($6.7\ M^{-1}\ ns^{-1}$).[17] Such estimates of the effective concentration of PBA in the micellar environment are plotted in Figure 12 against the concentration of alkyl group in $L_{0.25}$QPEI and CTAC. At a concentration of PBA of 1×10^{-5} M in bulk solution, its concentration in the hydrophobic cluster of $L_{0.25}$QPEI at 4×10^{-5} M solution concentration of lauryl groups was raised to 3×10^{-2} M; in solutions of CTAC with 3×10^{-4} cetyl group, the corresponding PBA concentration in the aggregate was raised 3×10^{-2} M. These results demonstrate quantitatively that the polymer cluster is more powerful by an order of magnitude than are low molecular weight detergents in ability to sequester hydrophobic substrates from bulk aqueous solutions.

Thus both spin-label and fluorescence experiments can be understood in terms of the model illustrated in Figure 3, which attributes the special features of the behavior of modified poly(ethylenimines) to the presence of hydrophobic clusters at intervals within the polymer matrix.

Registry No. I, 88337-17-1; pyrenebutyric acid, 25338-56-1; Tempyo ester, 37558-29-5; Tempyo ME, 88337-16-0.

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Forces between Two Layers of Adsorbed Polystyrene Immersed in Cyclohexane below and above the Θ Temperature

Jacob N. Israelachvili

Department of Applied Mathematics, Institute of Advanced Studies, Research School of Physical Sciences, Australian National University, Canberra, ACT 2600, Australia

Matthew Tirrell*

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Jacob Klein*,† and Ya'acov Almog

Department of Polymer Science, Weizmann Institute of Science, Rehovot 76100, Israel.

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ABSTRACT: Forces between polystyrene layers absorbed on mica and immersed in cyclohexane have been measured. The measurements were made on two different molecular weights (6×10^5 and 9×10^5) in two different laboratories and therefore support the quantitative reliability of the results. We have reproduced previous results of this type of measurement below the Θ temperature and extended the force measurement to (a) adsorbed layers at lower surface coverage and (b) temperatures above the bulk polystyrene–cyclohexane Θ temperature. At a coverage of about 1.1 mg/m^2 of polystyrene, which is on the order of 20–30% of saturation, we found strongly attractive forces below T_Θ, detectable at separations of about 300 Å between the bare mica surfaces. The forces can be measured very accurately and precisely in this situation. The force reaches a minimum at 46 ± 2 Å and becomes strongly repulsive closer in. The long-range attractive portion of the force curve is very nearly exactly exponential, with a decay length of 45 ± 2 Å. For saturated surfaces with about 4.5 ± 1 mg/m^2 the force is detectably attractive at larger distances (600–1200 Å) both below (23 and 26 °C) and above (37 ± 2 °C) the Θ temperature (34.5 °C). For each molecular weight the positions of the minimum in the $F(D)$ curve and of the short-range repulsive barrier are at smaller separations at $T > T_\Theta$. The magnitudes of the minima are smaller at $T > T_\Theta$ as well. Both of these new results suggest strongly that the forces, especially the attractive components, between the polymer surfaces are influenced by effects in addition to the usual segment–segment interactions which determine bulk thermodynamic properties.

Introduction

Forces between polymer surfaces, mediated by solvent, are the essence of the physics of adhesion,[1,2] steric stabilization of colloids,[3] tack in rubbers,[4] and other polymer particle aggregation and coalescence problems. We are most interested here in cases where two adsorbed polymer layers, covering other surfaces, interact. In this case the forces due to the polymer layers can be either attractive or repulsive, depending (a) on the polymer segment interactions, which in turn depend on solvent and temperature, and (b) on whether or not desorption occurs or

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[†] Also Cavendish Laboratory, Cambridge CB3 0HE, England.

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"bridges" form between the two surfaces. Here, bridge is used to mean a polymer chain spanning the gap between, and adsorbed simultaneously on, the two surfaces. We note also that it is possible that in the narrow near-2D region between two surfaces, thermodynamic interactions may not be exactly as in bulk fluid, and that properties such as the Θ temperature may be different from their bulk values.

We are interested here primarily in the case where the polymer layer is irreversibly adsorbed on the substrate surface, which appears to be attainable experimentally.[5] In this case, we expect that the forces measured between the adsorbed layers will be quite insensitive to the polymer concentration in the free solution once the surface has been saturated. Stable surface concentrations less than saturation can be produced easily as well, as long as the surface is only ever exposed to a subsaturating bulk concentration. Furthermore, in measuring the force vs. distance profile between the two surfaces we expect that a quasi-equilibrium situation will prevail. The forces that we measure at each gap separation will be the equilibrium forces for that certain constant amount of polymer in the gap; however, for true equilibrium the amount of polymer in the gap would diminish with decreasing separation due to increasing conformational restriction. This latter process is very slow compared to the time scale of force measurements.[6]

Several experiments have been done in attempts to make direct measurements of forces between polymer surfaces.[7-11] Some of these have suffered due to unreliability of the technique;[7,8] others used poorly characterized, very polydisperse polymers.[9,10] Only one previous effort[5,11] has, to date, produced quantitatively reliable results. One of the apparatuses in the present work was used to measure the forces between polystyrene surfaces adsorbed on mica and immersed in cyclohexane at 24 °C. Attractive forces were observed at separations of the mica surfaces between about 3 and 1 times the bulk polymer radius of gyration, and repulsive forces were measured closer in. The attractive forces were the novelty and were attributed to the poor solvent quality of cyclohexane for polystyrene at 24 °C. The Θ point (T_Θ) is 34.5 °C, and the critical temperature (T_c) for the molecular weight used (6×10^5) was 30 °C. The attraction was likened to the phase separation observed in bulk solution as polymer concentration is increased below T_c.

Fleer and Scheutjens[12,13] have disputed this explanation, arguing that if adsorption occurs then bridging can occur, and it contributes to the attraction. In particular, they assert that above T_c and T_Θ one may still see attraction due to bridging as long as wholesale desorption does not occur with increasing temperature.

The aim of the present work is to explore the lower surface coverage and higher temperature regimes further. The former favors bridging; the latter puts the explanation based on the analogy to bulk fluid phase separation to the test directly.

Experimental Section

The results reported here were obtained in two different laboratories, using both the apparatus developed by Israelachvili[14] and a modification developed by Klein.[11] The experiments with polystyrene (PS) of 9×10^5 molecular weight were performed by the first two coauthors in Canberra and will be labeled hereinafter the ANU experiments; the data on PS of 6×10^5 molecular weight were obtained by the second pair of coauthors and will be labeled the WI data. In each apparatus, the force between two molecularly smooth mica substrate surfaces can be determined to 10^{-7} N by measuring the deflection of a spring supporting one of the mica substrates, while their separation is determined with a resolution of better than 5 Å by an optical interferometry technique.[15] Temperature was controlled near ambient, i.e., at 23 ± 1, or 26 ± 0.5 °C, by a room thermostat; at 37 ± 2 °C the temperature control was by immersion heaters in the polystyrene–cyclohexane solution surrounding the surfaces in both apparatuses.

The forces $F(D)$ were first measured in pure cyclohexane, and then polystyrene was added to the cyclohexane and allowed to adsorb on the mica. In each laboratory, the cyclohexane used was spectroscopic grade, from Fluka. For the ANU experiments, it was prepared by storing for several days over 4A molecular sieve and silica gel, then distilled, and finally filtered through 0.05-μm Nuclepore filters immediately prior to use. Experience shows that the water content of cyclohexane treated in this way is less than 15 ppm.[16] In the WI experiments the cyclohexane was used as received after passage through a 0.22-μm Fluoropore filter. The polystyrenes were monodisperse standards from Pressure Chemical Co. The as-received samples were reprecipitated several times from the tetrahydrofuran into methanol and then vacuum-dried to remove detectable fluorescent impurities. The unperturbed radii of gyration of these molecules are approximately 210 and 250 Å for molecular weights 6×10^5 and 9×10^5, respectively.[17] The PS was dissolved outside the apparatus at a concentration of about 0.5 mg/mL in cyclohexane prepared as above. An aliquot of this solution was then injected through a 0.05-μm filter to establish the final concentrations in the apparatuses at $(11 \pm 2) \times 10^{-6}$ g/mL.

The low surface coverage polymer layer of 9×10^5 molecular weight studied in the ANU experiments was established by keeping the two mica surfaces very close together (≈0.1 mm) during the exposure to the polystyrene solution so that after 20 h of incubation the surface coverage, estimated by measuring the refractive index between the plates and from the minimum separation obtained at very high compressive force, was approximately 1.1 ± 0.2 mg/m^2, which appears to be roughly 20–30% of saturation coverage.[5,18] As long as the surfaces were held at a separation no greater than this small value, this low coverage was stable for several hours due to the slow diffusion of polymer into the small gap. In order to establish equilibrium saturation, after the low-coverage experiments, the surfaces were separated to about 2 mm and incubated 15 h more.

All distances reported here are relative to the measured air contact position of the bare mica surfaces. The mica surfaces between which the forces are measured are arranged in a crossed-cylinder configuration. For this reason, the forces are expressed here as force (F) divided by the geometric mean of the two principal radii of curvature (R) of the crossed cylinders. This is directly related, via the Derjaguin relation,[19] to the energy per unit are (E) of interaction between two flat parallel surfaces of the same nature and at the same separation (D):

$$F(D)/R = 2\pi E(D) \tag{1}$$

R (of order 1 cm) was slightly different in each of the different experiments here and was measured each time so that reporting F/R is a way of normalizing the data.

Results

Before discussing the results of forces between polystyrene layers, we must mention some significant features of the measurement of the forces between the bare mica surfaces immersed in pure cyclohexane. As noted above, the ANU experiments used dry cyclohexane. The $F(D)$ curves here showed not a monotonic van der Waals attraction but an oscillatory function of distance, where the spacing between successive minima corresponds to the molecular diameter of cyclohexane (i.e., about 6 Å). This behavior is documented and discussed in detail elsewhere.[16] The explanation of this behavior appears to be that there are ordered layers of cyclohexane molecules between the smooth mica surfaces which produce these so-called structural forces. In the WI experiments, with cyclohexane equilibrated with ambient humidity, a monotonic van der Waals type attraction was observed, the mica surfaces coming together smoothly to their air-contact position. This difference is due to the fact that water adsorbs at the

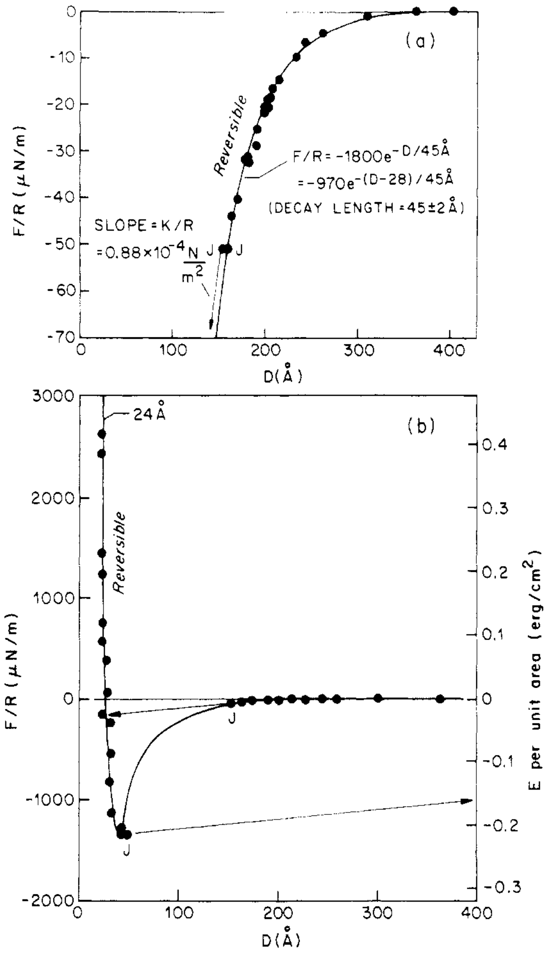

Figure 1. Low surface coverage experiment at 26 °C. (a) Long-range portion of force vs. distance curve plotted as F/R in μN/m vs. D in Å. Line drawn through points is plot of exponential function indicated. The symbol J indicates a point where a jump occurs due to the fact that the magnitude of the gradient of the force vs. distance curve exceeds the constant of the force-measuring spring. Precision of the measurement is about the same as the size of the data point. (b) Entire force vs. distance curve. Symbols J have the same meaning. Line drawn between jump points is schematic only. Precision is much better than the size of the data point. See text for details.

mica surface and presumably disrupts the order; and, it is possible to obtain a purely monotonic attractive force curve from previously dried cyclohexane by bubbling wet nitrogen through the cyclohexane.[20] Whether this is an important influence on the forces between polystyrene (PS) layers in cyclohexane (CH) is not clear. Moisture is known to affect the PS/CH Θ temperature markedly.[21] However, as will be shown below, we see quite comparable forces between the PS layers despite the difference in dryness of the cyclohexane used.

We describe first the results of the low surface coverage experiment with PS of 9 × 10^5 molecular weight (ANU), which are displayed in Figure 1. Figure 1a shows an expanded scale of the long-range portion of the $F(D)$ curve. Figure 1b gives the entire measured $F(D)$. This experiment was done at 26 °C. The amount of PS on each surface was estimated from the fact that at a separation of 24 Å, where the forces are strongly repulsive, the surface separation seems to have reached a limiting value; assuming that this value corresponds to essentially bulk PS between the mica surfaces, the density of bulk PS ($\sim$1.07 g/cm^3) enables us to estimate the surface coverage. This estimate, 1.1 ± 0.2 mg/m^2, is also consistent with refractive index measurements. We see in Figure 1 that the forces are detectably attractive at about 300 Å. It is possible that there is a very gradual decay to zero force farther out, but that is below the precision of force measurement in this experiment. As the surfaces are brought closer they jump toward one another at 158 ± 2 Å. These jumps occur whenever the magnitude of the gradient of the $F(D)$ curve exceeds the spring constant of the force-measuring spring which supports one of the mica surfaces.[13] The jumps go from 158 Å in until the repulsive barrier is hit at about 30 Å. Closer in than this the forces are strongly repulsive, with a very hard wall at 24 Å. On reversing the direction, traveling out from 24 Å, one finds a strong adhesive minimum, $F/R = -1320 \pm 20$ μN/m, and a jump out from 46 ± 2 Å. As the jump out follows the line of the local gradient of the $F(D)$ curve, these jumps out come to rest at 1530 ± 40 Å.

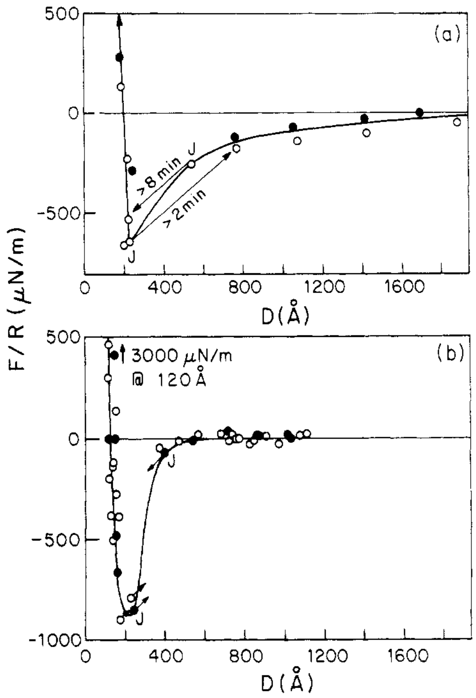

Figure 2. Saturated surfaces below T_Θ. Force vs. distance plotted as F/R vs. D: (a) 9 × 10^5 molecular weight (ANU), 26 ± 0.5 °C; (b) 6 × 10^5 molecular weight (WI), 23 ± 0.5 °C. Unfilled and filled circles represent separate experiments under the same conditions. Symbols J have same meaning as in Figure 1. Numbers on the repulsive portions of the force curves represent the closest approach of the two surfaces achieved for a very large force.

On the regions of the $F(D)$ curves where data points are given, the force measurements are reversible and reproducible over a number of cycles of movement in and out. A steady value of the force is measured within 5–10 s of establishment of some constant distance between the surfaces. The same $F(D)$ curve is followed on moving the surfaces toward or away from one another. In between the points of the two jumps the forces cannot be measured directly except by using a stiffer force-measuring spring. A semilogarithmic plot of the data between 158 and 300 Å reveals that the data there lie on a straight line; in order words, the forces here are exponentially attractive with a decay length of 45 ± 2 Å. This is the line drawn through the data in Figure 1a. We observe these exponentially attractive forces at distances beyond where van der Waals forces between the mica surfaces have become negligible. In the Discussion and Conclusions section we offer some qualitative reasoning to explain the exponential distance dependence.

The results of experiments with saturated adsorbed layers below T_Θ are shown in Figure 2 for the data on the 6 × 10^5 molecular weight PS (WI, Figure 2b); the amount of polystyrene adsorbed, determined by refractive index measurements and corroborated by independent microbalance measurements,[22] was 5.5 ± 0.5 mg/m^2. For the data on the 9×10^5 molecular weight PS (ANU, Figure 2a), refractive index measurements between the surfaces lead to an adsorbance value of 3.6 ± 0.6 mg/m^2, which we also believe to be saturation under the conditions of the ANU experiment.[18] The difference in the adsorbance values may be due to differences in the micas used or differences in the water content of the cyclohexanes. We do not believe that the difference is due to the difference in the molecular weights of the two polymers studied. Takahashi and coworkers have studied adsorption of PS on chrome plate and found the adsorbancy to be independent of molecular weight above 5×10^5.[23] The data of Figure 2b are in good agreement quantitatively with $F(D)$ published previously on the same polymer.

Comparing the data on the two molecular weights we see that the two curves are qualitatively similar. They can be made quantitatively similar if we scale the separation by the free solution radii of gyration (R_g) of the two polymers.[24] Thus, we find that the attractive minimum occurs at $D \gtrsim R_g$ in each case. Likewise, a very steep repulsive barrier is observed in each case at about $D \simeq {}^2/_3 R_g$. The distance at which attractive forces between the surfaces are first clearly detectable is somewhat larger for the 9×10^5 molecular weight sample than could be accounted for on the basis of radius of gyration scaling, which may be related to differences in the precision of the force measurement in the two experiments. The depths of the attractive minima, ~700 ± 50 μN/m, are reasonably close, too. It is noted that the depths of the minima here in these high surface coverage experiments is only about half that seen in Figure 1. Overall, these new results are in good accord with those published previously[5,11,24] at temperatures below T_Θ.

There are some differences between this experiment and the lower surface coverage experiment that do not show up directly in comparing Figures 1 and 2. Most important is the observation we made that the forces achieve steady values at a given separation in a *much* more sluggish fashion at higher coverage, especially at separations less than 400 Å in Figure 2a and 700 Å in Figure 2b. As noted on Figure 2, there are jumps in and jumps out from points where the magnitude of the local graident exceeds the spring constant. In contrast to the lower surface coverage experiment, where the jumps were complete in 5 s or so, here the inward jumps require more than 8 min in some cases to reach the final position and the outward jumps more than 2 min. Sluggish jumps at high coverage have been observed, and it has been suggested that either entanglement or hydrodynamic effects may be involved.[11,24]

Figure 3 shows the data at 37 ± 2 °C, about 3–5 °C above T_Θ. We again see the same general shape of the $F(D)$ curves in each case. There is definite attraction above T_Θ starting between about 500–1000 Å as in Figure 2, depending upon molecular weight. The attractive component of the force is somewhat weaker at each molecular weight than it was below T_Θ. The minima and the hard repulsive wall are moved closer in for both molecular weights to about 135 Å and 70 ± 5 Å, respectively. There seems to be little difference in the positions of the features of the $F(D)$ curves for the two molecular weights at $T > T_\Theta$ in spite of the differences in the magnitudes of the forces.

The new position of the repulsive wall is suggestive of some amount of desorption, a possibility upon which we shall comment in the discussion. (It was difficult to get accurate refractive index measurements for $T > T_\Theta$ due to thermal drifts.) We do note that if there are some desorption/adsorption phenomena occurring, they are readily reversible since the behaviors shown in Figures 2 and 3 can be produced, one from the other, within several minutes after making a rapid (several °C/min) temperature change.

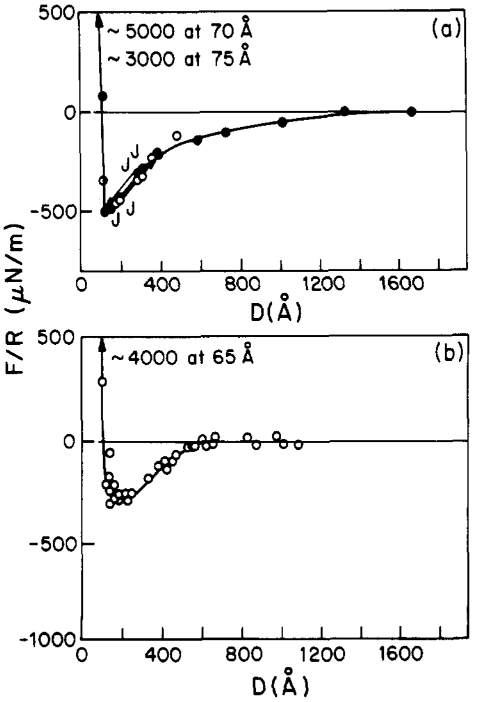

Figure 3. Saturated surfaces above T_Θ. Force vs. distance plotted as F/R vs. D: (a) 9×10^5 molecular weight (ANU), 37 ± 2.0 °C; (b) 6×10^5 molecular weight (WI), 37 ± 2.0 °C. All symbols have same meaning as in Figure 2.

The regions of the minima, on the distal sides, have more gradual slope than in Figure 2 so that, while jumps inward and outward do occur at the indicated places on the curves, they move virtually along the line connecting the accessible force measurements. A striking observation we made which does not show up in the figure is that the sluggishness which we noted in establishing equilibrium (Figure 2) is *not* observed here. Even the jumps are complete with 10 s, although it is also true that, due to the smaller slope of the $F(D)$ curve, the jumps are shorter. In any case, the key observation here is that at 5 °C above T_Θ there is still a definite *attraction* between the surfaces. We emphasize the word attraction since one might observe an adhesive minimum on separating the surfaces, even if they were intrinsically repulsive but became entangled when forced into close approach. Here we observe *jumps* inward on approach, which is a clear sign of intrinsic long-range attraction.

Discussion and Conclusions

These results show two new facts. Surfaces bearing adsorbed polystyrene immersed in cyclohexane exhibit long-range attractive interactions for one another both (a) at less than saturation coverage and (b) at temperatures above the bulk solution PS–CH Θ temperature.

The low surface coverage experimental conditions favor bridging due to the availability of surface sites, and this work clearly shows that whatever the origin of these long-range forces they are exponential in character. We have no *direct* evidence for bridging in these experiments; however, we feel that these data provide a very good touchstone for tests of theories of these attractive forces. We also note that if the strong adhesion (~0.2 erg/cm^2) we observe is due in part to bridging, then the adhesive

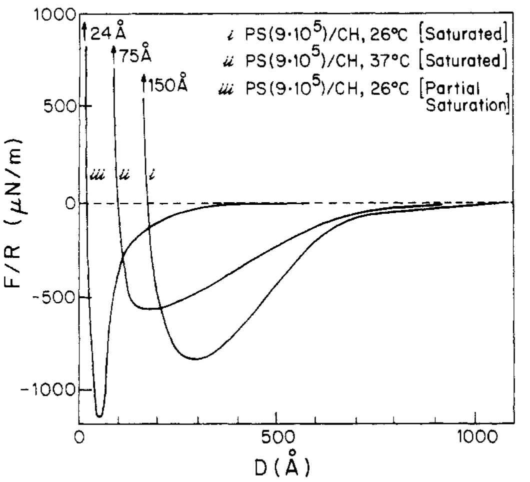

Figure 4. Schematic comparison of all data for PS of 9 × 10^5 molecular weight (ANU). All symbols have same meaning as in Figure 2.

energy, corresponding to the minimum in the $F(D)$ curve, may be related to the binding energy per segment of PS on mica.

The strength of the adhesion is decidedly greater in the case of partially saturated surfaces, indicating that some factor, in addition to interactions between PS segments, is contributing to the forces. It is well-known[25,26] however that the *long-range* portion of the polymer segment density distribution near an adsorbing wall varies exponentially with distance. Thus, polymer segment interactions probably do explain the long-range portion of the $F(D)$ curve.

Feasible explanations for the attractions at high surface coverage above the Θ temperature are less evident. It is apparent that polymer segment–segment interactions which are repulsive, albeit weakly, at this temperature do not dominate the scene. The forces are decidedly attractive. While we prefer to avoid too much speculation at this stage, several factors are worth noting. While bridging is less likely at high surface coverage,[12,13] we did notice an enhanced speed of the dynamic response at $T > T_\Theta$, much more than one would expect from the solvent viscosity change alone, which may mean that rearrangements of the macromolecules near the surface are now occurring sufficiently rapidly to allow bridges to form even at high coverage. The key role of surface dynamics in understanding these problems has been pointed out recently.[25] One plausible scenario is that there may be some amount of *desorption*[27,28] engendered by the increase in temperature which moves the repulsive barrier to smaller separations and frees additional surface sites for bridging. As noted previously, whatever surface rearrangement may be induced in traversing T_Θ is reversible as far as the $F(D)$ curve is concerned on a time scale of tens of minutes.

It is also true that these experiments were not done very far above the Θ point. The Θ point of 34.5 °C is for polystyrene and cyclohexane in unbounded solution. It, of course, is due to a delicate compensation of interactions which may be somehow altered in the space between the mica surfaces. For example, there is the clear evidence mentioned above that the cyclohexane is ordered between mica surfaces out to distances of 60 Å.[16] Likewise, a polymer molecule bound to a surface performs a different sort of self-avoiding walk than one in free solution.[26] Furthermore, the presence of the two mica sheets and the energetics associated with them may alter the thermodynamic state in the gap, irrespective of the above-mentioned ordering.[29] So, qualitatively speaking, it may be that the arguments advanced by Klein,[24] and later elaborated by Klein and Pincus,[30] for the attractive forces based on thermodynamics of unbounded solution may be correct if account is taken of the influence of the surfaces in the small gap. Whether any of these effects is large enough to explain our observations in this way is a question to pursue in future work.

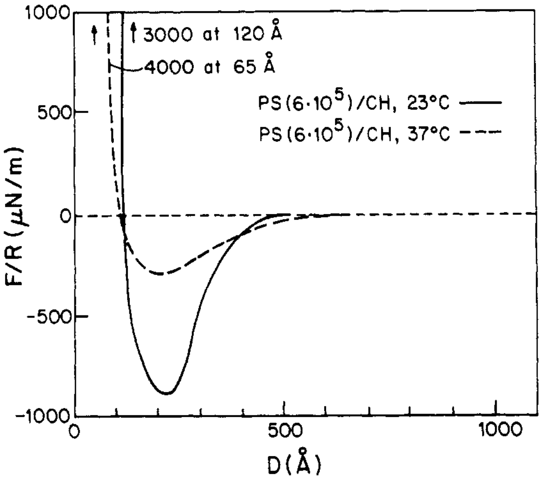

Figure 5. Schematic comparison of all data for PS of 6 × 10^5 molecular weight (WI). All symbols have same meaning as in Figure 2.

Summary

The results of all the experiments for the two molecular weights at different temperatures and surface coverages are summarized in Figures 4 and 5. These figures show only schematic smooth curves in place of the actual $F(D)$ data and are intended to summarize the data quantitatively and to facilitate comparisons of positions of various features and magnitudes of forces. The central findings are that (a) there are much stronger exponentially varying attractions at $T < T_\Theta$ between *partially* saturated PS-coated mica surfaces immersed in CH than between fully saturated PS-coated mica surfaces at the same temperature and (b) saturated PS-coated mica surfaces immersed in CH are decidedly attractive at T_Θ plus 3–5 °C.

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Registry No. Polystyrene, 9003-53-6.

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Degradation of Chain Molecules. 2. Thermodynamically Induced Shear Degradation of Dissolved Polystyrene

M. Ballauff[†] and B. A. Wolf*

Institut für Physikalische Chemie der Universität Mainz, Sonderforschungsbereich 41 "Chemie und Physik der Makromoleküle", D-65 Mainz, West Germany.

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ABSTRACT: The degradation of polystyrene ($2.60 \times 10^3 \le P_n \le 1.50 \times 10^4$) in semiconcentrated solutions (4.9–20 wt %) in *trans*-decalin (Θ solvent) has been studied at moderate shear rates (laminar flow, $5 \times 10^3 \le \dot{\gamma} \le 10^4$ s^{-1}). The results demonstrate that the scission of the C–C bonds is induced by the poor solvent quality. The breakage of chains leads to radical fragments that either recombine or react with added radical scavengers. Special attention has to be paid to the choice of the radical scavengers in order to avoid changes in solvent quality. The rate of degradation increases strongly with concentration. The breakage probability evaluated on the basis of the method described in part 1[1] is Gaussian along the chain. The standard deviation, expressed by the parameter R, amounts in most of the cases to 10–15% of the actual chain length. The exponent X describing the dependence of the rate of degradation on the individual chain length is comparatively small (0.1–0.9) and depends on temperature and shear rate. Since the effect is thermodynamically induced, the influence of temperature is very pronounced. All findings are compared to recent viscosimetric results[2] and can be explained in terms of the modified Graessley theory.[2,3]

Introduction

In the first paper of this series[1] the kinetic scheme describing the degradation process of chain molecules was solved exactly. It was demonstrated that each model of interest can be treated by this procedure. Thus the individual rate constants $k_{i,j}$ for the scission of a chain of length i into two fragments with j and $i - j$ subunits respectively can be obtained by fitting different models to experimental distributions. These rate constants $k_{i,j}$, i.e., the breakage probability as a function of chain length i and position of the jth bonds, clearly reflect the stress along the chain. This information is not available by any other method. Thus degradation experiments under suitable conditions can be used as a tool for studying special aspects of chain dynamics in a sheared liquid. In order to connect the kinetic data obtained by the above method with external forces applied to the molecules, the degradation experiment has to be carried out under laminar conditions; i.e., the acting shear rate must be well defined. But in many cases[4] the shear rate to be applied to cause the scission of the C–C bonds is of the order of 10^5 s^{-1}. Thus the degradation can be observed very often only under turbulent conditions. Some years ago it was observed[5] that polystyrene is degraded even at moderate shear rates (10^3–10^4 s^{-1}) when dissolved in a Θ solvent, whereas no scission occurs under the same conditions in a good solvent. This effect provides convenient access to degradation under laminar conditions. In this paper this "thermodynamically induced shear degradation" is studied with respect to molecular weight distribution, solvent quality, concentration, and shear rate. Since the scission of the C–C bond is homolytic, special attention is paid to the influence of added radical scavengers such as oxygen or DPPH (2,2-diphenyl-1-picrylhydrazyl). The results are compared to recent viscosimetric results,[3] leading to a semiquantitative understanding of the degradation process in terms of the modified Graessley theory.[2]

Experimental Section

Materials. Toluene, analytical grade (Merck, Darmstadt), was used without further purification. *trans*-Decalin (Merck-Schuchardt) was carefully fractionated before use. The final content of the cis isomer as checked by gas chromatography amounts to less than 0.2%. DPPH (Fluka, purum) was used without further purification. Solubility data of oxygen in *trans*-decalin, necessary for comparing the influence of different radical scavengers are not available from the literature but can be estimated from data of similar hydrocarbons to be ca. 0.1 cm^3 of O_2/cm^3 of solvent at 1 atm. This corresponds to a concentration of 4.5×10^{-3} mol/L.

[†] Present address: Department of Chemistry, Stanford University, Stanford, CA 94305.

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