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Dilational Viscoelasticity of PEO–PPO–PEO Triblock Copolymer Films at the Air–Water Interface in the Range of High Surface Pressures

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The dynamic dilational elasticity of adsorbed and spread films of PEO–PPO–PEO triblock copolymers at the air–water interface was measured as a function of surface pressure, surface age, and frequency. At low surface pressures (<10 mN/m), the surface viscoelasticity is identical to that of PEO homopolymer films. The results at higher surface pressures can be explained by the desorption of PPO segments from the interface and then mixing with PEO segments in water. Unlike some recent results, the spread and adsorbed films are not identical. Spread films exhibit a maximum real part of the dynamic surface elasticity of about 20 mN/m and probably begin to dissolve in water at surface pressures above 19 mN/m. However, the surface elasticity of the adsorbed films decreases beyond the maximum, indicating the formation of a loose surface structure.

Introduction

Amphiphilic block copolymers have attracted widespread interest for both scientific and practical reasons.¹ These macromolecules adsorb at various interfaces and play a significant role in dispersion stabilization, foaming, and emulsification. Examples of more specialized applications are bioprocessing and medicine. However, surface films of amphiphilic block copolymers are widely used in fundamental studies as convenient physical models of polymer brushes. The scaling^{2,3} and mean-field^{4,5} theories of brushes proved to be very useful for the description of grafted polymers at solid surfaces. The situation is more complicated for block copolymer films at liquid surfaces, mainly at the water–air interface. Although these systems have been studied for a few decades,^{1,6–18} the brush formation in

some copolymer films at the water surface is still a subject of discussion.^{13,18} Most of the authors investigated films of block copolymers containing poly(ethylene oxide) (PEO) blocks, which are hydrophilic and at the same time attracted by the surface. Special attention has been paid to films of triblock copolymers of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO).^{6–8,19–30} These polymers are commercially available, find various industrial applications,^{1,8} and are effective in sealing permeated cell membranes.^{19,20} The static properties of PEO–PPO–PEO spread and adsorbed films at the air–water interface were studied in detail by surface tension measurements,^{6–8,21} ellipsometry,^{21,22} neutron reflectivity,^{23–25} and Brewster angle microscopy.²¹ Recently, a few groups have investigated the dilational dynamic properties of these systems

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by various experimental techniques in broad frequency (0.1– 10^5 Hz) and concentration ranges.^{26–30} To the best of our knowledge, there is very little corresponding information on other block copolymer films at the air–water interface.

The first studies of PEO–PPO–PEO films at the air–water interface mainly concentrated on the interpretation of abrupt changes in the slope of the surface tension isotherm at concentrations below the critical micellar concentration (cmc).^{6–8} To explain these results, Alexandridis et al. assumed conformational changes in the surface layer of block copolymer solutions, in particular, the protrusion of PEO segments into the solution bulk beyond a critical concentration.⁸ At the same time, they considered that PPO segments are present at the interface over the whole concentration range. Munoz et al. further developed these ideas²¹ and discovered by ellipsometry that a rather abrupt increase in the film thickness is accompanied by changes in the slope of the surface tension isotherm. They proposed the formation of a brushlike structure in the PEO–PPO–PEO films, as was proposed independently by Sedev et al.²² The application of neutron reflectivity to these systems led to a somewhat more complicated structure. Sedev et al. studied commercial block copolymers in D₂O and fitted the reflection curve to a single-layer model.²³ The film thickness changed linearly with the PEO chain length in agreement with brush theory, but the segment density profile proved to be more diffuse than predicted by the brush model. More elaborate measurements by Vieira et al., who used deuterated polymers and fitted the experimental curve to a four layer model, led to some contradictions with the classical idea of a polymer brush.²⁵ The determined PPO segment density profile did not corroborate the previous assumptions and indicated that PPO and PEO segments can mix in the sublayer in accordance with the earlier mean-field calculations by Linse and Hatton.³¹ The extent of penetration increased with the copolymer bulk concentration.

Recent studies of the dilational viscoelasticity of PEO–PPO–PEO films are mainly focused on the comparison of adsorbed and spread monolayers at the water surface and the explanation of measured negative surface viscosities at high frequencies.^{26,27} Munoz et al. showed by capillary wave techniques that films of Pluronic F-68 (PEO₇₆–PPO₂₉–PEO₇₆) are mainly elastic and the elasticity did not depend on the method of film formation up to a surface pressure (π) of 18 mN/m.²⁶ The dependence of dynamic surface elasticity on surface pressure exhibited two local maxima and almost coincided with the corresponding dependence of the static elasticity for both F-68 and PEO homopolymer spread films at $\pi < 10$ mN/m. On the contrary, Kim and Yu discovered significant differences between the dynamic and static elasticities of spread films of PEO–PPO–PEO of lower molecular weight.²⁷ Although the authors explained their results in terms of a mushroom-to-brush transition, they did not investigate the compatibility of dilational surface viscoelastic properties with the brush model.

More recently, Hambardzumyan et al. have studied the elasticity of adsorbed films of PEO–PPO–PEO of different lengths of the blocks by bubble-shape tensiometry at low frequencies (0.1 s^{−1}) in the range of relatively low surface pressures (less than 15 mN/m for F-68).²⁸ Only the real part of the elasticity was taken into account. The results for F-68 were close to the data of Munoz et al., which correspond to higher frequencies (> 100 Hz).²⁶ The scaling model of the multiblock copolymer adsorption^{32–34} was applied to determine the transitions between various copolymer

conformations in the surface layer, and the formation of a quasibrush was assumed for increasing surface pressure.

Detailed data on the surface dilational viscoelasticity of PEO–PPO–PEO surface films have been obtained very recently by Rippner Blomqvist et al. using the oscillating ring method at a frequency of 0.13 Hz.³⁰ Unlike other studies, the authors measured surface elasticity as a function of surface age and at some concentrations observed nonmonotonic kinetic curves. Nevertheless, plotting the surface dilational modulus as a function of π gave a unique master curve for each copolymer independent of surface age. This result and similarities between spread and adsorbed PEO–PPO–PEO films led the authors to the conclusion that the surface structure is determined by the surface concentration. Although qualitative agreement with previous results^{26,28} was noted, the interpretation of experimental data at high surface pressures was different. The decrease in surface elasticity after the second maximum was explained by the formation of loops and tails by PPO segments and, consequently, by a structure somewhat different from a classic brush.

The important conclusions of Rippner Blomqvist et al., however, are based mainly on nonequilibrium experimental data. All results for adsorbed PEO–PPO–PEO films were obtained at a surface age of less than 1 h, which is not sufficient for equilibration at some concentrations.³⁰ Significant deviations from the master curve due to the slow time effects are clearly seen in Figure 6 of the work³⁰ just in the range of high surface pressures ($\pi > 20$ mN/m). Moreover, the barrier speed of 1 mm/s was also too high for measurements of equilibrium surface pressure of spread films where slow relaxation processes were expected.³⁰ Therefore, the similarity of spread and adsorbed PEO–PPO–PEO films and respective conclusions require special examination. With this aim, we applied a different experimental method to determine the dynamic surface elasticity at greater surface age and hence closer to the equilibrium state. Special attention was paid to the range of high surface pressures. Recently, the oscillating barrier technique has also been applied to nonionic homopolymer adsorption films.^{35–38} In the present study, we used this method to measure the dynamic surface elasticity of both adsorbed and spread PEO₇₆–PPO₂₉–PEO₇₆ films. In the latter case, the films were prepared by successive additions of the block copolymer solution to the water surface, and measurements began only if the rate of surface pressure decrease was less than 0.001 mN m^{−1} s^{−1}. The classic brush model cannot explain the experimental results in the range of high surface pressures. This point is in agreement with the results of ref 30, whereas several other conclusions are different. The surface pressure is not the only parameter determining all of the viscoelastic properties of PEO₇₆–PPO₂₉–PEO₇₆ surface films. The properties and, consequently, the structure of spread and adsorbed surface films can be different. For example, spread films have a maximum dynamic surface elasticity at $\pi \approx 19$ mN/m and do not exist at higher surface pressures, whereas the adsorbed ones exhibit much lower surface elasticity at much higher surface pressures.

Experimental Section

Triblock copolymer PEO₇₆–PPO₂₉–PEO₇₆ with an average molecular weight of 8750 was obtained from Polysciences (Germany)

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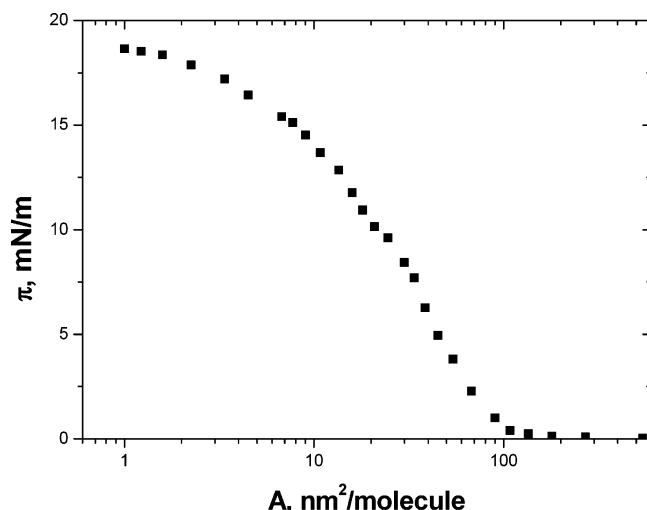


Figure 1. Surface pressure vs area per molecule for PEO₇₆-PPO₂₉-PEO₇₆ spread films.

and was vacuum dried at 50° C before used. Fresh twice-distilled water was used for the preparation of the solutions and the subphase for spread polymer films. An all-Pyrex apparatus and alkaline permanganate were employed in the second stage of distillation. All solutions were carefully stirred before measurements.

To produce spread films, the polymer was dissolved in chloroform, and solutions of concentrations between 0.02 and 0.05 g/L were carefully deposited onto the water surface in a PTFE Langmuir trough with the help of a Hamilton microsyringe. The surface concentration was changed by successive additions of polymer with the microsyringe.

All measurements were carried out at $20.0 \pm 1^\circ$ C.

The experimental setup for measurements of surface tension oscillations in a Langmuir trough together with the corresponding experimental procedure was described in detail elsewhere.^{37,39} We represent below only the basic principles of the employed technique. Low-frequency oscillations of the liquid surface area in the Langmuir trough were induced by a moving PTFE barrier.³⁹ A mechanical generator transformed the rotation of an electromotor to translational motion with reversion and provided the possibility to control the frequency and the amplitude. The moving part of the generator was connected to the PTFE barrier by a steel rod. In operation, the barrier glided back and forth along the polished brims of the Langmuir trough and produced sinusoidal oscillations of the liquid surface area S with a relative amplitude between 0.4 and 4%. The corresponding surface tension oscillations were measured by the Wilhelmy plate method using a roughened glass plate. The elasticity modulus $|\epsilon| = |d\gamma/d \ln S|$ was determined from the amplitude ratio of oscillations of surface tension γ and surface area, whereas the phase shift between the oscillations of the two parameters determined the phase angle of the dynamic surface elasticity. For oscillation frequencies below 0.2 Hz, the length of surface longitudinal waves in the Langmuir trough far exceeded the length of the trough, and the surface tension oscillations were homogeneous.

Results and Discussion

The surface pressure isotherm of PEO-PPO-PEO spread films (Figure 1) is in agreement with previous results;^{21,26} however, the range of surface pressures under investigation has been extended to higher values. If the surface area per molecule A before spreading an additional portion of polymer solution was less than $3 \text{ nm}^2/\text{molecule}$, then one could observe a relatively fast surface pressure relaxation. Just after the addition of the polymer solution, the surface pressure could be higher than 25 mN/m before decreasing over a few minutes (more than 10 min

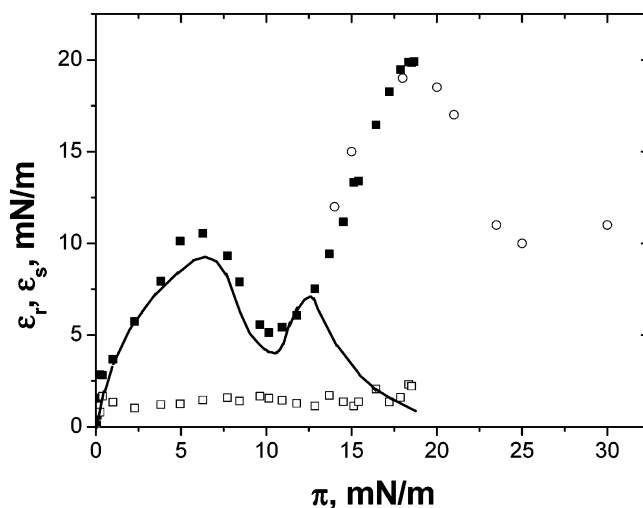


Figure 2. Real (solid squares, empty circles) and imaginary (empty squares) parts of the dynamic surface elasticity vs surface pressure for PEO₇₆-PPO₂₉-PEO₇₆ spread (squares) and adsorbed (circles) films. The line represents the static surface elasticity of spread PEO₇₆-PPO₂₉-PEO₇₆ films.

at $A < 1 \text{ nm}^2/\text{molecule}$) to the values shown in Figure 1. Subsequent surface pressure changes did not exceed 0.2 mN/m over 20 min. Therefore, one can consider that the experimental data in Figure 1 correspond approximately to the equilibrium state. Although successive additions of polymer solution to the water surface could lead to effective areas per molecule of less than about 3 nm^2 , the surface pressure after the corresponding relaxation never exceeded a value of about 19 mN/m. Obviously, values of A that are less than 3 nm^2 do not correspond to real areas, which the macromolecules occupy at the surface. For example, using neutron reflectivity Vieira et al. did not find values less than 3 nm^2 even for adsorbed PEO-PPO-PEO films of similar molecular weight and at higher surface pressures.²⁴ One can explain the significant decrease in the effective area per molecule below a critical value on the order of 3 nm^2 by the formation of polymolecular layers or dissolution of the polymer into the subphase. In the former case, one can assume that aggregates are formed in the surface layer because of the attraction between PPO segments of different macromolecules. The latter case, however, seems more probable if one takes into account that according to the previous conclusions^{25,30,31} PPO segments at the water-air interface are not located only at the boundary with the air phase but can be easily desorbed into the subphase. Thus, if the spread amount of PEO-PPO-PEO gradually increases, then an excess of polymer dissolves in the subphase or is transferred to aggregates and the surface layer tends to a certain state characterized by a surface pressure of about 19 mN/m. Even in the case of aggregate formation, one can assume that the dilational surface properties are determined by the polymer monolayer between the aggregates (cf. below).

It is accepted now that the dynamic surface elasticity is more sensitive to conformational changes in the polymer adsorption films than the surface pressure.^{26,30,35} Therefore, we also measured the real and imaginary components of the viscoelasticity at a frequency of 0.14 Hz simultaneously with the surface pressure (Figure 2). The main features of the experimental dependency of surface elasticity on surface pressure are in agreement with results for spread films of other triblock PEO-PPO-PEO copolymers.^{28,30} The imaginary part of the surface elasticity deviates from zero only slightly and is much less than the real part. The surface film is mainly elastic. At $\pi < 17 \text{ mN/m}$, the real component almost coincides with the results of Munoz et

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al.,²⁶ which were obtained by capillary wave techniques at frequencies of 800 Hz and higher. Consequently, the surface elasticity does not depend on frequency, at least in the range from 0.1 to 5000 Hz and for the high π values studied in this article.

Different authors propose almost the same interpretation of the nonmonotonic dependency of the real part of surface elasticity on surface pressure of spread PEO–PPO–PEO films.^{26–28,30} Up to the first local minimum ($\pi < 10$ mN/m), the dynamic surface elasticity depends only slightly on the length of PPO blocks and almost coincides with the elasticity of surface films of PEO homopolymer.^{39,40} At low surface pressures ($\pi \leq 5$ mN/m), all blocks have an almost flat conformation without long loops and tails protruding into the water phase. At higher surface pressures beyond the first elasticity maximum, the films are no longer two-dimensional, and PEO segments begin to protrude into the subphase, thus leading to the formation of a self-similar structure at the surface. The relaxation of surface stresses can proceed now at the expense of PEO segment exchange between the proximal, central, and distal regions of the surface layer, and the surface elasticity decreases with increasing surface pressure if the frequency is low enough.^{35,39,40} Beyond the local elasticity minimum ($\pi > 10$ mN/m), the PPO segments continue to have an almost flat conformation at the surface, but PEO chains extend further into the water phase. A brush structure consisting mainly of PEO segments begins to form.^{26–30} The interactions between the extended PEO chains, and also between PPO segments at the surface, lead to a gradual increase in the surface elasticity.

These ideas are also consistent with the experimental dependency in Figure 2. The main distinction of these data from previous data^{26–28,30} consists of a more extended range of surface pressures. When the surface pressure reaches the maximum value attainable for spread monolayers, about 19 mN/m, the real part of the dynamic elasticity of PEO₇₆–PPO₂₉–PEO₇₆ surface films gradually approaches a value of 20 mN/m. However, at this value of π , the static elasticity approaches zero.

This behavior is entirely different from the results of Rippner Blomqvist et al. for spread surface films of some other PEO–PPO–PEO triblock copolymers, where the surface elasticity decreases strongly after the second maximum in the range of high surface pressures.³⁰ These authors determined the surface elasticity by measuring the surface pressure as a function of surface area in a Langmuir trough with a constant barrier speed and by differentiating the obtained $\pi(\ln A)$ isotherm. In the limit of infinitely slow barrier speed, this procedure has to lead to static surface elasticity. However, one can expect significant deviations from the limiting value at a finite barrier speed (1 mm/s in the work³⁰). Note that the experimental points in Figure 2 represent the dynamic surface elasticity of almost equilibrium surface films, which is a different quantity.⁴¹ The continuous line in Figure 2 shows the static surface elasticity of PEO₇₆–PPO₂₉–PEO₇₆ surface films. It was obtained by differentiation of the surface pressure isotherm in Figure 1. The static and dynamic values almost coincide up to surface pressures slightly above the range of the local minimum (≤ 13 mN/m) but diverge strongly at higher surface pressures. When the real part of the dynamic surface elasticity tends to a constant value of 20 mN/m, the static elasticity approaches zero. The qualitative distinction of the results of Rippner Blomqvist et al.³⁰ from the static values in Figure 2 consists of the more extended region of the surface pressure increase beyond the local minima and

higher values of the second local maximum. Although the results³⁰ correspond to other PEO–PPO–PEO triblock copolymers, one can assume that these features are mainly consequences of the deviations from the static values due to the finite barrier speed.

A large difference between the dynamic and static elasticities of PEO₁₀–PPO₂₂–PEO₁₀ and PEO₈–PPO₂₂–PEO₈ surface films in the range of relatively high surface concentrations was also observed by Kim and Yu²⁷ in the kilohertz frequency range. The real part of the dynamic surface elasticity reached values of about 14 and 15 mN/m for the two copolymers, respectively, and remained constant after that, whereas the static elasticity approached zero. The former quantity increased monotonically with surface concentration, and the latter went through a single local maximum. These distinctions from the results in Figure 2 are probably connected with rather short PEO blocks in the copolymers investigated by Kim and Yu.²⁷ In this case, the lateral interaction between neighboring PPO blocks in the surface layer can begin at lower surface concentrations, thus leading to different concentration dependencies of surface elasticity.

If the dynamic surface elasticity significantly exceeds the static values at a given frequency, then one has to expect that the main relaxation processes proceed at lower frequencies according to the thermodynamic theory of surface viscoelasticity.^{37,41} However, the measurements of the real part of the surface elasticity as a function of frequency by the oscillating barrier method in the high-surface-pressure range led only to a small decrease of about 10% when the frequency decreased from 0.2 down to 0.01 Hz. This change in surface elasticity is close to the error limits, so it is not conclusive. The main relaxation processes probably correspond to lower frequencies. However, the significant difference between the static and dynamic surface elasticities of PEO₇₆–PPO₂₉–PEO₇₆ surface films is inconsistent with the conclusion³⁰ that the surface structure and, consequently, the surface viscoelasticity of triblock copolymer films are determined by the surface concentration. At relatively high surface pressures ($\pi > 13$ mN/m), the surface structure, although close to equilibrium, can depend on the method of film formation and on the stage of proceeding relaxation processes. This also follows from the fast relaxation of surface pressure after film formation at higher surface pressures (cf. above).

If the decrease in surface elasticity beyond the region of the second local maximum indicates the partial desorption of PPO segments and their mixing with PEO segments in water,³⁰ then the data in Figure 2 show that this process starts at much lower surface pressures in the case of quasi-static surface deformations as compared to deformations at frequencies higher than 0.1 Hz. In the former case, one can observe only very early steps of brush formation in the polymer film (at $10 < \pi < 13$ mN/m). At higher surface pressures, the surface stresses can be relaxed at the expense of PPO segment exchange between different regions of the surface layer. However, these processes are very slow and do not proceed even at a perturbation frequency of 0.1 Hz. For example, the surface contraction at this or higher frequencies can lead to a stretching of PEO chains protruding into the water phase and to relatively strong repulsion between PPO segments at the surface, as in the case of a polymer brush. As a result, the dilation elasticity of the PEO₇₆–PPO₂₉–PEO₇₆ surface film increases with surface pressure over the whole surface pressure range beyond the region of the local elasticity minimum (Figure 2). Consequently, if the mechanical perturbation is not too slow, then the response of the film can be similar to that of a brushlike structure, even if the real surface film contains some PPO segments mixed with PEO segments in the subphase and is consistent with

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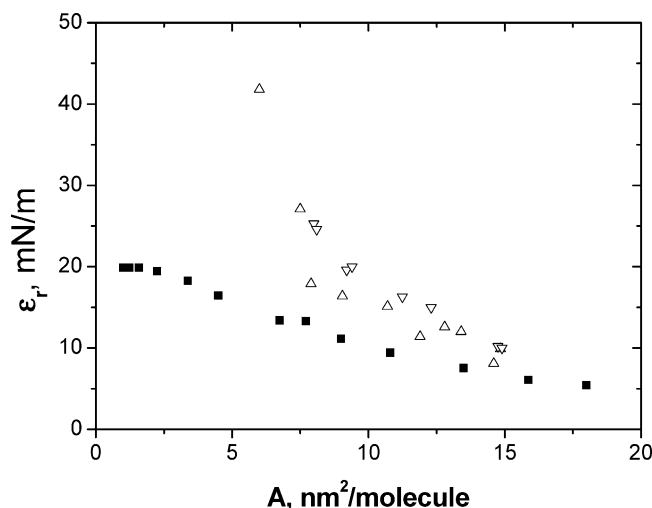


Figure 3. Real part of the dynamic surface elasticity vs area per molecule for spread films of PEO₇₆-PPO₂₉-PEO₇₆ (squares) and PS₃₈-PEO₂₅₀ (triangles).

the slow dissolution of excess macromolecules in water or their transfer into aggregates at high surface pressures.

This similarity, however, is incomplete. Figure 3 shows the real part of the dynamic elasticity as a function of area per molecule for spread surface films of PEO₇₆-PPO₂₉-PEO₇₆ and poly(styrene)-poly(ethylene oxide) (PS₃₈-PEO₂₅₀) diblock copolymer. The dynamic surface elasticity of the latter system has been measured recently by the oscillating barrier method at a frequency of 0.07 Hz and by the longitudinal wave method at a frequency of 1 Hz.¹⁵ PS₃₈-PEO₂₅₀ contains a PS block of high hydrophobicity, which forms compact globules at the water-air interface. The brush formation in spread films of PS₃₈-PEO₂₅₀ was confirmed by neutron reflectivity¹⁰ and surface dilational rheology methods,^{15,16} and one can consider these films to be physical models of polymer brushes. The rate of surface elasticity increase changes only slightly for real PS₃₈-PEO₂₅₀ surface films with decreasing area per molecule in the range of high surface concentrations, whereas the elasticity of PEO-PPO-PEO films tends asymptotically to a value of 20 mN/m (Figure 3). The different behavior is obviously connected with the deviations of the real PEO-PPO-PEO film structure from a classic brush model. Note that the deviations arise in the range of relatively high areas per molecule that correspond to surface pressures less than the maximal value of 19 mN/m.

Adsorption films of PEO₇₆-PPO₂₉-PEO₇₆ exist at surface pressures far exceeding 19 mN/m. The dynamic surface tension and elasticity change with surface age for more than 1 h after the formation of a fresh surface at concentrations of less than about 0.0002 mM. Figures 4 and 5 show some examples of the kinetic dependencies of the real and imaginary components of dynamic surface elasticity, which can be nonmonotonic at some concentrations as was first observed by Rippner Blomqvist et al.³⁰ They connected the complicated shape of the kinetic curves with the nonmonotonic concentration dependence of the surface elasticity. The dependencies of surface elasticity on surface pressure and also on bulk concentration for adsorbed films are similar to the curves in Figure 2 for spread films, at least for concentrations that are not too high.³⁰ At relatively low surface pressures, the elasticity is determined by the surface concentration³⁰ and, consequently, goes through a local minimum (Figure 4) when the surface concentration changes during adsorption in the range corresponding to the local minimum of elasticity versus concentration dependence. Munoz et al.⁴² showed that the adsorption kinetics of PEO₇₆-PPO₂₉-PEO₇₆ at the water-air

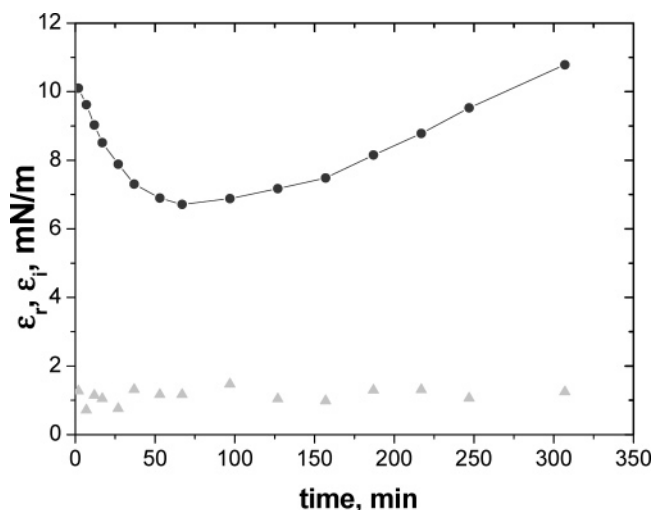


Figure 4. Real (circles) and imaginary (triangles) parts of the dynamic surface elasticity vs surface age for PEO₇₆-PPO₂₉-PEO₇₆ solutions at a concentration of 0.00004 mM. The line is a guide for the eye.

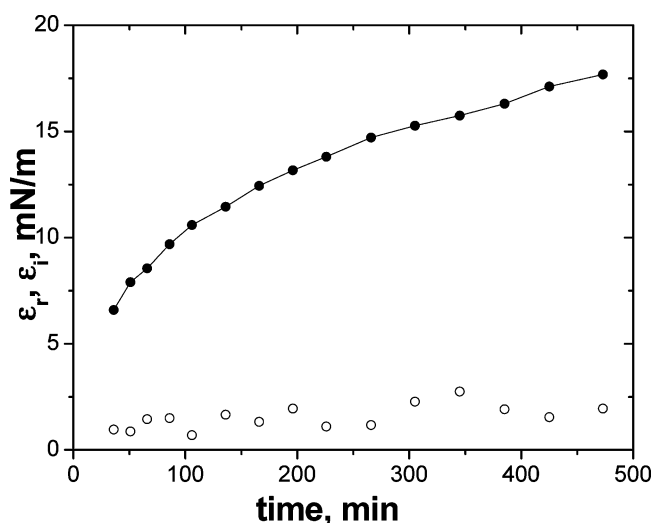


Figure 5. Real (circles) and imaginary (squares) parts of the dynamic surface elasticity vs surface age for PEO₇₆-PPO₂₉-PEO₇₆ solutions at a concentration of 0.000055 mM. The line is a guide for the eye.

interface is determined by polymer diffusion from the bulk to the surface at small surface lifetimes but the subsequent slow step of adsorption is controlled by conformational transitions in the surface layer.

The viscoelastic behavior of spread and adsorbed PEO₇₆-PPO₂₉-PEO₇₆ surface films is similar at surface pressures of less than 19 mN/m. The imaginary part of the surface elasticity of adsorbed films is also much less than the real part. When plotting the real part as a function of surface pressure, the data for spread and adsorbed films lie on the same curve for $\pi < 19$ mN/m (Figure 2), in accordance with previous results.^{26,30} However, this similarity breaks at higher surface pressures. The spreading of PEO₇₆-PPO₂₉-PEO₇₆ solution in chloroform at the water surface leads only to an increase in the real part of the dynamic surface elasticity, which tends asymptotically to about 20 mN/m. The increase in polymer concentration in the bulk phase can lead to a decrease in surface elasticity at $\pi > 19$ mN/m (Figure 2). One can assume that the structures of the two kinds

(42) Munoz, M. G.; Monroy, F.; Ortega, F.; Rubio, R. G.; Langevin, D. *Langmuir* **2000**, *16*, 1094.

(43) Svitova, T. F.; Radke, C. J. *Ind. Eng. Chem. Rev.* **2005**, *44*, 1129.

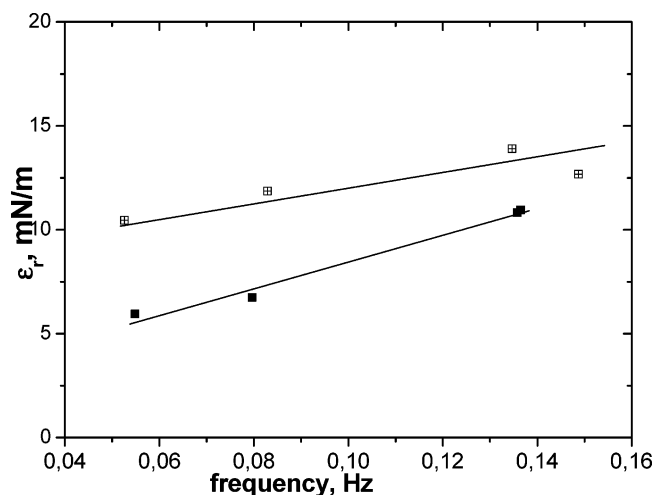


Figure 6. Real part of the dynamic surface elasticity vs frequency for PEO₇₆–PPO₂₉–PEO₇₆ solutions at concentrations of 0.033 mM (solid squares) and 0.24 mM (crossed squares). The lines represent linear best fits.

of films are similar indeed in the range of $13 < \pi < 19$ mN/m and lead to the same response to relatively fast surface expansions and compressions. However, the adsorbed and spread polymer films are not entirely identical even in this range because the static surface elasticities and the polymer activities in the bulk phase are different. Unfortunately, the experimental data on surface rheological properties do not allow us to discuss the reason for these deviations.

Any further increase in the polymer activity leads to strong changes in the adsorption film structure, which are accompanied by a strong decrease in surface elasticity. Note that Svitova and Radke obtained similar absolute values of the surface elasticity of PEO₇₆–PPO₂₉–PEO₇₆ adsorbed films at the mineral oil/water interface in the same concentration range.⁴² The present level of knowledge does not allow us to discuss details of the film structure. The mean-field calculations³¹ and the data from neutron reflectivity²⁵ show that there is a mixing of PEO and PPO segments beneath the PPO layer at the boundary with the air phase. The decrease in surface elasticity also indicates that the adsorbed film structure becomes looser with increasing concentration, thus the main relaxation processes can be faster. Ferri et al. report that PEO₇₆–PPO₂₉–PEO₇₆ “is highly mobile in the adsorbed phase” in comparison with other polymers.²⁰ The confirmation of relatively fast processes in adsorbed films at high surface pressures follows also from the frequency dependence of the real part of dynamic surface elasticity (Figure 6).

The surface elasticity increases by more than 30% when the frequency increases about 3-fold, unlike the situation for spread PEO₇₆–PPO₂₉–PEO₇₆ films. This means that the main relaxation time is on the order of the oscillation period (10 s). This value coincides with estimates of the characteristic rearrangement time scale in a mixed monolayer of copolymers with DPPC.²⁰

Conclusions

The measurements of the complex dynamic dilational elasticity of adsorbed and spread films of PEO₇₆–PPO₂₉–PEO₇₆ by the oscillating barrier method allowed us to refine the existing model of film structure. At $\pi < 13$ mN/m, the two kinds of films are almost identical, and their viscoelasticity is determined by the surface concentration, in agreement with preceding studies.^{21–30} At $\pi < 10$ mN/m, the surface viscoelasticity is determined only by PEO blocks and is close to the properties of the PEO homopolymer surface film.^{39,40} Any further compression of the film at $\pi > 10$ mN/m leads to a stretching of PEO blocks in a direction perpendicular to the interface and a repulsion between neighboring PPO blocks at the boundary with the air phase. At $\pi > 13$ mN/m, the static and dynamic elasticities diverge, and the surface dilational viscoelasticity cannot be determined only by the surface concentration, as recently assumed.³⁰ If the surface pressure is high enough, then the PPO segments can probably desorb from the surface and mix with PEO segments in water.^{25,30,31} However, the possibility of aggregate formation in the surface layer cannot be entirely excluded. The beginning of these processes is not necessarily connected with the range of maximum surface elasticity³⁰ but can proceed at lower surface concentrations. Although the dynamic response of spread and adsorbed surface films is identical at $\pi < 19$ mN/m, their structures can be different, as follows from the difference in the static surface elasticities. Spread films begin to dissolve in water at $\pi \approx 19$ mN/m when the real part of the surface elasticity has a maximum value of about 20 mN/m. However, this quantity for adsorbed films drops dramatically after the maximum upon bulk concentration increases. Adsorbed films at relatively high concentrations (> 0.001 mM) have a loose structure with a main relaxation time of about 10 s.

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