degree of freedom of the surface layer. It is connected with the start of the formation of a second layer on top of the dense monolayer. On further compression until point A_2^0 the surface entropy and enthalpy increase. It corresponds to the continuous phase transition from the monolayer to the bilayer.

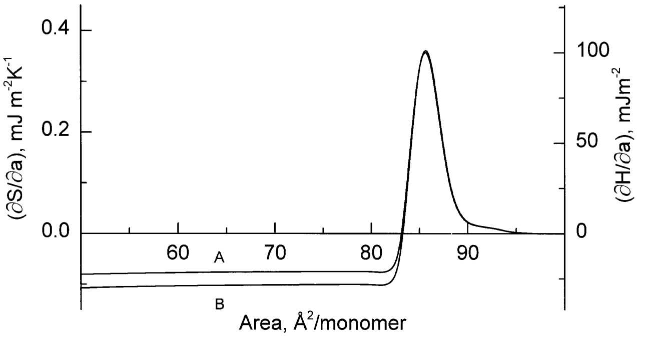

Fig. 10 Dependences of the differential surface entropy (A) and enthalpy (B) of PMPhCS-6a on the area per monomer unit on water at 23 °C

The transition from the monolayer to the bilayer can be treated as the first-order phase transition. The latent heat Q and entropy change ΔS can be estimated from the values of the equilibrium surface pressure by means of the two-dimensional Clausius–Clapeyron equation [29]:

$$(\partial\pi/\partial T) = Q/(T\Delta a) = \Delta S/\Delta a\,, \qquad (2)$$

where Δa is the change in area per repeating unit of the surface film.

Within the temperature interval from 15 to 40 °C $(\partial\pi/\pi T)$ of PMPhCS-6a is constant $(-0.072\ \mathrm{mJ/(m^2 \times K)})$ and Δa is not strongly dependent on the temperature (43 ± 1 Å^2/monomer). From Eq. (2) we obtain $\Delta S =$ 19 J/(mol × K); and at 23 °C $Q = 5.5$ kJ/mol. The latent heat can be simply converted into a change of the surface energy $\Delta E = Q/\Delta a$. $\Delta E = 21\ \mathrm{mJ/m^2}$ for PMPhCS-6a at 23 °C. The change in the surface energy value can be compared with 24 mJ/m^2 obtained for monomer organosiloxane smectogens [15]. But in the case of PMPhCS-6a the contribution of the removal of macromolecules from the air/water interface ($\pi = 5.5\ \mathrm{mJ/m^2}$) is much lower than 15 mJ/m^2 for these smectogens. The origin of the additional 15.5 mJ/m^2 is still not clear. The Clausius–Clapeyron equation is not applicable to the transition from the bilayer to the trilayer and the following ones, because the value of the surface pressure in these cases is strongly non-equilibrium.

To explain the process of formation of additional layers in CLPOS, we use the model proposed recently [21]. According to this model, macromolecules of CLPOS are treated for simplicity as parallel cylinders. Parallelization of macromolecules is a result of formation of the thermodynamically stable mesophase. Pressure, caused by a barrier, forces the polymer chains to slide relative to each other along sliding planes, lying with the angle 60° respective to the water surface. The decrease in the area occupied by polymer occurs at the expense of displacement of molecules from the n-layer to the $n+1$ layer, leaving the surface pressure constant.

The additional dynamic increment of the surface pressure $\Delta\pi_{\text{step}}$ could be expressed as

$$n\Delta\pi_{\text{step}} = \frac{2F_{\text{slide}}}{l} = 4nr\sigma_{\text{slide}} \ , \tag{3}$$

where F_{slide} is the sliding force of a polymer chain with length l and average diameter of the chain $2r$, σ_{slide} the plastic sliding stress for irreversible plastic deformation. F_{slide} is a function of the number of layers, and its increase on formation of each new layer should be a constant value. σ_{slide} is connected by a simple relation with sliding deformation $\varepsilon_{\text{slide}}$ through shear module G [30].

$$\sigma_{\text{slide}} \cong G\varepsilon_{\text{slide}} \ .$$

By substitution in Eq. (3) we obtain that value of the increase in the surface pressure at the expense of sliding of macromolecules is directly proportional to the shear module.

$$\Delta\pi_{\text{step}} \cong 4rG\varepsilon_{\text{slide}} \ .$$

Sliding deformation does not depend on the length of a polymer chain (MW of polymer), because deformation occurs in direction, perpendicular to the axes of the macromolecules. Thus, change in the height of surface pressure steps is determined by a change in the shear module. The observed change in the height of the surface pressure steps with MW seems to be the result of an increase in the shear module with MW. The change in the shear module with temperature is also a possible reason for the decrease in the height of the surface pressure steps and even for their disappearing with temperature.

Acknowledgements This work was supported by Sonderforschungsbereich 239 University of Ulm (project A11), Russian Foundation for Basic Research (grant 96-03-32497) and CRDF (grant RC-210). Yu. K.G. is greatful to the Alexander von Humboldt foundation for the Research Award.

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