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Thermodynamic and Kinetic Factors in Adsorption of Polymers on a Plane Lattice

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ABSTRACT: The rate of formation of an adsorbed polystyrene monolayer onto silica/carbon tetrachloride interfaces is studied by a radioactive tracer method with ^{3}H-labeled polymers. The influence of the temperature on the amount of the polymer adsorbed is determined, and the kinetic law of the adsorption is formulated. At low solution concentrations, the polymer adsorbs with a very flattened conformation, and the kinetic parameter of the adsorption process is quantitatively analyzed with use of a mechanism corresponding to a two-dimensional lattice filling. This process may be regarded as a "solution" process such as the mixing on a molecular scale, which involves, beside surface forces, local conformational changes and entropy of mixing effects. At higher solution concentrations, loops and/or tails emerge from the surface at a very low rate.

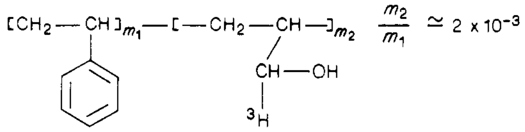
Introduction

Several studies of the adsorption of polystyrene onto silica, carbon, and metal surfaces under various solvent conditions have been reported in the literature.[1-8] Several characteristics of the polymer layer adsorbed on these substrates were determined: macromolecular interfacial area, hydrodynamic and ellipsometric thicknesses, and relative importance of trains and loops at adsorption equilibrium. Special interest was also directed toward the variation of the number of chain segments in contact with the solid surface, resulting from the increase in the degree of coverage. These adsorption studies were done on plane, porous, or finely divided adsorbents, suited to the selected techniques of investigation.[9]

In the present study, we focused attention on the kinetics of the formation of a polymer layer on a nonporous silica adsorbent of particular interest. By choosing an adsorbent, fully hydrated silica, bearing only silanol groups and carbon tetrachloride as solvent, we were able to generate strong polymer–surface interaction forces and to follow the early stages corresponding to the formation of a flat carpet.[10] Information relative to the layer structure and to the successive conformations of the adsorbed polymer was obtained by varying the polymer concentration in the solution at adsorption equilibrium. Similarly the influence of temperature on the shape of the adsorption isotherms furnished a scheme complementary to the observed unusually stable structure of the adsorbed polymer. It then proved interesting to establish the relationship for the kinetics of the establishment of the adsorbed layer and therefore to determine the main mechanism of the process.

Experimental Section

Materials. Polymer. The radiolabeled polystyrene was prepared by radical polymerization in the presence of traces of acrolein. After purification, the polymer was reacted in freshly distilled dioxane with tritiated potassium borohydride to yield the following chemical structure:


$\frac{m_2}{m_1} \simeq 2 \times 10^{-3}$

The characteristics of the polymer are as follow: $M_w = 3.6 \times 10^5$, M_w/M_n (GPC) = 1.6; specific radioactivity $R_s = 2 \times 10^8$ cpm g^{-1}. The polymer concentration was obtained by determining the specific radioactivity of the solution. Because the carbon tetrachloride exerts a strong quenching, the solvent was extracted before the liquid scintillator (Instagel Packard) was added to the polymer sample.

Adsorbent. The adsorbent was nonporous glass beads (Verre et Ind.) of 34-μm average diameter and 7.8×10^{-2} m^2 g^{-1} specific surface area. This adsorbent was treated with hot hydrochloric acid to extract or exchange with H$^+$ all surface ionic exchangeable species. Moreover, this treatment generates a hydrated silanol surface. The beads were then washed free of acid. Excess water was evaporated under reduced pressure at 40 °C. This soft drying process maintains the fully hydrated silanol surface.[11]

Solvent. Carbon tetrachloride was dried over CaH$_2$, distilled under N$_2$, and maintained over molecular sieves. The polystyrene solutions were kept at the selected temperature for 5 days before use in adsorption experiments to reach conformational equilibrium.

Procedures. Adsorption Isotherms. Silica beads were suspended in the solvent and degassed under reduced pressure to generate the true solid–liquid interface. The required mass of polymer solution was then added to the suspension. Great care was taken to isolate the suspension from atmospheric moisture. Mild controlled agitation was used to renew the sediment/supernatant interface. The amount of adsorbed polymer was determined by counting the radioactivity of the supernatant solution. This was done at different time intervals, and the actual adsorption was calculated when no systematic variation could be detected over 3 days.

Adsorption Rate Determination. Glass beads (1 g) and approximately 20 mL of carbon tetrachloride were introduced into

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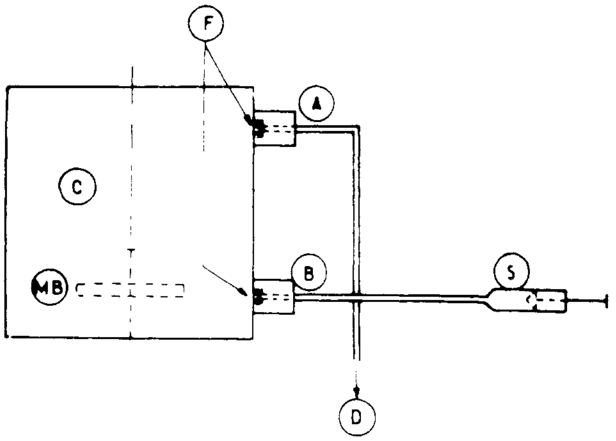

Figure 1. Diagrammatic representation of the cell (C) used in adsorption experiments: (A) outlet and (B) inlet for polymer solutions, (F) Millipore Teflon filter, (MB) magnetic bar, (S) automatically driven syringe, (D) to sample collector.

the cell reactor ($V = 50$ mL; Figure 1), and the suspension was degassed. The cell was then filled with the solvent. A constant homogenization of suspension was achieved by stirring with a magnetic bar. At time zero, the labeled polymer solution at concentration C_0 (cpm/mL) was injected at constant rate J_v (mL/min) into the reactor at inlet B, with use of a regularly driven calibrated glass syringe (Tacussel). Simultaneously, the solution flowed through the outlet A after filtration through a Millipore Teflon filter (F) to retain the glass beads inside the cell reactor. This effluent was collected for a time Δt (minutes), and the successive samples n were analyzed for radioactivity with a liquid scintillator spectrophotometer (Roche Kontron). A detailed analysis of the procedure is given in ref 12. The increase in adsorption ΔA_s for an increment of time Δt was obtained with the following relationship:

$$[\Delta A_s]_{n+1} = J_v C_0 \Delta t - A_{n+1} - \frac{V}{2J_v\Delta t}\{A_{n+2} - A_n\} \qquad (1)$$

where A_n represents the total radioactivity of the nth sample. At time t = zero, $n = 0$.

The increase ΔN_s (mol/cm^2) is related to A_s through eq 2:

$$\Delta N_s = \Delta A_s/(S R_s M_w) \qquad (2)$$

where S, R_s, and M_w are respectively the specific area of the adsorbent, the specific radioactivity, and the mean molecular weight of the polymer.

The value n corresponding to the end of the adsorption process was obtained by comparing the experimental variation of A_n versus n with the variation calculated by use of the following relation:

$$A_n \equiv C_0 J_v \Delta t\left\{1 - \exp\left(\frac{J_v\Delta t}{V}[n_f - n]\right)\right\} + A_f \exp\left(\frac{J_v\Delta t}{V}[n_f - n]\right) \qquad (3)$$

A_f and n_f are the sample radioactivity and the sample number corresponding to the end of the adsorption. Relation 3 means that the exponential behavior of A_n, which exists in the case of no adsorption, is recovered when the adsorption has reached completion. In Figure 2, the experimental variation of A_n is represented as a function of n for several values of J_v, Δt, and C_0.

Viscosity Measurements. The viscosity of polystyrene in carbon tetrachloride was measured between 45 and −10 °C, with an automatic Ubbelohde viscosimeter surrounded with a glass thermostating jacket. The temperature was fixed with the aid of a commercial temperature bath (Haake).

Results

Adsorption as a Function of Polymer Concentration and Temperature. The adsorption isotherms of polystyrene on hydrated silica at 4, 25, and 35 °C are reported in Figure 3. As the concentration N of the polymer in the solution at adsorption equilibrium increases from 10^{-12} to 5×10^{-11} mol/mL, two well-separated values of the amount of adsorbed polymer are shown.

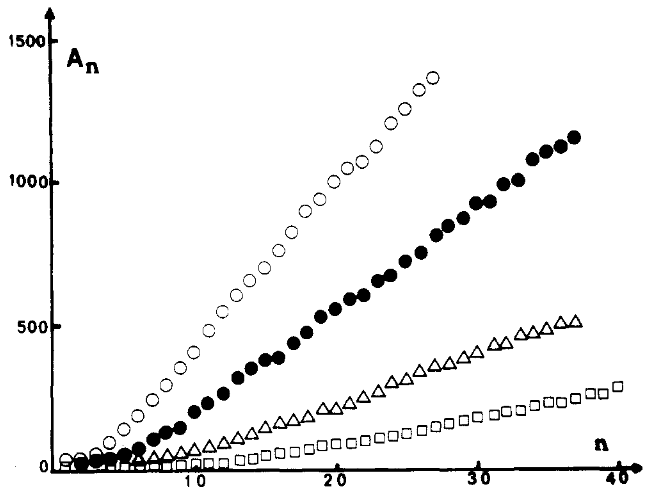

Figure 2. Radioactivity A_n (cpm) of effluent as a function of the sample number n for different experimental conditions referring respectively to the specific radioactivity of the injected polymer solution C_0 (cpm/mL)–the solution injection rate J_v (mL/min)–the period of the sample collection T (min): (○) 4500–0.15–6; (●) 8200–0.15–3.3; (△) 7100–0.06–6; (□) 4500–0.06–6.

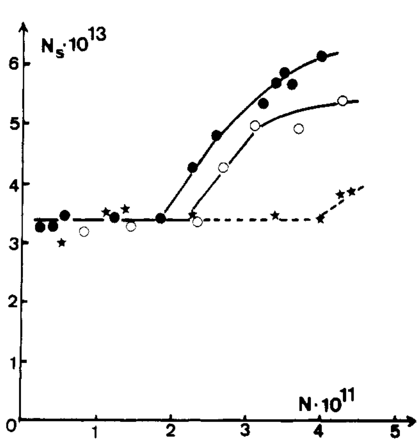

Figure 3. Adsorption isotherms at different temperatures. Representation of the surface coverage N_s (molecules/cm^2) as a function of the polymer concentration N (molecules/mL) in solution at adsorption equilibrium: (○) 4 °C, (●) 25 °C, (★) 35 °C.

Irrespective of the temperature, a first plateau region corresponding to $N_s = 3.4 \times 10^{-13}$ mol/cm^2 is observed. The persistency of the plateau at 35 °C up to $N \simeq 4 \times 10^{-11}$ mol/mL implies the existence of a very stable interfacial structure under good solvent conditions. At 25 °C, the first equilibrium structure is modified at $N = 1.7 \times 10^{-11}$ mol/mL, and the surface covering grows as the concentration N at adsorption equilibrium increases. Similarly, at 4 °C a second stable structure of the polymeric interface is also displayed. In Figure 4, the intrinsic viscosity of polystyrene in carbon tetrachloride is represented versus $1/T$. Between 45 and −10 °C, the mean radius of gyration of polystyrene in this marginal solvent is decreased by 20%. Below 5 °C and up to −10 °C, the mean conformation is not greatly modified, and the polymer may be regarded as a compact globe. Thus the temperature modifies on a large scale the energies of the forces that interact between the solvent and the chain segments and also between the segments and the chain itself. However, the adsorption in the first plateau region does not depend on this parameter.

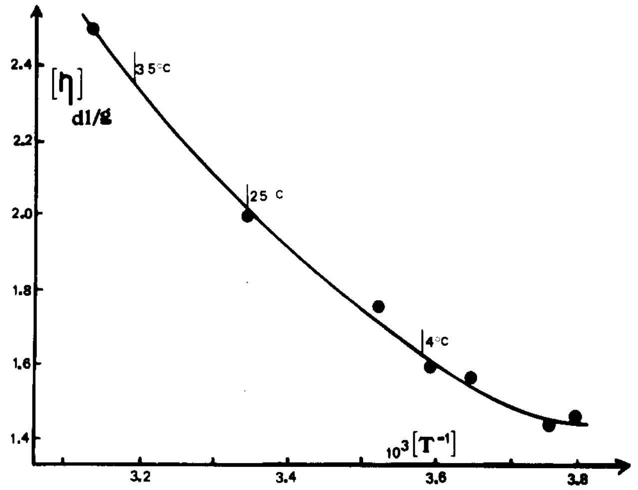

Figure 4. Intrinsic viscosity (η, dL/g) versus T^{-1} (K^{-1}).

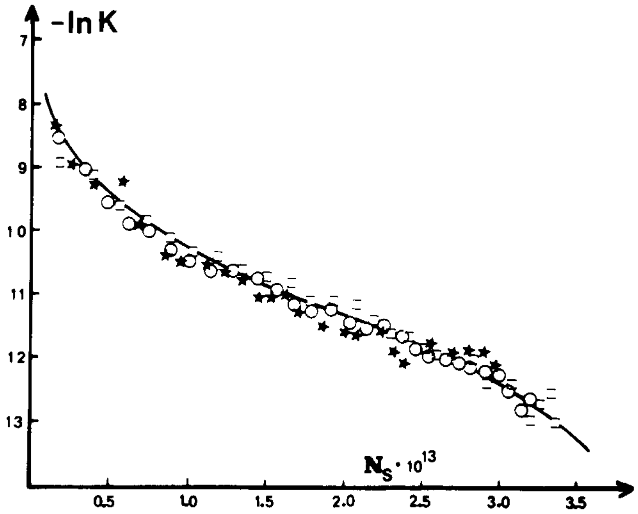

Figure 5. Adsorption rate at 4 °C. Representation of -ln K (K cm/s, being the kinetic coefficient in eq 5) as a function of the surface coverage N_s (molecules/cm^2). The different points correspond to different values of the polymer injection rate C_0J_v (cpm/min): (○) 320, (□) 800, (★) 1600. The full line corresponds to eq 14.

Kinetics of the Interfacial Layer Formation. Assuming the adsorption process corresponds to first-order kinetics

$$N \text{ (solution)} \rightarrow N_s \text{ (interface)} \tag{4}$$

(desorption is not considered at this stage), the elementary formulation of the kinetics of the adsorption is as follows:

$$\mathrm{d}N_s/\mathrm{d}t = N(t)\ K(N_s) \tag{5}$$

the coefficient $K(N_s)$ being more or less related to the coverage N_s. It was necessary to verify the validity of the commonly used relationship (eq 5) between $\mathrm{d}N_s/\mathrm{d}t$ and $N(t)$.[1,13] This was done with the representation (Figure 5) and 6) of the variation of ln $K(N_s)$ as a function of N_s. Each point corresponds to the $K(N_s)$ value calculated in the multiple situations, where the polymeric interface bearing the same number N_s of adsorbed molecules per square centimeter is brought into contact with solutions of different concentration $N(t)$. This is realized by using different values of J_vC_0 (cpm/min), which characterizes the kinetics of the polymer transfer into the reactor, where the macromolecules come into contact with the glass beads. At the two temperatures where the influence of $N(t)$ was studied, relationship 5 was found to be valid. Rather unexpected was the large decrease of $K(N_s)$, which represents the kinetic characteristic of the surface coverage up to the first plateau region.

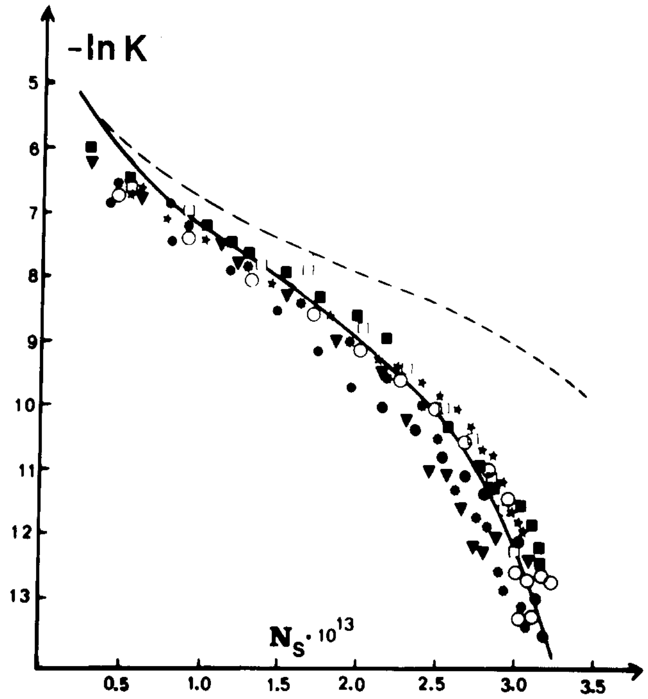

Figure 6. Adsorption rate at 25 °C. Representation of -ln K as a function of the surface coverage N_s (molecules/cm^2). The different points refer to different values of the polymer injection rate (cpm/min): (■) 260, (●) 430, (○) 600, (*) 750, (★) 1185, (▼) 1230, (□) 1250. Curves correspond to eq 14 (dashed line) and 18 (full line).

Model of the Lattice Adsorption. Polystyrene adsorption on silica in carbon tetrachloride is consecutive to the rupture of the SiOH-CCl_4 link and requires the formation of the SiOH-phenyl ring hydrogen bond.[7] If the adsorption of one polystyrene elementary segment can be compared to the adsorption of toluene, it is possible to evaluate the adsorption enthalpy. With use of the results of Basila[14] and Curthoys et al.,[15] the enthalpy of adsorption is found to be of the order of 1 kcal/mol, which largely exceeds the segmental loss of entropy. It follows that if the silica surface bears only SiOH groups, it may be possible that each elementary segment of the polymer is paired to a surface hydroxyl group and, as a result, that the adsorbed macromolecule lies flat on the solid surface. If this scheme is correct, up to formation of the first plateau, the density of the surface silanol groups must be equal to the density of the polymer constitutive units in the monolayer: 6.7×10^{14} styrene segments/cm^2. This value is close to the value of the density of the hydroxyl groups on fully hydrated silica: 7.9×10^{14} OH groups/cm^2.[11,16,17]

If we return to another monolayer model the regular packing of the polymer coils in one plane,[18] the following relation should be established if the coil dimensions of the polymer in solution are conserved during the adsorption process:

$$N_s^* = (N_v/M)^{2/3}\frac{1}{(N^0)^{1/3}} \tag{6}$$

$$N_v = 0.77/[\eta]_{\mathrm{mL/g}} \tag{7}$$

where N^0 is Avogadro's number. N_v represents the number of coils per milliliter in the three-dimensional packing.[19] N_s^* corresponds therefore to the two-dimensional close-packing. The following values of N_s^* were calculated at the different temperatures: 0.52×10^{-13} mol/cm^2 (35 °C),

0.57×10^{-13} mol/cm^2 (25 °C), and 0.66×10^{-13} mol/cm^2 (4 °C). This latter interfacial layer model, which actually gives different coverages at the different temperatures, is in fact far from the reality. The two-dimensional flat lattice model holds true in the first plateau region. Evidently at higher coverage, a distinct population appears, due to the formation of extended loops and/or tails.[20]

Rate-Controlling Process in the Lattice Adsorption. The large decrease of $K(N_s)$ as a function of N_s may result from the difficulty encountered by the polymer to find systematically an unoccupied –OH surface group and from the necessity to dispose of the expected number of sets of contiguous –OH sites to bind the unwound macromolecule to the surface. Using the relation of Arrhenius to express the kinetic coefficient $K(N_s)$ as a function of the adsorption energy $\Delta\mu$(ads), one obtains the following equation:

$$K = K_0 \exp(-\Delta\mu(\text{ads})/kT) \qquad (8)$$

One assumes that $\Delta\mu$(ads) is mainly determined by the variation of the chemical potential of the polymer resulting from the transfer of the macromolecules from the solution to the surface:

$$\Delta\mu(\text{ads}) = \mu(\text{surf}) - \mu(\text{soln}) \qquad (9)$$

where in each case, the chemical potential is split into the enthalpic h and the entropic Ts contributions.

The course we adopt is the following: (1) The adsorption enthalpy h(surf) – h(soln) results actually from the exchange in the interface of adsorbed molecules of solvent with polymer segments (train adsorption only) and from the exchange in the solution of polymer–solvent interactions for solvent–solvent interactions. This same scheme is encountered throughout the surface covering and the enthalpic balance is constant. (2) The entropy of the polymer in the solution s(soln) does not vary greatly in very dilute solution and may also be taken as constant.

To a first approximation, the term $\Delta\mu$(ads) in relation 9 is determined by the variation of Ts(surf.):

$$\Delta\mu(\text{ads}) \simeq \text{constant} - Ts(\text{surf}) \qquad (10)$$

The term s(surf) is evaluated as follows: the entropy S of the polymeric interface can be estimated from the general law $S = k \ln W$, where W represents the number of ways of putting the polymer at the N_0 sites of a plane lattice:[21]

$$W = \frac{N_0!}{(N_0 - xN_s)!N_s!}\left[\frac{z-1}{N_0}\right]^{N_s(x-1)} \qquad (11)$$

z is the lattice coordination number and x the mean degree of polymerization.

The entropy s(surf) of the isolated macromolecule in the situation $[N_0,N_s]$ is thus given by the relation:

$$s = \mathrm{d}S/\mathrm{d}N_s \qquad (12)$$

With the usual assumption of Flory, relation 8 may be expressed as follows:

$$K = K_0\left(\frac{z-1}{z}\right)\frac{1}{N_s}\{\nu_{N_s+1}\} \qquad (13)$$

$\{\nu_{N_s+1}\}$ represents the expected number of sets of x contiguous sites available to the $(N_s + 1)$th molecule, if N_s molecules are previously adsorbed at random. Relation 13 can be developed into

$$K = K_0\frac{N_0 - xN_s}{N_s} = K_0 x\frac{(N_0/x) - N_s}{N_s} \qquad (14)$$

The corresponding variation of ln K is represented in Figure 5 (solid line, K_0 is arbitrary). To a first approximation, this procedure proved satisfactory at low temperature. In this situation, the adsorption mechanism could be easily described if as suggested by relation 14 the sorbent surface is composed of N_0/x fictive adsorption sites. Henceforth, the N_s entities are anchored at random on the corresponding N_0/x equivalent adsorption sites. In this sense, the macromolecule may not unroll in all possible orientations in the adsorption plane but rather preserves a plane and circular configuration. In Figures 6 and 7, the variation of ln K (eq 14) is represented as a dashed line. The actual variation of ln K diverges gradually as N_s increases. At these higher temperatures, the polymer may unroll, but the rather slight deviation seems to indicate that the macromolecule conserves a privileged (or imposed) direction ($z = 2$).

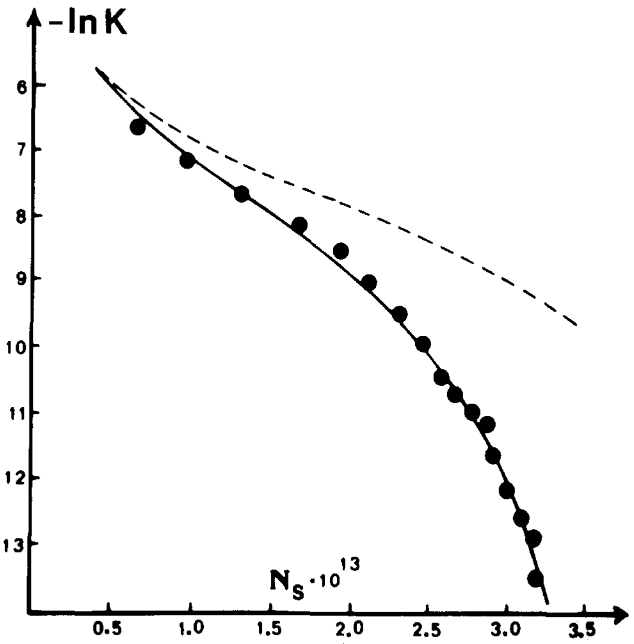

Figure 7. Adsorption rate at 35 °C. Representation of –ln K as a function of the surface coverage N_s (molecules/cm^2; C_0J_v = 320 cpm/min). Curves correspond to eq 14 (dashed line) and 18 (full line).

To approximate more exactly the term ν_{N_s+1} in eq 13, Flory proposed a better evaluation of f_i, which represents the "expectancy that a given cell adjacent to a previously vacant one is occupied":

$$\nu_{N_s+1} = (N_0 - xN_s)z(z-1)^{x-2}(1 - f_i)^{x-1} \qquad (15)$$

where

$$1 - f_i = \frac{N_0 - xN_s}{N_0 - 2(x-1)N_s/z} \qquad (16)$$

If as expected f_i remains of low value for the full coverage, one obtains relation 17, where f_i is of the order of 1.7×10^{-3} at maximum coverage:

$$f_i \simeq \frac{N_s}{N_0 - xN_s} \qquad (17)$$

Relation 14 is therefore modified into

$$K = K_0\frac{N_0 - xN_s}{N_s}\left(1 - \frac{N_s}{N_0 - xN_s}\right)^{x-1} \qquad (18)$$

Silberberg gives the relationship for the entropy in this case, taking into account all contacts of the polymer with its neighbors in its environment.[22] The corresponding variation of ln K with N_s is shown in Figures 6 and 7 (solid line) with K_0 arbitrary. Taking into account the inherent limitations in the development of the lattice model, this approach gives a simple representation of the kinetic behavior of the adsorption process. The scheme of one-dimensional lattice adsorption may be attributed to the ultimate structure of the polymeric glass.[23] This structure may impose some constraints on the polystyrene in the course of the adsorption. In fact, the pure silica model refers to tetrahedra which form complex polymeric structures more or less linearly.[11] The microstructure of glasses is actually of greater complexity. Following this reasoning, it is difficult to establish the real mechanism of this flat layering which is modeled by the one-dimensional lattice adsorption.

Discussion

Structure of the Polymeric Interface. The hydration of the sorbent may change drastically the polymer/surface interaction or influence the interfacial structure of the adsorbed polymer. Two examples are presented to introduce the discussion.

Griot and Kitchener demonstrated the influence of silica hydration on polymer adsorption if hydrogen bonding is responsible for the polymer–surface linking.[24] Polyacrylamide does not adsorb on hydrated silica. Polyacrylamide–silica interactions are effective only on fused or grafted silica where free hydroxyl groups emerge from the surface.[25]

With IR spectroscopy measurements, Joppien observed structural changes of a polyester adsorbed layer on an alumina/carbon tetrachloride interface that accompanied the adsorption of water.[26] The hydration of the dry Al_2O_3 surface promotes the formation of train adsorption: the fraction of chain segments in direct contact with the sorbent varies from 0.4 (value in dry CCl_4) to 0.8 in the hydrated form within 15 min. Joppien showed that the structural modification of the layer develops into a very flattened conformation with time. This experiment illustrates the influence of the chemical nature of the sorbent surface on the layer structure.

In fact, the absence of polyacrylamide/silica interactions[18] demonstrates the electrochemical homogeneity of our sorbent, which bears neither siloxane links nor isolated silanol groups. This chemical pecularity of the sorbent and the chosen domain of very low concentrations make possible the formation of a flat polymeric layer. On the other hand, the energy of the polymer–surface interaction also plays an important role. Barnett et al. observed train adsorption at intermediate coverage of poly(vinylpyridine)–silica interfaces.[27] In our case, the flat monolayer is characterized by its stability if the solution concentration is increased, especially under good solvent conditions where contact between adsorbed polymers and nonadsorbed polymers are less probable. Collisions between adsorbed polymers and solution polymers become more efficient at lower temperature. As the concentration is increased, these collisions may induce partial interfacial exchange[28] between surface segments and solute segments, which favors the formation of loops and/or tails. The layer corresponding to the second plateau region of the isotherm (Figure 3) contains about 40% of chain segments in the diffuse zone. This over-adsorption phase is very slow and was never observed under the experimental conditions (J_v, C_0) used to measure the initial adsorption rate.

Rate of Surface Coverage. Temperature Effect. The diffusional mass transfer through the Nernst layer from the stirred solution (at homogeneous concentration $N(t)$) to the solid surface (at local concentration $N_D(t)$) is not the rate-controlling process for establishment of the adsorbed layer. In fact, in the case of a diffusion-controlled mechanism,[29] relation 5 would be modified to

$$\mathrm{d}N_s/\mathrm{d}t = N_D(t)\ K(N_s) \qquad (19)$$

with $N_D(t) < N(t)$. $N_D(t)$ depends on the actual concentration $N(t)$ and on the concentration gradient that develops within the interfacial unstirred zone. The existence of a unique curve representative of the variation of $K(N_s)$ with N_s indicates that the degree of coverage N_s is the pertinent parameter that governs the adsorption rate, by varying the adsorption entropy.

It is interesting to note that under good solvent conditions (35 and 25 °C) the variation of $K(N_s)$ as function of N_s is weakly influenced by temperature. On the contrary, at 4 °C $K(N_s)$ is markedly decreased. Heatley and Wood studied the molecular motion of polystyrene in different solvents as a function of temperature.[30] These authors concluded that the viscosity of the solvent has a strong influence on the segmental motion of polystyrene. In carbon tetrachloride, it varies little above 25 °C but is decreased by half at 4 °C. The slowness of the adsorption process at 4 °C results thus partly from the restricted chain motion. This shows that the molecular rearrangement in the interfacial zone prior to flat adsorption also constitutes an important stage in the kinetics of the polymer adsorption. This step exerts a constant influence throughout the process of surface covering.

Polydispersity Effects. If one assumes the adsorption favors the fixation of polymers of high molecular weight to the detriment of polymers of lower molecular weight,[6] the molecular weight distribution of the polymer remaining in solution will depend on the concentration $N(t)$. As for the various $N(t)$ values, if no such influence on the variation of $K(N_s)$ with N_s is observed (within experimental error), one may conclude that selective adsorption is unlikely in the formation of the flat layer (train adsorption).

Conclusion

The establishment of a flat polymeric layer by the adsorption process requires the existence of a well-defined situation that allies a large adsorption enthalpy and a solvent having homogeneous surface characteristics. In fact, when the hydroxyl groups are sparsely dispersed on the sorbent (as for fused silica or metal surfaces), only isolated links may be established, and it is suggested that loops and tails are formed immediately.

The kinetics of the formation of flat layers is hardly lowered during the adsorption process. The formulation of the kinetic parameter $K(N_s)$ gives an idea of the two mechanisms that slow down the adsorption: (1) ν_{N_s+1} determines the number of x connected sites that are available for polymer fixation. In our case, this variation parallels more or less the variation of the number of free sites that may anchor the polymer; (2) N_s^{-1} determines the probability that solution polymer will encounter a hydroxyl group as yet unencumbered by a polystyrene phenyl ring. N_s^{-1} also takes into account the time wasted when a solution polymer runs against a patch of the adsorbent surface already covered with polymer and is repelled.

The development of the diffuse layer at higher polymer concentrations may be promoted by the exchange of macromolecules between the sorbent and the bathing solution, which becomes efficient at higher concentrations. Since the early stages corresponds to train adsorption, if this dense layer tends to be glassy, it will be very difficult for a newly arriving polymer to reach the adequate number of binding sites on the surface.

This means that part of an adsorbed macromolecule will leave the solid surface to form a tail and that at the same time part of another polymer (leaving the solution) will occupy the freed hydroxyl. This exchange mechanism, which gives rise to over-adsorption if the exchange rate is low, will be of interest in the future.

Registry No. Polystyrene, 9003-53-6.

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Polyureas Containing Diaza Crown Ether Units: Synthesis and Influence of Ring Size on the Glass Transitions and Secondary Relaxation Processes

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ABSTRACT: A series of polyureas have been prepared by linking together diaza crown ether units of sizes 12, 18, and 24 atoms by using diisocyanates of differing rigidity. Measurement of the glass transition temperature, T_g, showed that as the ring size increased from 12 to 24 atoms, T_g decreased in polymers with a common linking unit. When the ring size was held constant, T_g varied with the flexibility of the spacing unit. Several secondary relaxations were located. It was possible to identify intramolecular relaxation processes in the diaza crown ring that occurred at decreasing temperatures as the ring size increased in the order 200 K (12-crown) > 152 K (18-crown) > 148 K (24-crown) when methylenedi-*p*-phenylene diisocyanate was the linking unit. Tentative assignments for other relaxation processes were also made that involved rotation of the amide unit.

Introduction

Studies of the dynamic mechanical behavior of polymers containing large ring units, in excess of six atoms, have largely been confined to structures in which the ring is pendant to the main chain. Intramolecular relaxations in cycloalkyl rings attached to polyitaconate[1,2] and polymethacrylate[3] backbones have been studied in some detail from investigations of the glassy state in these systems. We have recently reported[4] the effect of incorporating cycloalkyl rings with sizes from 8 to 22 carbon atoms into linear polyurethane structures and have now extended this to aza crown ether rings, which might be expected to be inherently more flexible. In this paper an examination of the dynamic mechanical response of polyureas, containing in the main chain 12-, 18-, and 24-membered aza crown ether structures, is presented.

Experimental Section

Diaza crown ethers were synthesised by using a high-dilution technique and following the general procedures described by Lehn.[5] The major steps are outlined for the 12- and 24-membered rings, which had to be prepared, whereas the diaza-18-crown-6 ether (kryptofix 2,2) was available commerically and purchased from Merck.

Synthesis of 5,9-Dioxo-1,7-dioxa-4,10-diazacyclododecane. A solution of 3.24 g of 1,5-diamino-3-oxapentane in 32 cm^3 of anhydrous benzene and a solution of 2.68 g of diglycolic acid dichloride in 32 cm^3 of anhydrous benzene were added to 500 cm^3 of benzene over a 50-min period, under a nitrogen atmosphere, with vigorous stirring. After the residue was filtered and washed, the solutions were evaporated to dryness, leaving a solid that was recrystallized from a hot mixture of chloroform and heptane to give the required product: mp 172 °C; ^{1}H NMR (CDCl$_3$) 3.6 (m), 4.5 (s), and 7.65 (br) ppm.

Synthesis of 1,7-Dioxa-4,10-diazacyclododecane. A suspension of 5,9-dioxo-1,7-dioxa-4,10-diazacyclododecane (0.6 g) in hot anhydrous tetrahydrofuran (20 cm^3) was added to LiAlH$_4$ (0.6 g) in THF (15 cm^3) over a period of 1 h. The mixture was refluxed with stirring under nitrogen for 18 h and then cooled to room temperature. Excess LiAlH$_4$ was removed by adding a water/THF mixture (50/50) followed by sodium hydroxide and more water. The mixture was then filtered, and the solvent evaporated to leave a residue that was passed through a neutral column with benzene as eluant. Recrystallization from benzene gave the desired product: mp 83–84 °C; ^{1}H NMR (CDCl$_3$) 2.4 (s), 2.8 (t), and 3.66 (t) ppm; trivial name diaza-12-crown-4 ether.

Synthesis of 1,7,10,13,19,22-Hexaoxa-4,16-diazacyclotetracosane. A high-dilution technique was used to prepare first the precursor 5,15-dioxo-1,7,10,13,19,22-hexaoxa-4,16-diazacyclotetracosane. Benzene solutions of 1,11-diamino-3,6,9-trioxaundecane (8 g/300 cm^3) and tetraglycolyl chloride (5.4 g/300 cm^3) were added, with vigorous stirring, over a period of 20 h to anhydrous benzene (800 cm^3) under a nitrogen atmosphere. A viscous oil was isolated from this reaction, and this was reduced

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