tance in the overall process of relaxation back to the ground state. Although no compelling evidence for the formation of charged species has been encountered in this work, it is suggested as a subject for future study especially in view of the recent interpretation of the mechanism of delayed fluorescence production in PVK subjected to laser excitation.[11]

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Adsorption Kinetics of Poly(ethylene oxide) at the Air/Water Interface

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ABSTRACT: With the aid of surface quasi-elastic light scattering (SLS) at the air/water interface, we established that the viscoelastic parameters of poly(ethylene oxide) (PEO) films, formed either by spreading from a methylene chloride solution or by spontaneous adsorption from aqueous solution, were identical over the entire surface pressure range. This identity was taken to infer that the PEO segments anchored at the surface are in the same physical state for both spread and adsorbed films. On this basis, the time dependence of the static surface pressure of adsorbed PEO films was used to deduce the corresponding surface concentration as a function of time. The adsorption kinetics by this method were found to be diffusion limited under certain conditions, and the resulting diffusion coefficients were shown to be in accord with those obtained by quasi-elastic light scattering on the same PEO samples in dilute aqueous solutions.

Introduction

Poly(ethylene oxide) (PEO) is known to form stable spread films[1-4] at the air/water (A/W) interface. PEO is also one of few polymers that forms such films at the A/W interface yet is water soluble in all proportions. The stability of a high molecular weight polymer film arises from its cooperativity, the large amount of interfacial contacts even if the monomer segments themselves being only mildly amphiphilic, and PEO is one of such instances. It has been shown to be extremely surface active in aqueous solutions[5-7] and thus is well suited for a comparative study of *spread* and *adsorbed* films. The schematic extremes of chain conformation adopted by a polymer adsorbed to an interface from dilute solution are as follows. At one extreme, the polymer exists in a random coil conformation, as in solution, with only a few segments in contact with the interface; a case in point is poly(methacrylic acid).[8] At the other extreme, a chain adopts a flattened, two-dimensional conformation with the majority of the segments in contact with the interface, and PEO is such a case.[1,2] In reality, the chain conformation at the interface probably comprises a certain combination of the two extremes. Since the random coil conformation arises from the predominance of configurational entropy and the planar conformation from that of adsorption enthalpy, a given combination of the two extremes reflects a manifestation of interplay of the entropic and enthalpic contributions to the adsorption free energy. For most of the spread polymer films in the dilute limit of surface segment density, the chain conformation is deduced to be in a flattened, two-dimensional one, and there are many examples of this case.[9]

Surface quasi-elastic light scattering (SLS) is a useful tool to probe the mechanism of adsorption to an interface since the film rheological parameters can be determined without knowing the surface concentration of such films; these rheological parameters are obtained by characterizing the dynamics of surface capillary waves. In a previous study,[3] we compared the dynamic longitudinal elasticity of spread PEO films determined from SLS with the static Gibbs surface elasticity. The first part of this paper deals with an extension of the SLS technique to the study of the dynamic viscoelasticity of adsorbed films for which the static Gibbs elasticity is not accessible because the surface

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concentration is not explicitly defined. This reveals the advantages of SLS in gaining access to dynamic surface viscoelastic parameters.

The SLS measurements indicate that the PEO segments at the interface are in a similar physical state in both adsorbed and spread films. This result motivates the second part of this paper. The polymeric nature of the films was used to our advantage, where the increased stability of the adsorbed species with respect to surface desorption allows the surface pressure–surface concentration (Π–Γ) isotherm for spread PEO to define implicitly the value of Γ at any value of Π for adsorbed films. This was put to use in the analysis of kinetic data of the adsorption process where the time dependence of Γ was considered in terms of a diffusion-limited process. Others studying the adsorption of macromolecules have almost universally found convection to play a role.[10-13] We have developed methodologies to overcome convective problems and have found good agreement between diffusion coefficients obtained by the adsorption experiment with those obtained from quasi-elastic light scattering (QELS) over a wide surface concentration range.

Experimental Section

Materials. PEO samples with molecular weights of 18K, 145K, 252K, and 996K with M_w/M_n less than 1.05 were acquired from Toyo Soda Co. through its distributor in the US (Varian, Sunnyvale, CA). Here, the letter K stands for kilodalton in molecular weight units. The 145K sample was dehydrated under vacuum for 48 h at room temperature and was indistinguishable from an undried 252K sample with respect to surface pressure isotherms. This was intended to check for whether there should be a problem with wet samples. On the other hand, we have found that one 594K sample was found to have degraded after dehydration and storage at room temperature for 2 months. Hence, all other PEO samples, 18K, 252K, and 996K, were stored at 4 °C and no dehydration step was taken before their use.

The aqueous phase for the surface measurements was house-distilled water, further deionized with a Milli-Q filtering system (Millipore) with one carbon and two ion-exchange filters. Dichloromethane (Aldrich, spectro grade, Gold Label) was used without further purification as the spreading solvent. All glassware and Teflon were cleaned with a sulfuric acid–Nochromix (Godax Labs. Inc., New York) mixture with no exposure to detergents of any sort.

Methods. The details of the SLS experiment have been given elsewhere.[14,15] All instrumental constants are the same as reported previously.[3,15] Both SLS and static measurements were performed simultaneously in a Teflon trough having dimensions of 28.5 cm × 11.1 cm × 1.0 cm, enclosed in a Plexiglass box (68 cm × 30 cm × 24 cm) with the relative humidity kept at 70%. A 1.0 cm × 2.5 cm × 0.01 cm sandblasted platinum plate, suspended from a Cahn 2000 electrobalance by fine stainless steel wire, was used for the Wilhelmy plate surface tension measurements. The precision in the surface pressure measurements was ±0.02 dyn/cm. The surface temperature was controlled to ±0.1 °C at 25 °C by circulating temperature-regulated water from a Lauda bath through a glass coil placed at the bottom of a trough.

For spread films, PEO was introduced to the interface by adding dropwise a methylene chloride solution of the polymer (approximately 0.5 mg/mL) onto the surface with a microsyringe. The surface concentration was controlled by a sliding Teflon barrier, allowing compression and expansion of the monolayer.

The PEO adsorption experiments were started (1) by rapidly lowering the platinum Wilhelmy plate to a fresh surface and acquiring the force signals from the Cahn balance via an A/D converter, which were subsequently converted to the surface tension values, and (2) by accumulating simultaneously the SLS spectral signals. A dilute (≅1–3 mg/L), well-mixed PEO solution was placed in the trough, and after sweeping the surface with the Teflon barrier, providing a clean surface to the polymer solution, the experiment was started. The second, and less successful, method of initiating the adsorption kinetics was to inject about 20 mL of a polymer solution into about 100 mL of water in the trough and stir for a few seconds in an attempt to mix the solution. With both methods at low PEO concentrations, however, the polymer adsorption was found to occur too rapidly, giving rise to apparent D values much too large. This is ascribed to convective motions in the solution underneath the surface. Others have seen the same trend with the adsorption of surfactant and proteins at lower concentrations, giving larger apparent D values.[11,16] As for the second method, failure is attributed to insufficient mixing upon injection of PEO solution to the subphase water before the start of an experiment; if the solution was not well mixed then concentration-rich regions would bring the material to the surface rapidly enough to give apparent diffusion coefficients varying from 2 to 10 times too large.[13,17]

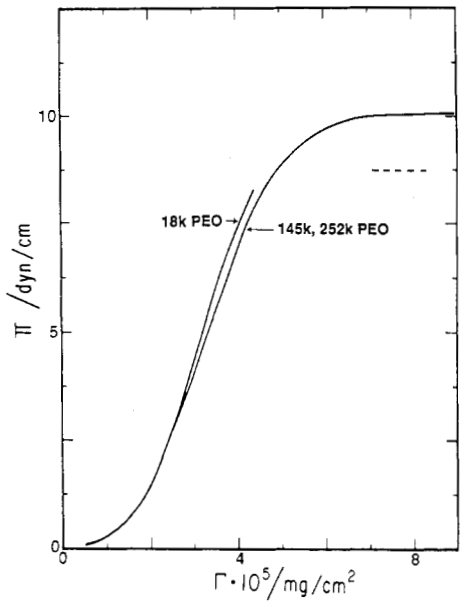

Figure 1. Static Π–Γ isotherms for 18K, 145, and 252K PEO. The results for 145K and 252K were identical. A noticeable difference was seen for the 18K sample starting at about 3 dyn/cm. The solid curve for 18K PEO stops at 8.5 dyn/cm because of monolayer collapse and the horizontal dotted line indicates a steady-state value found by continued compression past the collapse pressure for 18K PEO.

Quasi-elastic light scattering (QELS) was used to determine PEO diffusion coefficients in bulk solution. The instrumental details and scattered signal analysis method are detailed elsewhere.[18] Self-beating (homodyne) scattered intensity is analyzed by the second-order cumulant function.[19] The error for our D_{LS} values is estimated from 95% confidence interval of the fitted slope of the exponential time constant versus the scattering wave vector squared. The QELS experiments were performed periodically to check for sample degradation and the sample integrity was proved intact as inferred from the observed reproducibility of D_{LS}. The limiting value of D_{LS} at infinite dilution was found by lowering the PEO concentration until the observed D_{LS} became concentration independent.

Results and Discussion

Static isotherms for 18K and 252K PEO are given in Figure 1. A noticeable difference is seen between 18K, which was the lowest molecular weight sample, and higher molecular weight samples, 145K and 252K PEO. The 18K and 145K PEO isotherms start to deviate from each other at a static surface pressure Π of 3 dyn/cm and the 18K sample has a sharp collapse pressure around 8.5 dyn/cm which was indicated by a rapid decrease of Π upon reaching this pressure. Hence, the isotherm was terminated at 8.5 dyn/cm in Figure 1. The higher molecular weight samples collapsed less steeply as some segments were forced into solution with only a very small amount of time dependence above 8 dyn/cm. PEO with molecular weights between 145K and 996K was previously found to be molecular weight independent with respect to static

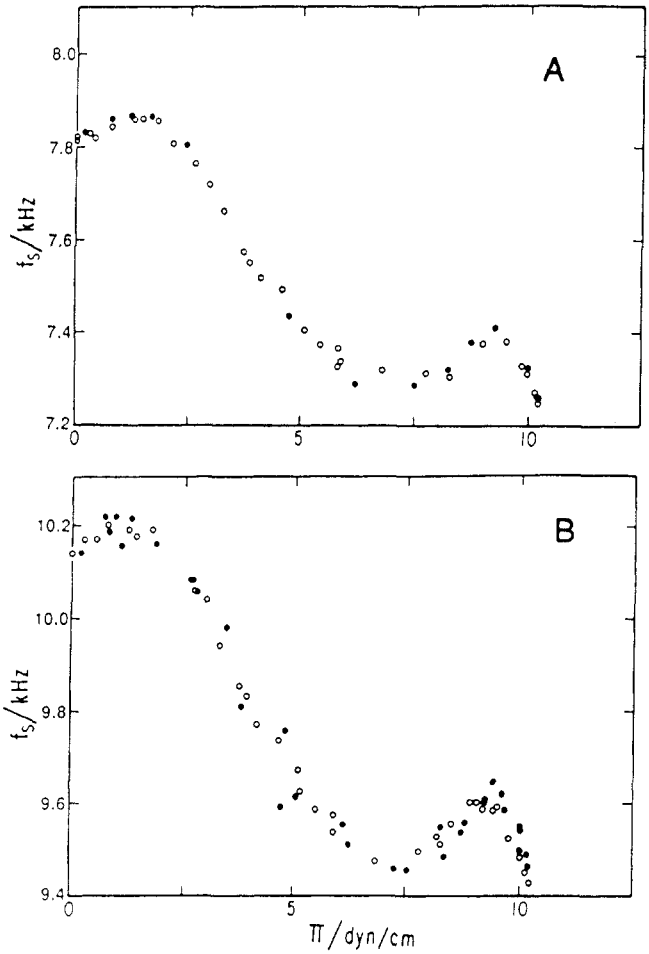

Figure 2. Frequency shifts versus Π for spread (open circles) and adsorbed (filled circles) monolayers of 252K PEO at (A) k = 323 cm^{-1} and (B) k = 385 cm^{-1}. The spread and adsorbed PEO are identical within experimental error for both k values.

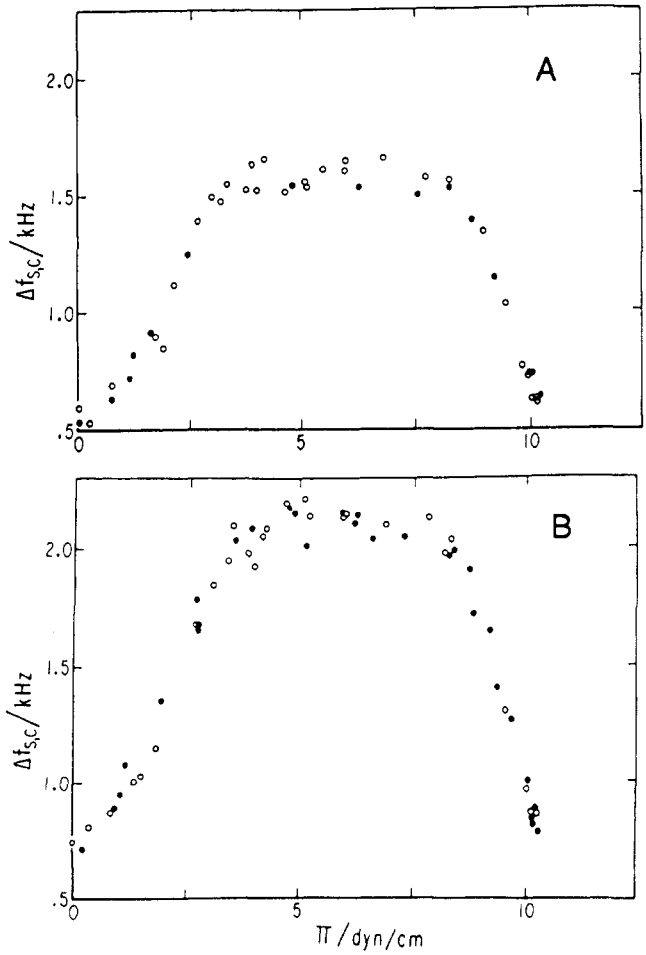

Figure 3. Corrected width versus Π for spread (open circles) and adsorbed (filled circles) monolayers of 252K PEO at (A) k = 323 cm^{-1} and (B) k = 385 cm^{-1}. The spread and adsorbed PEO are identical within experimental error for both k values.

isotherms[20] as was the case here. The abrupt collapse for 18K PEO was experimentally observed when the surface pressure became time dependent and decreased steadily by about 0.1 dyn/cm per min when first compressed past 8.5 dyn/cm; we suggest that such a collapse might be attributed to complete desorption of some of the PEO molecules. Upon compressing to higher surface densities and waiting for Π to stabilize between each compression step, an asymptotic value of about 8.75 dyn/cm was reached, and this is indicated by the horizontal dotted line in Figure 1. A possible reason that the asymptotic value is slightly larger than the collapse pressure of 8.5 dyn/cm is that the compression may force the monolayer into a nonequilibrium state. The molecular weight dependence of the collapse pressure has also been reported previously.[2,4] The higher molecular weight polymers did not exhibit a drastic collapse but gradually reached a common plateau value of about 10.2 ± 0.2 dyn/cm, as shown in Figure 1.

Surface Light Scattering Results. SLS spectra for adsorbed and spread films were acquired on the spectrum analyzer with an accumulation time of about 1 min. The static surface pressure was also monitored while the spectra were being taken, at various values of Π for four separate adsorption experiments at different bulk concentrations of 252K PEO ranging from c = 0.0001% to c = 0.0005%. (In keeping with the concentration unit of weight % adopted by Glass,[5] we begin with weight % but henceforth replace it by mg/L for 10^{-4}%, which is just one part per million.) The spectral characteristics were independent of c and thus independent of the rate of adsorption as long as the adsorption rate was slow enough that Π did not change significantly during the minute or so it took to obtain a spectrum.

A comparison of the values of the frequency shift f_s versus Π for the surface adsorption experiments and for spread monolayers is shown in parts A and B of Figure 2, for fifth and sixth orders, respectively, of the diffracted beam positions where fifth- and sixth-order diffraction spots correspond to k = 323 and 385 cm^{-1}, respectively. The quantity k for SLS equals $(2\pi/\lambda_0)$ cos ϕ sin θ, ϕ is the incident angle measured from the normal to the interface, θ is the scattering angle, and λ_0 is the laser wavelength in vacuo (632.8 nm). The values of f_s for adsorbed and spread PEO are identical as can be seen by comparing the open and filled circles. The values of f_s increase slightly, starting at low Π, and attain a small maximum at 1.5 dyn/cm with a value of about 80 Hz above the pure water value. After the peak, f_s decreases rapidly, following the surface tension decrease. There is another small bump, of about 200 Hz in magnitude, at 9.25 dyn/cm, and eventually Π reaches a plateau value at 10.2 dyn/cm and the graph is terminated here. Both the small peaks at 1.5 and 9.25 dyn/cm are ascribed to efficient coupling of the longitudinal and capillary waves, and they may not be identified with any telltale sign of conformational changes at the respective surface pressures.[3]

The frequency width was corrected for the instrumental broadening as previously described,[15] giving the corrected frequency width $\Delta f_{s,c}$. These values of $\Delta f_{s,c}$ are plotted as a function of Π in parts A and B of Figure 3 for fifth and

sixth order, respectively. These results also indicate that the SLS results for spread and adsorbed PEO are identical within experimental error. The values of $\Delta f_{s,c}$ rise rapidly for both spread and adsorbed monolayers at about 1.5 dyn/cm, following the increase in the dynamic surface longitudinal elasticity ϵ, remain relatively constant between $\Pi = 4$ and 7.5 dyn/cm, and then begin to decrease as ϵ decreases.[3]

This comparison between spread and adsorbed films makes full use of the SLS technique in a situation where no other technique would appear to be adequate. The advantage of the SLS technique over static methods is that values of ϵ for adsorbed films are determined via the wave dynamics, whereas knowledge of the Π–Γ isotherm is needed to determine the static Gibbs elasticity ϵ_s defined by

$$\epsilon_s = \Gamma(\partial \Pi/\partial \Gamma)_T \quad (1)$$

The values of ϵ and the dynamic surface longitudinal viscosity κ were calculated in a previous paper[3] by substituting the experimental values of f_s and $\Delta f_{s,c}$ into the dispersion equation[21,22] for monolayer-covered interfaces. The similarity of the spectra over the entire range of Π indicates that values of ϵ and of κ for adsorbed or spread PEO are indistinguishable at any given value of Π. We take this to infer that the conformation of the adsorbed and spread PEO segments at the surface are similar over the entire surface pressure range and that there is a very small activation energy barrier for adsorption over the range.

Another point in support of the low-energy barrier for adsorption is made by observing that the surface pressures at the fully saturated interfacial state for both adsorbed and spread films are rather similar and that the absolute value of collapse pressure for spread films is at $\Pi = 10.2$ dyn/cm. The small collapse pressure of PEO and corresponding low-energy barrier for adsorption is in contrast to earlier results on proteins which indicated that there was a substantial energy barrier for adsorption even at very small surface pressures[10] (above 0.1 dyn/cm).

Adsorption Kinetics. Having thus established the identity of spread and adsorbed films, we now turn to the adsorption kinetics results. It is essential to have a reliable means of determining the surface concentration. To this end many approximate forms of the Π–Γ isotherm have been derived[23] in order to calculate values of Γ from the experimental observable, i.e., Π. These give at best marginal results. Other techniques such as ellipsometry can be used to determine Γ with some success but only for relatively thick protein and polymer monolayers.[11,13] On the other hand, according to the measurements described in the first section of this paper, once the PEO molecules arrive at the interface from the solution side or the air side, they are adsorbed and form a film whose state is path-independently defined at a given surface pressure. Thus, Γ for *adsorbed* films can be determined by interpolating points from the Π–Γ isotherm for *spread* films of PEO.

We report only adsorption experiments initiated by sweeping the surface, as was discussed in Experimental Section, with PEO samples with molecular weights of 18K and 145K. Representative results of Π versus $t^{1/2}$ for the 145K sample are given in the inset of Figure 4. We emphasize that a saturation limit of $\Pi = 10.2$ dyn/cm is eventually reached after a long time, i.e., 3 h, which is the same as the collapse pressure of spread 145K films, which again illustrates the similarity between the spread and adsorbed films. Although it is not shown here explicitly, the 252K and 996K PEO samples were also found to reach a saturation limit of about $\Pi = 10.2$ dyn/cm[17] while the

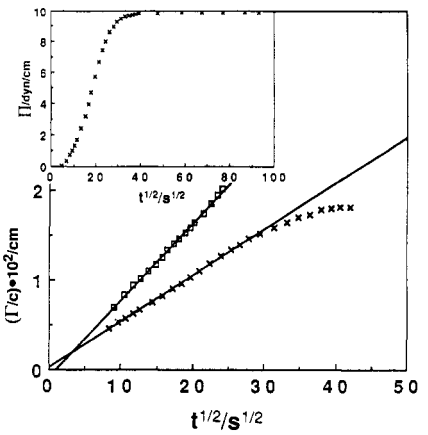

Figure 4. Interpolated values of the surface concentration Γ/c versus $t^{1/2}$ are plotted for 18K (upper points) and 145K PEO (lower points) at $c = 2.22$ mg/L and $c = 3.53$ mg/L, respectively, for PEO adsorbing at the air/water interface. The solid lines are the least-squares fits showing that the adsorption follows the predicted $t^{1/2}$ behavior over a wide range of surface density. The same data which were given in Figure 4 for 145K PEO are plotted in the inset as Π versus $t^{1/2}$.

18K sample only reached 9.4 dyn/cm, consistent with the lower collapse pressure shown in Figure 1 for this sample.

The kinetic results can be analyzed considering the adsorption to be a diffusion-limited process. The rate of adsorption of a diffusion-limited process with no back-diffusion was given long ago by Langmuir and Schaefer[24] as

$$\Gamma(t) = 2c(Dt/\pi)^{1/2} \quad (2)$$

where c is the polymer concentration in bulk solution and D is the diffusion coefficient for the adsorption process. As stated earlier, $\Gamma(t)$ was determined by fitting numerically the Π–Γ isotherms for 18K and 145K PEO (Figure 1) to seventh-order polynomials, although lesser order (fifth or sixth) polynomials would have been precise enough in most cases. Thus, for every experimental value of $\Pi(t)$, the corresponding $\Gamma(t)$ value could be determined. One polynomial could not fit the whole isotherm, so two separate equations for different regions of a Π–Γ isotherm with some overlap were used. Once $\Gamma(t)$ is thus found, the ratio $\Gamma(t)/c$ is easily calculated since c is assumed to be time independent because of a negligible amount from the solution being depleted for adsorption to the air/water interface even at the saturation limit. Thus, the plots in Figure 4, $\Gamma(t)/c$ versus $t^{1/2}$, amply demonstrate applicability of eq 2 to our experiments. The solid lines represent the least-squares fit, and the $t^{1/2}$ dependence is seen to hold for the whole surface concentration range for 18K PEO (upper curve) which corresponds to 0–8 dyn/cm. The static Π–Γ isotherm for the 18K sample (Figure 1) ends at 8.5 dyn/cm because of the abrupt collapse as was mentioned earlier, and up to $\Pi = 8$ dyn/cm there is no departure from the linearity in Figure 4. Systematic departure from $t^{1/2}$ dependence for 145K PEO commences at $\Gamma(t)/c = 1.6 \times 10^{-2}$ cm, corresponding to $\Pi \cong 9$ dyn/cm. Some departure is to be expected as the process can no longer be diffusion controlled in the vicinity of saturation; volume exclusion effects would likely set in and this should inhibit further adsorption. At $\Pi > 9$ dyn/cm, repulsive interactions (steric hindrances) come into play, preventing the molecules from completely adsorbing at the interface or possibly causing some reflection from the interface. This departure was found to be extremely reproducible for the 145K sample, so we only show one set of data.

The diffusion coefficient values D calculated from the slopes of the plots are summarized in Table I along with

Table I
Summary of PEO Diffusion Coefficients from Two Types of Experiments at 25 °C

sample	10^7D,[a] cm²/s	c, mg/L	10^7D_{LS},[b] cm²/s	c, mg/L
18K PEO			5.5 ± 0.4	3900
	5.3 ± 0.4	1.13		
	5.4 ± 0.3	2.22		
145K PEO			1.96 ± 0.1	1200
	3.8 ± 0.3[c]	1.00		
	2.2 ± 0.2	3.53		
252K PEO			1.47 ± 0.2	220
996K PEO			0.82 ± 0.1	140

[a] The deduced diffusion coefficients from the adsorption kinetics experiment. [b] The measured diffusion coefficients in dilute solutions by the quasi-elastic light scattering experiment. [c] An example of the diffusion coefficient by adsorption kinetics that was complicated by convection problems (see text).

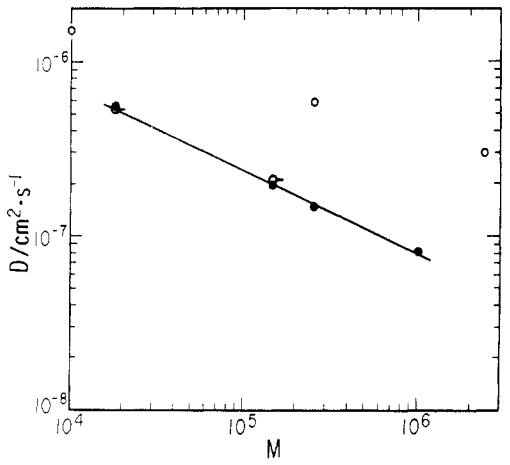

Figure 5. Diffusion coefficient versus PEO molecular weight is plotted on a log–log scale. The filled circles are D_{LS} by QELS and the line is drawn through the data giving a slope of −0.47 ± 0.03. The open circles with pips to the right are the D values deduced from the slopes in the plots in Figure 4 according to eq 2. The open circles without pips are the diffusion coefficients determined by reanalyzing the PEO adsorption data of Glass.[5]

the D_{LS} values. It is evident that the values of D and D_{LS} are identical within experimental error. The error for D was determined from one standard deviation between separate experiments. To illustrate more completely the molecular weight dependence, the values of D for 18K and 145K are shown along with the infinite dilution QELS diffusion coefficients D_{LS} for 18K, 145K, 252K, and 996K PEO in Figure 5. The points not on the solid line are those of Glass' which will be discussed presently. The D_{LS} values scale with $M^{-0.47\pm0.03}$ which is in qualitative agreement with the predicted $M^{-0.5}$ for Θ-solvent conditions.[25] The data obtained by the rapid mixing method have been omitted from Figure 5 because of the previously discussed convection problems; they are fully presented elsewhere.[17] The experiment done at c = 1 mg/L with 145K PEO is included in Table I to give an idea of at what concentrations convection contributes to the adsorption process for this molecular weight. This is strongly dependent on the molecular weight because that is what controls the duration of the experiment and it is the long-duration experiments which suffer from convective motion. The surfaces for this and all other experiments in Table I were cleaned at the start by the sweeping method discussed earlier, yet the dilute experiment at 1 mg/L still gives an apparent diffusion coefficient about 2 times too large. We saw a similar trend for other experiments performed at concentrations less than this for molecular weights of 145K, 252K, and 996K.[17]

Table II
Reanalysis of the Adsorption Kinetics Results of Glass[5]

	10^7D, cm²/s	c, mg/L		10^7D, cm²/s	c, mg/L
10K PEO	18	5	2400K PEO	5.1	9
	12	10		2.3	20
430K PEO	8.2	8		2.7	30
	6.6	10			
	3.6	20			

For a comparison sake, we now attempt to amend the analysis of the adsorption data of Glass[5] who was one of the first to do a systematic study of the adsorption kinetics of PEO solutions. We have crudely reanalyzed his raw data of Γ versus t in terms of eq 3 which is the analogue of eq 2 for adsorption at a spherical interface[26]

$$\Gamma = 0.736c(Dt)^{1/2} \quad (3)$$

The values of D calculated from Glass' data are listed in Table II for representative PEO concentrations c and also plotted in Figure 5. Averages of Glass' results for each molecular weight are given in Figure 5 (open circles with no pips). They are shown to be slightly more than a factor of 2 larger than the bulk solution values but not by several orders of magnitude as he had earlier stated. To explain the higher values, it is possible that the results of Glass[5] were affected by convective problems as is indicated by the dependence of D on c in Table II for his data at a given molecular weight. We close here with a parenthetical remark. There has been no impediment to pursue the adsorption experiment with higher molecular weight samples beyond 145K PEO, and these are being planned. Though our case could be strengthed further with a wider range of molecular weight, we think that a clean case of diffusion-controlled adsorption is established with two samples after successfully controlling convection problems.

We have shown here a method and recipes for controlling convection problems[10-13] and have obtained good agreement between the diffusion coefficients deduced by the adsorption method and measured by QELS in bulk solutions. Hence, we put forth a claim that the combination of surface light scattering and kinetic techniques can provide an unambiguous means to probe the polymer adsorption process quantitatively. This study thus sets the stage for applications to a wide variety of water-soluble polymers including polyelectrolytes, flexible and rigid polymers, and biopolymers.

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Registry No. PEO, 25322-68-3.

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Holography as a Tool for Mechanistic and Kinetic Studies of Photopolymerization Reactions: A Theoretical and Experimental Approach

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ABSTRACT: An original method based on the study of the time evolution of the refractive index modulation that results from a spatially inhomogeneous polymerization is developed with an aim at providing information on the initiation mechanism of the reaction. This study is restricted to the case where the intensity response of the material is not linear, i.e., when the polymerization rate is proportional to the square root of the absorbed dose of light. The equations that are arrived at are deduced from the simultaneous study of the bleaching of the sensitizer, the conversion of the monomer, and the diffusion of the species involved. The interest of this original approach for the study of the reactivity of polymerizable mixtures is exemplified by a concrete application. The system used to demonstrate the promising character and the flexibility of this nondestructive technique utilizes the photoredox reaction of methylene blue in its triplet state with an electron donor, as the source of initiating species. By use of the time-resolved holographic technique, the yield of the initiation step of this polymerization, which is almost impossible to measure by classical techniques, can be readily determined in the highly viscous environment of an incipient polymer film. Moreover, several pieces of mechanistic information can be collected from the kinetic study of the hologram growth curves.

1. Introduction

During recent years, holographic techniques have drawn the attention of many physical chemists owing to their potent applications as a nondestructive means for the study of physical transformations that occur in particular media where the conventional methods of investigation cannot be put into operation. One of the most immediate applications of these techniques is the study of local deformations or microdisplacements.[1,2] They have also been used for the production of holographic optical elements such as gratings, lenses, or prisms with better performances than conventional optical components or for the design of optical memories, able to store large amounts of information in small volumes of photosensitive materials.

The kinetic analysis of chemical reactions conducted in photopolymerizable films is another very interesting field in which holographic techniques show promise.[3-6] Thus, highly viscous or solid systems form an attractive class of compounds that lend themselves to this type of investigation.[7-10]

In fact, in such systems, polymerization takes place only in the bright areas of the pattern created by the interference of two plane waves, and volume-phase holograms exhibiting high diffraction efficiencies are created. However, a better comprehension of the physical and chemical processes that induce the refractive index modulation in a photopolymerizable active material is still required.

In this context, great care must be taken when dealing with the available theories that are generally used to rationalize the experimental observations and draw information from the study of the building up of the hologram.

The propagation of optical waves in thick gratings has been studied thoroughly, and it is possible in the present state of the art, to calculate from the theoretical analysis, the amplitude, phase, or polarization of the waves emerging in the reconstruction step.[10,11] Owing to the periodicity of the interference pattern, a Fourier representation of the grating can be employed. With this approach, the general coupled wave theory allows the first and higher orders diffraction efficiencies to be examined for a given grating with any index profile. The approach introduced by Kogelnik for thick sinusoidal gratings that uses simple analytical expressions leads to satisfactory analysis provided the underlying assumptions are satisfied.[12]

Braüchle and Burland have exemplified the usefulness of holography in many systems where the spatial modulation of the refractive index or of the absorption coefficient has the same profile as the interference pattern.[3] In particular, they used this technique with continuous-wave lasers to obtain detailed information on reversible or irreversible photoprocesses (rate constants, quantum yields, number of photons involved in a process, polymer lengths, etc.). For this type of applications, they are satisfied with using the Kogelnik expression reduced to its first two

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