

# Dynamic Surface Properties of Solutions of Poly(ethylene oxide) and Polyethylene Glycols

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The damping coefficient and the length of transversal (at the frequencies from 100 to 300 Hz) and longitudinal (at the frequencies from 0.1 to 3 Hz) surface waves have been measured as a function of the concentration of solutions of poly(ethylene glycol)s (PEG) and poly(ethylene oxide) (PEO), and the molecular weight of the polymer. A local maximum of the damping coefficient of transversal waves has been discovered for dilute solutions of PEG 400. This maximum disappears and the damping coefficient decreases monotonically with the concentration of polymers of higher molecular weight in the region of dilute solutions. A fast increase of the damping with concentration has been discovered for semidilute solutions. These experimental data are used for the calculation of the real and imaginary components of the dynamic surface elasticity as a function of concentration and frequency. The obtained dependencies can be explained with the help of a dynamic model of the surface layer of polymer solutions where the main relaxation processes are connected with the monomer exchange between different regions of the surface layer. In the investigated concentration range, the corresponding relaxation time determined from the experimental data changes by more than 2 orders of magnitude.

## 1. Introduction

Surface properties of aqueous polymer solutions have been investigated for more than half a century.<sup>1,2</sup> The area of the liquid surface can be easily controlled and the experimental results on adsorption films can be easily correlated with data on spread polymer films where the adsorption value can be controlled too. These considerations make the boundary between two fluid phases particularly attractive for validating the theory of adsorption of polymer chains.<sup>3–5</sup> On the other hand, the behavior of macromolecules at liquid surfaces determines the efficiency of various industrial compositions and, consequently, the corresponding information is also important from the point of view of applications.<sup>6</sup>

Meantime, progress in the studies of the surface layer of polymer solutions turned out to be rather slow. This is mainly due to experimental difficulties. Traditional methods of investigation of liquid surfaces often give too scarce information when they are applied to polymer systems. For example, the static surface tension of many polymer systems is almost independent of concentration in a broad concentration range and the application of the Gibbs adsorption equation leads to large errors when used to determine the polymer adsorption.<sup>7,8</sup> Only recently,

the application of neutron reflection has been introduced to determine not only the adsorption but also the distribution of monomers in surface films of poly(ethylene oxide)s (PEO).<sup>7,9,10</sup>

At the same time, information on the dynamics of polymer chains at the liquid surface is rather restricted as, for example, Richards and Taylor noted in their article on spread polymer films.<sup>11</sup> Nonequilibrium surface properties of polymer solutions are mainly investigated via measurements of the dynamic surface tension<sup>2,12–15</sup> and by comparison of the results with the solution of the corresponding boundary problem for the diffusion equation.<sup>13,14</sup> However, it has rarely been taken into account that surface tension can be insensitive to the state of the surface layer. Thus, for example, conformational transitions are possible in adsorption films of PEO and poly(ethylene glycol)s (PEG) although the surface tension is almost constant.<sup>16</sup> Relaxation processes in the surface films at high frequencies ( $\geq 10$  kHz) can be investigated by quasi-elastic surface light scattering.<sup>8,10,11,13</sup> In this frequency range, the rheological behavior of adsorbed polymer films is analogous to insoluble monolayers,<sup>13</sup> indicating that the characteristic times of the main relaxation processes correspond to lower frequencies. It is noteworthy that the surface dilational viscosity turns out to be negative in the course of application of the method of quasi-elastic light scattering to both solutions of conventional surfactants<sup>17</sup> and polymer films.<sup>11,18</sup> For surfactant solutions, this effect was connected originally with adsorption barriers.<sup>17</sup> However, it was

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shown later that the surface viscosity must be positive for equilibrium systems regardless of the adsorption mechanism.<sup>19</sup> It seems that a more realistic interpretation is given in the articles<sup>18,20</sup> where the authors characterize the negative surface viscosity as an effective quantity and connect it with inadequacy of the theory of the applied experimental method. For example, the apparent negative surface viscosity can be explained, if one assumes that a small fraction of the polymer aggregates into a superstructure below the normal adsorbed monolayer.<sup>20</sup>

It is possible to expect that these difficulties will disappear, at least partly, when one applies low-frequency ( $\ll 10$  kHz) externally excited surface waves to polymer solutions. In fact, in this frequency range one can neglect the influence of the surface transverse viscosity and the sign of the surface dilational viscosity, which was earlier determined for solutions of conventional surfactants to be always in accordance with the requirements of the thermodynamics.<sup>19</sup> On the other hand, the results for quasi-elastic surface light scattering indicate that the surface elasticity of adsorbed polymer films is close to its high-frequency limit at the frequencies higher than about 10 kHz.<sup>13</sup> If one takes into account that the static surface elasticity of solution is zero, it follows that the main relaxation processes in the surface layer can be expected in the low-frequency range ( $< 10$  kHz).

Low-frequency surface waves have been used until now mainly in studies of spread polymer films.<sup>21–24</sup> Only Scott and Stephens have presented results of measurements of the characteristics of capillary waves for PEO solution at a single concentration.<sup>22</sup>

The aim of this work is to study the dynamic surface properties of solutions of PEG and PEO of different molecular weights in a broad concentration range by means of transversal and longitudinal surface waves.<sup>25</sup> The following section summarizes the main conclusions of a recently developed theory of dilational surface viscoelasticity of solutions of surface-active polymers.<sup>26</sup> The main quantity is the dynamic surface elasticity, which can be determined from the characteristics of surface waves by means of the dispersion relation. After a description of the experimental technique, measured damping coefficients and wavelengths are represented. In the last section, the concentration and frequency dependencies of the dynamic surface elasticity are calculated from the experimental data and are compared with the theoretical conclusions.

## 2. Theoretical Considerations

The dynamic surface properties of polymer solutions have been considered until recently only in the framework of the dumbbell model,<sup>27,28</sup> which can lead to reasonable results only for dilute solutions. A more general theory<sup>26</sup> based on the Rouse model and on the reptation model by de Gennes<sup>3,29</sup> was proposed a few years ago. The main conclusions of ref 26 have been corroborated for insoluble polymer films.<sup>30,31</sup> Reference 30 contains also a review of the theoretical results. We will present below only some relations relevant to adsorbed polymer films.

The characteristic time of surfactant diffusion to the surface increases with the molecular weight of the solute. Consequently, for macromolecules the exchange between the surface layer and the bulk phase can be neglected at frequencies characteristic for surface waves ( $\geq 1$  Hz). However, the exchange of monomers between different regions of the surface layer has to be taken into account.

Two main parts of the surface film have been considered: a relatively narrow concentrated region I contiguous to the gas phase and the region II of “tails” and “loops” protruding into

the bulk of the liquid where the global concentration of monomers is essentially lower. This model is in agreement with both the results of the scaling theory<sup>5</sup> and the experimental data on neutron reflectivity.<sup>7</sup> In ref 26, the region I is called “monolayer” but it is necessary to take into account that the meaning of this term is different from what is usually used in discussions of insoluble surfactant films, and the width of region I can exceed the characteristic size of the monomer. It is only essential that the width of region II exceeds that of region I and the monomer concentration in the latter region is essentially higher. The second important assumption is that the surface tension depends first of all on the concentration in region I and the relaxation of surface stresses to a surface dilation proceeds at the expense of drawing chains up to the surface (transition of monomers from II to I) or squeezing chains out of the surface (the reverse transition). If we consider a linear theory of surface viscoelasticity (small deformations), the departure of a polymer coil from the surface (disentanglement of the coil) or the reverse process of entanglement of a free coil to the surface turns out to be relatively rare events and we can neglect their influence. Then the exchange of monomers between the regions I and II under expansion (compression) of the surface can take place as a result of two processes: the relaxation of inner strains of a polymer chain or the drawing up (squeezing in) of the chain as a whole. The first process can be described mathematically by means of a solution of the corresponding boundary problem for the Rouse equation.

The surface activity of the polymer leads to high monomer concentration in region I and, consequently, to interaction between the adsorbed polymer trains. Then the motion of a train as a whole can be considered in the framework of the two-dimensional reptation model by de Gennes.<sup>3</sup> The neighboring adsorbed polymer trains form a two-dimensional network of entanglements. The real nature of the entanglements is not important. In the two-dimensional case the entanglements can be formed, for example, by the transitional parts of the chains where a polymer chain transits from region I to region II. Then the adsorbed train wriggles (reptates) inside a network of entanglements which form a two-dimensional tube. The velocity of the train with one transitional region from region I to II (a tail lying on the surface) can be proportional to the acting force  $\Delta\tilde{\pi}a$

$$\Delta\tilde{\pi}a = \frac{N_2}{B} \frac{dL_2}{dt} \quad (1)$$

where  $a$  is the mean distance between the walls of the two-dimensional tube of entanglements,  $B$  is the mobility constant,  $\Delta\tilde{\pi}$  is the deviation of the surface pressure from the equilibrium value,  $N_2$  is the number of monomers in the train under consideration,  $L_2$  is the length of the train, and  $t$  is the time.

These simple assumptions allow us to calculate the frequency dependence of the dynamic surface elasticity. If the number of loops and tails (in the region II) per chain  $n$  is large ( $n \gg 1$ ), the following expression for the complex dynamic surface elasticity can be obtained<sup>26</sup>

$$\epsilon = - \frac{\partial \sigma}{\partial \ln \Gamma} \left[ \frac{2\Gamma_3}{\pi\Gamma} \sum_p \frac{8i\tau_B\omega}{p^2\pi^2(1 + i\omega\tau_B/p^2)} + \left( 1 - \frac{2\Gamma_3}{\pi\Gamma} \right) \frac{i\omega\tau_2}{1 + i\omega\tau_2} \right] \quad (2)$$

where  $p$  changes from 1 to infinity and the sum includes only the odd terms,  $\omega$  is the angular frequency,  $\sigma$  is the surface

tension,  $\Gamma$  is the number of moles of monomers per surface element of unit area in region I,  $\Gamma_3$  is the number of moles of those monomers per unit area in region I that belong to trains with two transitional regions from I to II,  $\tau_B$  is the time of relaxation of the inner stresses of a polymer chain

$$\tau_B = \frac{b^2 N_0^2}{3\pi^2 k_B T B} \quad (3)$$

and the relaxation time  $\tau_2$  corresponds to the motion of a train in the region I as a whole

$$\tau_2 = \frac{N_2 L_2}{B \Gamma_2 a (\partial \pi / \partial \Gamma)} \quad (4)$$

$\Gamma_2$  is the number of moles of monomers per unit area in the region I, which belong to trains with one transitional region from I to II,  $N_0$  is the number of monomers inside the two-dimensional tube of entanglements,  $b$  is the mean separation between the Rouse segments,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature.

It follows from relation 4 that the relaxation time decreases with  $\Gamma_2$  and, consequently, with the number of tails protruding into the bulk phase. Actually, each additional tail creates a new path for the relaxation of stresses in the region I of the surface layer and decreases the resistance to this relaxation. Similarly, the increase of the number of loops leads to the decrease of  $N_0$  and, consequently, to the decrease of  $\tau_B$  according to eq 3.

If the chains are short enough and the number of adsorbed chains with more than one loop (train) in the region II is small ( $n < 1$ ,  $\Gamma_3 \ll \Gamma_2 < \Gamma$ ), the relaxation of surface stresses at the frequencies comparable with  $1/\tau_2$  will mainly take place at the expense of squeezing separate trains out of the region I (drawing in the region I). In this case the relaxation of local surface dilational stresses can proceed mainly at the expense of reptation of trains with a tail in the bulk phase. Then

$$\epsilon = - \frac{\partial \sigma}{\partial \ln \Gamma} \frac{i \omega \tau_2}{1 + i \omega \tau_2} \quad (5)$$

Consequently, the surface dilational viscoelasticity is described by the Maxwell model.

Measurements of the frequency dependence of the dynamic surface elasticity give a possibility to determine the important characteristics of the surface layer  $\partial \sigma / \partial \ln \Gamma$  and  $\tau_2$ . The former quantity is an analogue of the Gibbs elasticity of solutions of conventional surfactants<sup>39</sup> and characterizes the interaction of polymer chains in the surface layer. The relaxation time  $\tau_2$  can be connected with the dynamic characteristics of macromolecules (eq 4). This equation contains a number of parameters and cannot be applied for the determination of the molecular properties without additional information. However, such determination is beyond the scope of this work. Even the reliable estimation of the main relaxation times in the surface films of PEG and PEO is still lacking and the data of different authors are not always in agreement.<sup>11–13,21,22,25</sup> In this work, eq 4 is used only for qualitative comparison with the results of the methods of transversal and longitudinal surface waves.

It was shown also in ref 26 that the conventional dispersion relation, which connects the characteristics of surface waves with the surface properties, holds at least for dilute polymer solutions. Different forms of this equation have been presented in the literature.<sup>8,11,13,16–18,20–25</sup> In this work we will use the

dispersion relation for surface waves in the liquid of finite depth<sup>32</sup>

$$\epsilon = \epsilon_r + i \epsilon_i = \frac{\rho \omega^2 [\rho \omega^2 - (\sigma k^3 + \rho g k) \tanh(kh)] + 4i \rho \mu \omega^3 k^2 + 4 \mu^2 \omega^2 k^3 [m \tanh(kh) - k]}{m k^2 [\rho \omega^2 - (\sigma k^3 + \rho g k) \tanh(kh)] + k^3 (\sigma k^3 + \rho g k)} \quad (6)$$

where  $k = 2\pi/\lambda + i\alpha$  is the complex wavenumber,  $\alpha$  is the damping coefficient,  $\lambda$  is the wavelength,  $g$  is the gravitational acceleration,  $m^2 = k^2 - i\omega\rho/\mu$ ,  $\sigma$  is the surface tension,  $\mu$  is the viscosity,  $\rho$  is the density, and  $h$  is the depth of the liquid in the trough (in our work  $h = 15$  mm).

Relation 6 can be considered to be a complex algebraic relation relative to  $k$ . The two main roots of this equation correspond to transversal and longitudinal surface waves. Both wave modes arise as a result of thermal spontaneous fluctuations at the liquid surface or can be excited by a wave generator. However, the longitudinal waves disappear if the complex dynamic surface elasticity tends to zero. The detection of longitudinal waves is a more difficult problem in comparison with transversal waves because the former ones almost do not change the geometrical shape of the surface.

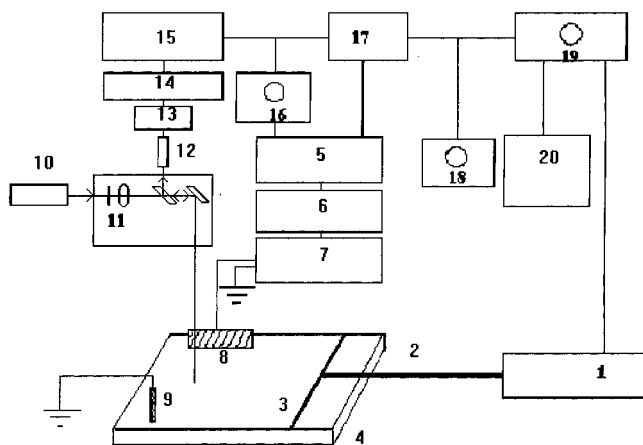
Note that although the specific energy dissipation in the surface layer, where the monomer concentration is higher, exceeds the specific dissipation in the bulk solution, the energy of waves dissipates mainly in the bulk solution because the wavelength (the penetration depth of the motion into the bulk liquid) exceeds the thickness of the surface layer by about 6 orders of magnitude. The surface rheology influences the wave characteristics only as a result of alterations of the boundary conditions for the equations of the liquid dynamics.<sup>39</sup> Therefore, the damping coefficient of surface waves is a function of both components of the dynamic surface elasticity. Even if the imaginary part of the surface elasticity is zero (pure elastic film), the damping coefficient can be a complicated (nonmonotonic) function of the elasticity modulus.

### 3. Experimental Section

Many authors used the transversal capillary waves in their studies of surface phenomena.<sup>8,16,25,32–35</sup> The main features of our experimental setup for studying characteristics of transversal surface waves, and the corresponding procedures of measurements were described in detail elsewhere.<sup>33–35</sup> The characteristics of transversal capillary waves were measured with the help of an electromechanical method based on the principle of a dynamic condenser. One side of the condenser was a thin metal plate of a thickness less than half the wavelength. The other side was the investigated liquid surface in a Teflon Langmuir trough. Waves were excited by a mechanical generator. Propagation of capillary waves caused the capacity of the condenser to oscillate and as a result an alternating electric current proportional to the wave amplitude appeared in the circuit. Measurements of the amplitude and the phase of the electric signal allowed us to determine the damping coefficient and the length of transversal capillary waves.

Figure 1 shows the scheme of our setup, which was used in the measurements of the characteristics of longitudinal surface waves.<sup>36</sup> A generator of low-frequency mechanical oscillations (1) transformed the rotation of the electromotor to the translational motion with reversion and gave a possibility to regulate the frequency and the amplitude. The moving part of the generator was connected by means of a hollow steel rod (2) with a Teflon frame (3). A metal wire covered with paraffin





**Figure 1.** Schematic illustration of the longitudinal wave setup. Explanations are in the text.

was tightened inside the frame. When the frame lay on the polished brims of a Teflon Langmuir trough (4) the wire was wetted by the liquid and was in parallel to the liquid surface. In operation, the frame glided back and forth along the polished brims and the oscillations of the wire excited longitudinal surface waves in the trough. The diameter of the wire was 0.05 mm and the amplitude of the oscillations of the wire varied from 0.5 to 5 mm.

The electrocapillary method was used to create transverse surface waves. The sinusoidal voltage of the given frequency (180 Hz) from an electric generator of high precision (5) was applied in series to an amplifier (6), to a frequency divider (1:2) (7), and after that to a metal blade (8). The distance between the blade and the surface of the grounded solution under investigation determined the initial amplitude of the transverse waves and was less than a millimeter. A reference platinum electrode (9) was immersed into the solution. Under the action of strong alternating electric field in the gap between the blade and the liquid surface, transverse capillary waves were excited and propagated in the direction perpendicular to the direction of propagation of longitudinal waves. The frequency of transverse waves equalled the double frequency of the voltage at the blade and thus was 180 Hz. Transverse surface waves were detected by the optical method. The beam of the laser (10) went through a focusing optical system (11) and was reflected from the liquid surface and directed by an optical fiber (12) to a position-sensitive photodetector (13). The main part of the optical system (11) was placed on a translation stage which was moved by means of a microscrew. The alternating electric current appearing as a result of the oscillations of the laser beam incident on the photodetector was amplified by a preliminary unit (14) and by a selective unit (15), and was applied to a scope (16). Another signal to the scope was applied from the electrical generator (5). A comparison of the changes of the phase difference of these two signals at simultaneous measurements of the displacements of the point where the laser beam reflected from the liquid surface allowed us to determine the length of transverse waves.

Propagation of longitudinal waves led to oscillations of the surface concentration of the surfactant and thereby to oscillations of the surface tension. In its turn this induces oscillations of the length of transverse waves according to the Kelvin equation (a dispersion equation for transverse capillary waves). Moreover, this was the only observable effect connected with the propagation of longitudinal waves because the length of longitudinal waves exceeded the length of transverse waves by more than one order of magnitude and only linear waves had been used.

In other words, we could ignore the nonlinear interaction of surface waves. The oscillations of the length of transverse waves could be observed as oscillations of phase of the electric signal (relative to the phase of the signal from the electric generator (5)). A phase difference gauge (17) converted the oscillations of the phase to a low-frequency signal with the frequency equal to that of the longitudinal surface waves and with the amplitude proportional to the amplitude of these waves. This signal was observed on the screen of the oscillograph (18) and was recorded in the memory of a special oscillograph (19). The recording was synchronized with the motion of the Teflon frame (3).

The change of the distance between the mechanical generator of longitudinal waves (3) and the region where the laser beam is reflected from the liquid surface led to corresponding changes of the amplitude and the phase of the signal applied to the oscillograph (19). This allowed us to determine the length and the damping coefficient of longitudinal waves by the same method that was used frequently in the course of measurements of the characteristics of transverse capillary waves. From 10 to 15 patterns of the signal in the numerical form were recorded in the memory of a computer (20) for each position of the mechanical generator (3) and were averaged after that. The averaged data were used for the determination of the amplitude and of the phase shift relative to oscillations of the generator (3) by means of the nonlinear regression analysis. The derivative of the dependence of the logarithm of amplitude on the distance between the oscillating wire and the region where the laser beam was reflected from the surface equalled the damping coefficient of longitudinal waves and the derivative of the phase shift against this distance allowed us to determine the wavelength.

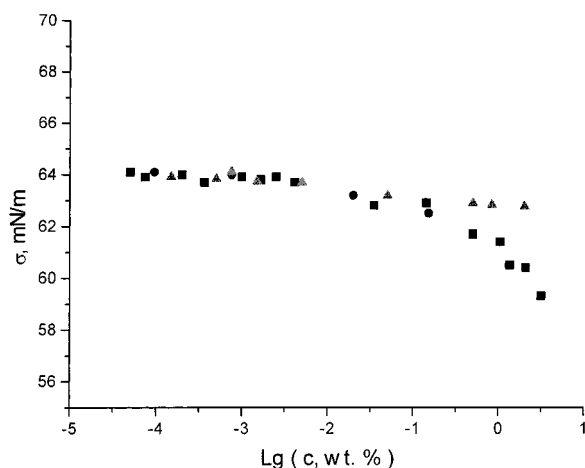
Both experimental setups were constructed on separate basements without mechanical connections with the building. The surface tension was measured by the Wilhelmy plate method. All the measurements were carried out at  $20.0 \pm 0.5$  °C.

PEG (Merck, with the averaged molecular weights  $M = 4000$  and  $20\,000$ ) and PEO (Aldrich,  $M = 100\,000$ ) were used as received. All the solutions were freshly prepared before each measurement and were mixed up carefully for about 15 min. Fresh twice-distilled water was used for these purposes. An all-Pyrex apparatus and alkaline permanganate were employed in the second stage of distillation.

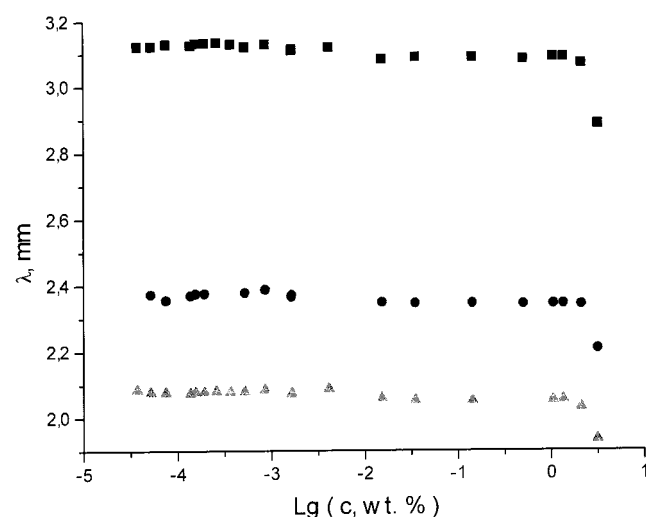
Before the measurements of the wave characteristics the surface of the solution under investigation was swept by the moving barrier and cleaned with a Pasteur pipet.<sup>33</sup> The time of the subsequent recovery of the equilibrium surface tension depends on the concentration  $c$  and the molecular weight of the polymer and varied from several hours at  $c < 0.0001$  wt % for PEO up to less than 1 min at concentrations close to 1 wt %.

#### 4. Results and Discussion

Static surface tension of the solutions under investigation does not depend on the molecular weight of the polymers in a broad concentration range (Figure 2) and changes only by about 1 mN/m when the concentration increases by more than 3 orders of magnitude (from 0.000 05 wt % up to 0.15 wt %). The decrease of the surface tension of solutions of PEG 20 000 and PEO with concentration becomes faster at higher concentrations at the transition from dilute to semidilute solutions. The changes of the surface tension of solutions of PEG 4000 in the same concentration range remain slow. The fast decrease of the surface tension with concentration has been noted also by Kim and Cao<sup>37</sup> in the range of semidilute solutions. Similar changes



**Figure 2.** Concentration dependence of the surface tension of solutions of PEG 4000 (triangles), PEG 20 000 (squares), and PEO 100 000 (circles).

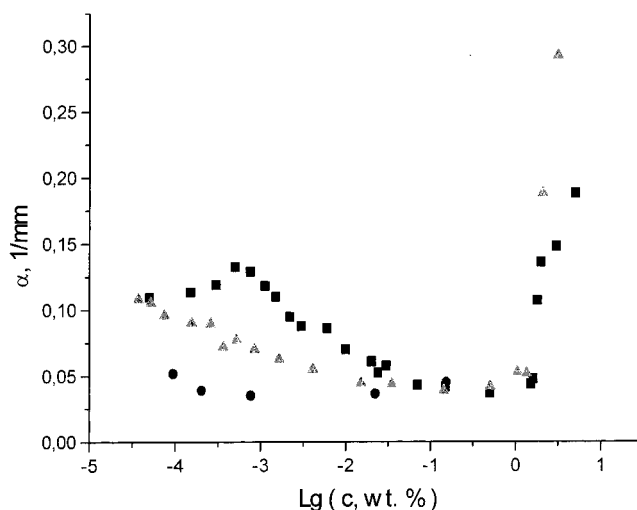


**Figure 3.** Concentration dependence of the wavelength of capillary waves for solutions of PEG 4000 at the frequencies 120 Hz (squares), 180 Hz (circles), and 220 Hz (triangles).

of the surface tension have been observed for solutions of poly(vinylpyrrolidone).<sup>8</sup>

The changes of the wavelength of transversal capillary waves with concentration for all polymers studied in this work have the same features in the frequency range under investigation (from 100 to 400 Hz). As an example, Figure 3 shows the measured wavelengths for solutions of PEG 2000 at three different frequencies. The wavelength almost does not change with concentration similar to the corresponding dependence of the surface tension except at high concentrations. Note that the similarity of the dependencies  $\lambda(c)$  and  $\sigma(c)$  follows from the dispersion relation (6). Actually, it is easy to show by separating the real part of eq 6 that the wavelength is determined first of all by the surface tension and the surface elasticity gives only a small correction (about several percent) to the expression for  $\lambda$ .<sup>17</sup>

Unlike the surface tension and the wavelength, the damping coefficient of capillary waves proved to be a nonmonotonic function of concentration and depended on the molecular weight. Figure 4 shows the corresponding experimental data at a frequency of 200 Hz. The general shape of the dependence  $\alpha(c)$  is preserved also at other applied frequencies (from 100 to 400 Hz). At first sight the concentration dependence of the PEG 4000 solutions resembles the corresponding curves for conven-



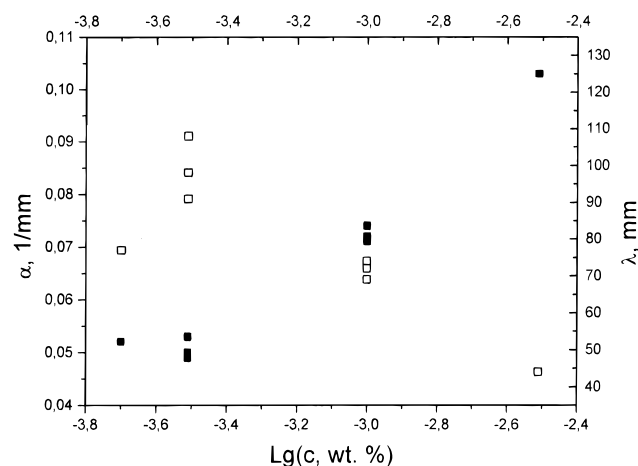
**Figure 4.** Concentration dependence of the damping coefficient of capillary waves at the frequency 200 Hz for solutions of PEG 4000 (squares), PEG 20 000 (triangles), and PEO 100 000 (circles).

tional surfactants.<sup>33–35</sup> a local maximum is followed by a local minimum and the damping coefficient increases again at higher concentrations. However, more careful comparison allows us to detect some peculiarities. First, the damping coefficient of the polymer solutions under investigation changes significantly slower with concentration. For most of conventional surfactants all changes of the damping coefficient in the region below the cmc take place in a concentration range of about 1 order of magnitude. In contrast, the concentration range in Figure 4 spans over 5 orders of magnitude. Second, for conventional surfactants the damping coefficient in the region of the local minimum corresponds to the approximation of an infinite surface elasticity and equals to about  $3\alpha_0$ , where  $\alpha_0$  is the damping coefficient at zero surface elasticity. In addition, the obtained  $\alpha$  values in the region of the local minimum are essentially lower for all investigated polymers. Finally, the rate of increase of the damping coefficient at high concentrations also exceeds significantly the corresponding rate for conventional surfactants.

For solutions of PEG 20 000 the decrease in damping for dilute solutions proceeds more slowly and the local maximum disappears. One can assume that this maximum shifts to the range of lower concentrations where measurements of the surface properties are difficult because of the slow equilibration. For PEO solutions the damping coefficient is almost constant in the range of dilute solutions and the increase in damping can be observed only at low concentration up to about 0.0001 wt %.

Obviously the observed changes of the damping coefficient are connected first of all with the corresponding changes of the dynamic surface properties. Only the fast increase of  $\alpha$  at concentrations higher than 1 wt % can be explained partly by the increase of the viscosity of the bulk phase. However, it will be shown below that the increase of the viscosity is insufficient in order to induce the observed increased damping and at  $c > 1$  wt % the modulus of the dynamic surface elasticity increases too.

It is well-known that the local maximum of the damping of capillary waves usually corresponds to a resonance between the longitudinal and transversal components of the wave motion and is observed when the surface elasticity modulus is about  $0.14\sigma$ .<sup>17</sup> The maximum value of the damping coefficient for dilute aqueous solutions can be calculated according to eq 6 and equals  $0.125 \text{ mm}^{-1}$  when  $\epsilon_i = 0$  and the other parameters



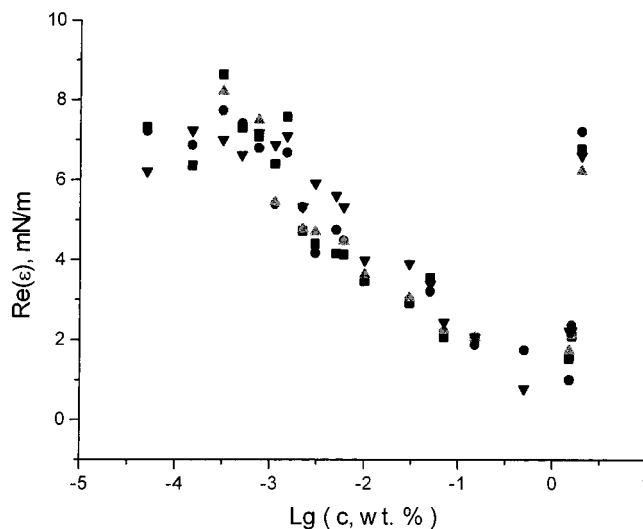
**Figure 5.** Concentration dependence of the damping coefficient (solid symbols) and of the length (open symbols) of longitudinal surface waves for solutions of PEG 4000 at the frequency 2 Hz.

correspond to the system represented in Figure 4. This value decreases with the increase of  $|\epsilon_i|$ . Therefore, the maximum in Figure 4 corresponds to the maximum possible damping and, consequently,  $\epsilon_r \approx 9$  mN/m,  $\epsilon_i \approx 0$  in the region of the maximum, and the adsorption film proves to be elastic there. In the general case, the decrease of the damping after the maximum can be connected with both the increase and decrease of the dynamic surface elasticity modulus. However, it is possible to assert that the surface elasticity modulus of solutions of PEG 4000 and PEG 20 000 decreases with concentration (at  $c < 0.1$  wt %) because  $\alpha$  is essentially less than  $3\alpha_0$  in the region of minimum damping.

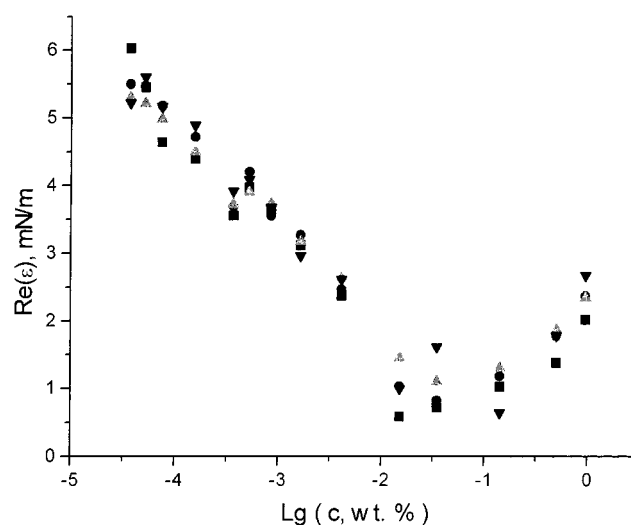
At lower frequencies in the interval between 0.1 and 3 Hz the dynamic surface elasticity was determined by means of longitudinal surface waves. Note that the amplitude of longitudinal waves for all investigated solutions exceeds the error limits only at concentrations lower than 0.05 wt %. The damping coefficient of longitudinal waves increases fast while approaching this concentration and the wavelength decreases. This behavior of the wave characteristics is illustrated in Figure 5 for solutions of PEG 4000 at a frequency 2 Hz. These results also indicate that the dynamic surface elasticity decreases with concentration for two different frequency ranges.

The obtained results give evidence that the dynamic surface elasticity is a complex function of concentration. This can be a consequence of the corresponding changes of the surface structure and of the relaxation times. In order to study this problem in detail the concentration dependencies of the components of surface elasticity were calculated according to eq 6. In the course of these calculations the density of solution was taken equal to the density of water but its viscosity was measured separately. The viscosity of the bulk increases significantly at concentrations  $> 1$  wt % at the transition to semidilute solutions as the result of interactions between polymer coils.

It is noteworthy that the characteristics of different wave modes depend on the dynamic surface elasticity in different ways. The influence of  $\epsilon$  on the characteristics of transversal capillary waves is only a consequence of the coupling between transversal and longitudinal waves. This influence is relatively weak and the dynamic surface elasticity modulus can be estimated with a reasonable accuracy only at  $|\epsilon| \leq 0.14\sigma$ .<sup>17,39</sup> Fortunately, for the solutions under investigation this condition holds for the whole concentration range. At the same time the possibility to excite longitudinal waves is a direct consequence



**Figure 6.** Real part of the dynamic surface elasticity of solutions of PEG 4000 vs concentration at the frequencies 120 Hz (squares), 180 Hz (circles), 220 Hz (triangles pointing up), and 270 Hz (triangles pointing down).



**Figure 7.** Real part of the dynamic surface elasticity of solutions of PEG 20 000 vs concentration at the frequencies 120 Hz (squares), 180 Hz (circles), 220 Hz (triangles pointing up), and 270 Hz (triangles pointing down).

of the fact that the surface film exhibits elastic properties. Therefore, the precision of the determination of  $\epsilon$  in the latter case is comparable with the precision of the experimental determination of wave characteristics. This is evident from the approximate dispersion equation of longitudinal waves which follows from relation 6

$$\epsilon ik^2 = \mu m \omega \quad (7)$$

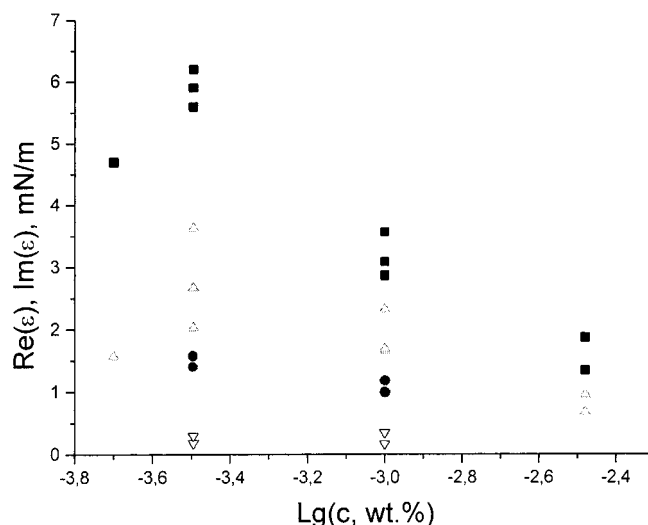
Figures 6 and 7 show the results of calculation of the real part of the dynamic surface elasticity from experimental data on the characteristics of transversal surface waves for solutions of PEG 4000 and PEG 20 000. The imaginary part of the surface elasticity for these systems was in the interval 0–1.5 mN/m and hence in the range of experimental accuracy. The results of Figures 6 and 7 let us conclude that the precision of determination of  $\epsilon_r$  does not allow to investigate the frequency dependence of the surface elasticity and that the investigated frequency interval of the capillary waves is insufficient for this purpose. At the same time, the concentration dependence of  $\epsilon_r$

proves to be accurate to a sufficient extent and agrees with the preliminary conclusions from the shape of the dependence  $\alpha(c)$ . The real part of the surface elasticity for solutions of PEG 4000 decreases by several times in the concentration interval from 0.001 to 0.1 wt %. For solutions of PEG 20 000  $\epsilon_r$  decreases in a broader concentration range. At concentrations of about 1 wt % the surface elasticity begins to increase again for both polymers. At low concentrations  $\epsilon_r \gg \epsilon_i$  and the adsorption film is elastic. In the concentration range from 0.01 to 1 wt % both components of the elasticity are comparable and we can assert that the adsorption film is viscoelastic. This means that the characteristic times of the surface relaxation processes are comparable to the period of capillary waves.

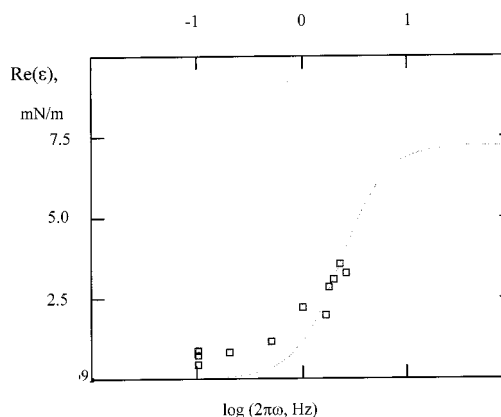
The only relaxation process, which has been studied until now for PEO adsorption films, was the diffusional exchange of macromolecules between the surface layer and the bulk phase.<sup>12,13</sup> However, the determined characteristic times of the diffusion of macromolecules exceed the period of applied capillary waves by many orders of magnitude. Consequently, this process cannot influence the surface viscoelasticity at frequencies of about 100 Hz.

The influence of the monomer exchange between different regions of the surface layer, which has been considered in the second part of this paper, seems to be more probable. Actually, in this case the decrease of the surface elasticity with concentration can be explained by the corresponding increase of the number of loops and tails of the polymer chains protruding into the bulk phase. This leads to the increase of  $\Gamma_2$  and to the decrease of  $\tau_2$  in agreement with eq 4. According to the results of the quasi-elastic surface light scattering the adsorption films of PEO behave like insoluble monolayers.<sup>13</sup> In this case the polymer chains are entirely unfolded in the surface layer and do not form long loops and tails<sup>10</sup> at least at concentrations  $< 0.4$  mg/m<sup>2</sup>. This situation is probably realized for adsorbed films of PEG 4000 in the region of maximum damping of capillary waves. Further increase of the concentration leads to a gradual appearance of loops and tails and, consequently, to a decrease in surface elasticity (Figure 6). At the increase of the molecular weight the loops and tails start to appear at lower concentrations but their number increases more slowly leading to a slower decrease of the dynamic surface elasticity (Figure 7). For PEO solutions the monomer distribution in the surface layer does not change significantly in the whole concentration range. This fact has been discovered by means of the neutron reflectivity.<sup>7</sup> Therefore, the suggested model allows us to explain qualitatively the observed behavior of the dynamic surface elasticity in the frequency range from 100 to 400 Hz.

The dispersion eq 6 gives also a possibility to calculate  $\epsilon$  from the characteristics of surface longitudinal waves. The absolute error of this quantity is lower than in the preceding case of transversal waves. The real and the imaginary parts of the dynamic surface elasticity turn out to be comparable at low frequencies (Figure 8). At low concentrations ( $c < 0.005$  wt %) the real part decreases with the concentration of PEO 4000 similar to the behavior at higher frequencies. At  $c > 0.005$  wt % it approaches zero. The imaginary part of the surface elasticity changes in the same way (Figure 8). Both components of the elasticity also decrease with the polymer molecular weight and for solutions of PEO their maximum values exceed the error limits only slightly. Thus, the surface film proves to be viscoelastic at frequencies close to 1 Hz and at low polymer concentrations. On further increase of concentration both components of the surface elasticity approach zero. This behavior is also in accordance with the suggested model. At



**Figure 8.** Real (squares, triangles pointing up) and imaginary (circles, triangles pointing down) parts of the dynamic surface elasticity of solutions of PEG 4000 (solid symbols) and PEO 100 000 (open symbols) vs concentration at the frequency 2 Hz.

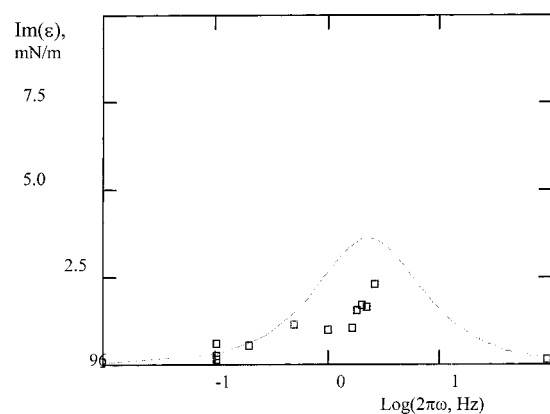


**Figure 9.** Frequency dependence of the real part of the dynamic surface elasticity for solutions of PEG 4000 at the concentration 0.001 wt %. The continuous line is the best fit to eq 5.

slow deformations (low frequencies) a relatively low number of loops and tails, which is insufficient to induce a viscous dissipation of energy in the surface layer at the frequencies about 100 Hz ( $\omega^{-1} \ll \tau_2$ ), can lead to the appearance of the surface viscoelasticity ( $\omega^{-1} \approx \tau_2$ ) at dilute solutions. The growing number of loops and tails resulting with increasing concentration leads to an abrupt acceleration of the relaxation processes and expansion (compression) of the surface is not any longer accompanied by changes in surface tension ( $\omega^{-1} \gg \tau_2$ ).

For solutions of PEG 4000 at low concentrations the dynamic surface elasticity proves to be maximal in comparison to the other systems investigated here (Figure 8). In this case the frequency dependence of the surface elasticity can be determined by the longitudinal wave method. Figures 9 and 10 show the results of this determination together with the dynamic surface elasticity determined from transversal surface waves. The latter value corresponds to the high-frequency limit ( $\epsilon(\omega \rightarrow \infty)$ ) (Figure 9). For PEG 4000 the polyoxyethylene chain is relatively short and we can assume that the number of loops and tails per adsorbed chain is low ( $n < 1$ ). Then relation 5 can be applied to the description of the frequency dependence of the dynamic surface elasticity. The parameters  $\partial\sigma/\ln \partial\Gamma$ ,  $\tau_2$  have been determined by a nonlinear regression analysis and the curves in Figures 9 and 10 represent the results of calculation according



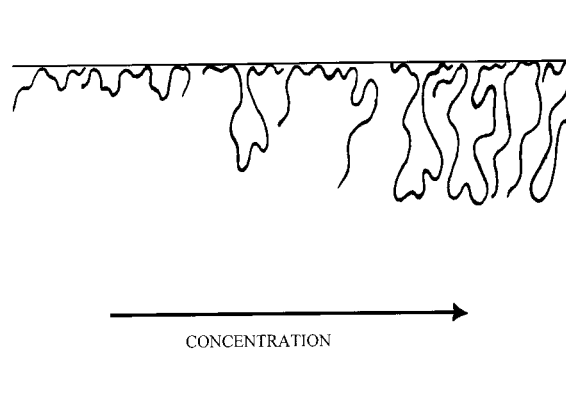


**Figure 10.** Frequency dependence of the real part of the dynamic surface elasticity for solutions of PEG 4000 at the concentration 0.001 wt %. The continuous line represent the results of calculations according to eq 5.

to eq 5. The deviation of the values of the real part of the surface elasticity from the curve at low frequencies probably indicates an influence of other relaxation processes. Note that eq 5 describes only the main contribution to the surface elasticity. The accuracy of the determination of the imaginary component is lower and this leads to the worse agreement between two sets of the data shown in Figure 10. The quantity  $\partial\sigma/\ln \partial\Gamma$ , which in the present case is equal to 7.2 mN/m, is an important characteristic of the surface layer. It depends on the molecular interactions in the surface layer and is one of the most important parameters in the physicochemical hydrodynamics of capillary systems.<sup>39</sup> For solutions of conventional surfactants,  $\partial\sigma/\ln \partial\Gamma$  can be determined from the surface tension isotherm by means of the Gibbs adsorption equation. This is not possible for polymer solutions and relation 5 is a method of its determination. Another important characteristic is the relaxation time. From the results in Figures 9 and 10 it follows  $\tau_2 = 0.06$  s. This parameter is related to both the properties of the polymer chain  $a$ ,  $B$ , and the characteristics of the chain packing in the surface layer  $N_2$ ,  $L_2$  (cf. eq 4). The latter parameters cannot probably be estimated now by an independent method. A possible method of their determination can consist, for example, in a more precise measurement of the dependence  $\epsilon(\omega)$  and a simultaneous estimation of both relaxation times  $\tau_2$  and  $\tau_B$ .

The applied experimental methods do not allow to construct the frequency dependence of the dynamic surface elasticity for higher concentrated solutions of PEG 4000. However, it is possible to obtain a rough estimate of  $\tau_2$  in the region of the minimum damping coefficient of the transversal capillary waves, where these waves indicate viscoelastic behavior of the polymer film. We can assume that  $\tau_2$  is comparable to the wave period or  $\tau_2 \sim 0.001$  s. Thus, the relaxation time changes by about 2 orders of magnitude for solutions of PEG 4000 in the investigated concentration range. For solutions of PEG 20 000 these changes become slower and for PEO solutions only slight changes of  $\tau_2$  are possible at the concentrations  $c < 0.001$  wt %.

The region of semidilute solutions ( $c > 1$  wt %) deserves special attention. Here the interaction of polymer coils in the solution leads to an increase in viscosity of the bulk phase. However, this increase is not sufficient to explain the observed increase of the damping coefficient of capillary waves (Figure 4), which is also connected with the increase of the surface elasticity (Figures 6 and 7). The interaction of macromolecules in solution also means that loops and tails at the surface cannot be considered as noninteracting with other loops and tails, and



**Figure 11.** Schematic illustration of the structural changes with concentration in the surface layer of polymer solutions.

with the neighboring macromolecules. Therefore, the dynamic model of the surface layer represented in the second section of this work cannot be applied any more and a more general theory must be derived taking into account the interactions of polymer chains outside the region I of the adsorbed film which is out of the scope of this work. However, it seems probable that some additional restrictions arise for the motion of monomers in loops and tails at the surface in the region of semidilute solutions and the adsorbed chains form a polymer brush similar to adsorbed block copolymers at high surface concentrations.<sup>20</sup>

Therefore, the changes of the state of polymer chains in the surface layer at increasing concentration can be imagined symbolically with the help of the scheme in Figure 11. The chains are stretched at the surface at low concentrations, then some long and noninteracting loops and tails protruding into the bulk phase arise, and finally the motion of loops and tails becomes restricted for semidilute solutions.

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