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Molecular Weight Effects in the Relaxation of Orientation of Polystyrene Chains As Revealed by Infrared Dichroism

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ABSTRACT: The relaxation of orientation of narrow distribution polystyrenes of different molecular weights is studied over 4 decades of time by infrared dichroism and compared to the predictions of the Doi–Edwards and related models. The behavior at short times appears to be independent of the molecular weight, whereas molecular weight effects at longer time are observed, as predicted by the theory. A careful comparison between theory and experiment shows that the kinetics of the relaxation at short times are slower than predicted by the model. The experimental behavior at longer times is in good agreement, especially for the highest molecular weights, with the predictions of a self-consistent treatment including a process of equilibration across slip-links.

Introduction

The viscoelastic properties of polymer melts have been widely investigated from experimental and theoretical points of view. The presence of molecular relaxation motions, especially in the case of deformed polymers, plays an important role in many processing methods such as fiber spinning, film blowing, and thermoforming. Practically, the state of orientation of the macromolecular chains allows the control of mechanical properties in the final product. It is therefore necessary to know, as precisely as possible, how the orientation is influenced by macroscopic parameters such as deformation ratio, temperature, and strain rate and by molecular quantities like length and structure of the chains. Besides an experimental approach, theoretical work has been recently developed from a molecular point of view via the reptation concept introduced by de Gennes[1] and its application to highly deformed amorphous polymers by Doi and Edwards.[2,3]

This model describes the relaxation of a deformed and highly entangled polymeric medium through three different processes which are well separated in time.

The first relaxation motion (A) is a Rouse motion of a part of chain between two entanglements, considered here as fixed points, and is characterized by a relaxation time τ_A, which is independent of the molecular weight of the

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chain. This relaxation time is very short for temperatures corresponding to the terminal flow region but can be on the order of seconds closer to the glass transition temperature.

The second relaxation stage (B) is a retraction of the deformed chain inside its deformed tube to recover its equilibrium curvilinear length. This process only appears for large deformations. The relaxation time τ_B scales as the square of the molecular weight.

The third relaxation motion (C) corresponds to the reptation of the chain in order to disengage from its deformed tube and attain an equilibrium isotropic conformation. The associated relaxation time varies with the third power of the molecular weight.

During the last few years, new processes have been introduced to improve this model.

Viovy[4] has remarked that the curvilinear monomer density is constant between two entanglement points at the end of the A process but not necessarily equal on each side of an entanglement. The mathematical treatment of stage B assumes it to be constant along the chain at the beginning of the B process. It has therefore been proposed to account for this discrepancy by introducing a mechanism of diffusion of monomers through entanglements in order to equilibrate the forces acting on each side. This process will be referred to hereafter as the A′ process. Although the mathematical approach is different, the same physical ideal has been suggested by Lin.[5]

On the time scale of τ_B, retraction may also be coupled with another process: chain length fluctuation as first introduced by Doi.[6] The coupling of these two processes in the case of deformed polymers has been also treated by Viovy.[7] It has been shown that length fluctuations are able to screen retraction in practical situations.

The original Doi–Edwards model (DE) can also be improved by introducing the concepts of tube relaxation[8] and of constraint release[9] or tube renewal[10] that arise from a self-consistent treatment of the relaxation of all the chains. During the B process, retraction of the surrounding chains leads to the disappearance of topological constraints acting on a chain. Thus, a chain can be partially relaxed by the motion of its surroundings rather than its own equilibration motion. This concept has been called tube relaxation.

A self-consistent treatment of reptation requires the concepts of tube renewal or constraint release. The idea of tube renewal was first proposed by Daoud and de Gennes.[10] A detailed discussion of constraint release has been made by Graessley[9] and an equivalent treatment has been provided by Viovy.[11]

Thus, many ways to modify the original DE model exist and it is useful to see which processes can be experimentally observed. This can be achieved through an accurate comparison between experimental behavior and theoretical predictions.

The behavior of the stress in deformed polymers has already been studied[12] and compared with the basic version of the DE model.[13] A similar comparison which includes recent improvements of this theory will be reported soon.[14]

This paper deals with the relaxation of chain orientation in uniaxially stretched polystyrenes of different molecular weights as studied by infrared dichroism over a large time domain. Attention will be given to molecular weight effects and to the comparison between experimental observations and theoretical predictions of the Doi–Edwards and related models.

Experimental Section

Preparation of the Samples. Two anionically polymerized polystyrenes of molecular weights around 100 000 and 900 000 g/mol were used in this study, together with three hydrogenated and deuteriated block polystyrenes having intermediate molecular weights. Some experiments have also been carried out with a polydisperse polystyrene. Appelation and number- and weight-average molecular weights are given in Table I. In the block copolymers, the deuteriated part represents ca. 15% of the chain. The purely monodisperse hydrogenated polymers were supplied by E.A.H.P. (Strasbourg, France) and the isotopically labeled block polystyrenes were provided by L. J. Fetters (Exxon Co., Annandale, NJ). The polydisperse sample was obtained from CdF Chimie.

Table I

name	M_n	M_w	M_w/M_n
Hydrogenated Polystyrene Samples			
PS 100	105 500	117 200	1.11
PS 900	891 000	999 000	1.12
PSP	150 000	254 000	1.7
Isotopically Labeled Block Polystyrenes[a]			
PS 180	175 000	184 000	1.05
PS 180	179 000	188 000	1.05
PS 500	465 000	502 000	1.08

[a] The block copolymers having M_w = 184 000 and M_w = 188 000 show the same behavior for the average orientation and have therefore been considered together here as PS 180.

Clearly, the study of the orientation of D and H sequences in block copolymers yields richer information than the average orientation that will be considered here. Preliminary results have been already published,[15] and a more detailed discussion of block relaxation will be presented in a subsequent paper.

The polystyrene films (50 μm thick) were obtained by casting a distilled benzene solution of each polymer on a glass plate, followed by drying at room temperature. Strips 2 cm in width were annealed under vacuum for 48 h at 140 °C in order to remove any trace of solvent and internal stress. The films' support during the drying treatment was chosen to provide an irregular surface for the films in order to avoid interference fringes during the recording of the FTIR spectra.

Stretching Conditions. Stretching experiments were performed on a hydraulic apparatus designed in our laboratory.[16] Elongations were made at constant strain rate and at temperatures above the glass transition temperature (T_g = 105 °C measured by DSC at a heating rate of 10 °C/min). The draw ratio was limited to λ = 4 (λ being the ratio of the final over the initial length) to avoid breaking of the samples. For the same reasons the temperature domain was limited to a range of 110 to 135 °C, the strain rate being in the range 8×10^{-3} to 0.1 s^{-1}. After they were stretched, the samples were rapidly quenched to room temperature in order to freeze the state of orientation of the polymer chains.

Infrared Dichroism. The infrared spectra were obtained on a Nicolet 7199 Fourier transform infrared spectrometer at a resolution of 2 cm^{-1} with a total of 32 scans. The polarization of the infrared beam was obtained by use of a SPECAC gold wire grid polarizer, and the samples rather than the polarizer were rotated 90° in order to obtain the two polarization measurements. Dichroic ratios were calculated as $R = A_\parallel/A_\perp$ (where $A_\parallel$ and $A_\perp$ are the measured absorbances parallel and perpendicular to the stretching direction, respectively).

For a given absorption band, the dichroic ratio R allows one to calculate the second moment of the orientation function $\langle P_2(\cos\theta)\rangle$ in which θ is the angle between the chain axis and the stretching direction. The following relation is used:

$$\langle P_2(\cos\theta)\rangle = \frac{R_0 + 2}{R_0 - 1}\,\frac{R - 1}{R + 2} \qquad (1)$$

in which $R_0 = 2\cot^2\alpha$ where α is the angle between the dipole moment associated with the considered vibration and the chain axis.

For normal polystyrene, the 906-cm^{-1} and the 1028-cm^{-1} absorption bands were used. In the case of H sequences in copolymers the 906-cm^{-1} band does not overlap with any absorptions of the deuteriated species and is therefore convenient for orientation studies. Orientation of the D sequences has been deter-

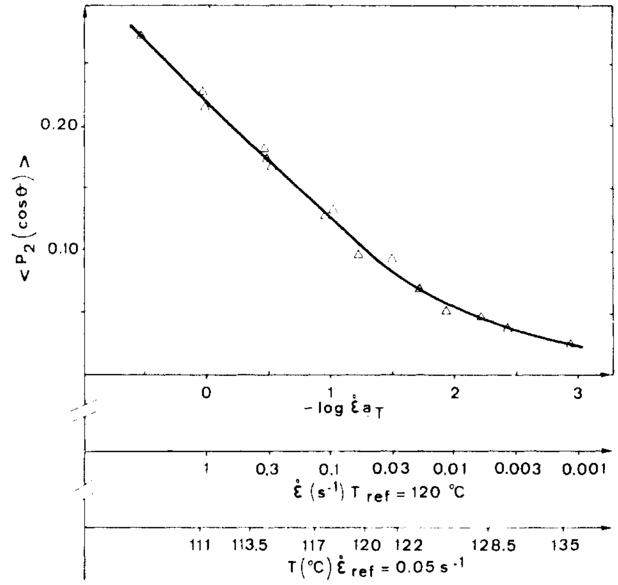

Figure 1. Master curve of the relaxation of orientation for the PSP polymer at a reference temperature of 120 °C. The two axes below represent respectively the strain rate domain at a reference temperature of 120 °C and the temperature domain at an intermediate reference strain rate of 0.05 s^{-1}.

mined with the 2195- and 2273-cm^{-1} absorption bands corresponding to an asymmetric stretching vibration of CD_2 groups and stretching vibrations of the aromatic CD groups, respectively. Because of the low concentration of deuteriated units in the sample (15 wt %), the intensity of the 2100-cm^{-1} band, assigned to the CD_2 symmetric stretching vibration, was too weak to yield reliable results. The orientation function of the deuteriated blocks has been calculated by using the following relationships:

$$\langle P_2(\cos\theta)\rangle = A((R-1)/(R+2))_{2195\text{cm}^{-1}}$$

$$\langle P_2(\cos\theta)\rangle = B((R-1)/(R+2))_{2273\text{cm}^{-1}}$$

with $A = -3.8$ and $B = -2.7$.

The coefficients A and B have been determined previously[15] from the study of a blend containing 15 wt % of deuteriated polystyrene chains mixed with hydrogenated chains of roughly the same molecular weight.

For the copolymers, the orientation of the whole chain has been calculated as the weight-average orientation of each block.

Results

Influence of Temperature and Strain Rate. As in the work of Lefebvre et al.,[17] the orientation function was found to increase linearly with draw ratio at all of the temperatures and strain rates studied. In the same way, a decrease of orientation, at a given draw ratio, was observed when either the stretching temperature was raised or the strain rate was lowered. This behavior reflects the existence of relaxation phenomena at a molecular scale, as has already been mentioned. Moreover, the influence of temperature and strain rate obeys the time–temperature superposition principle. The orientation, measured at a given draw ratio, for a strain rate $\dot{\epsilon}_1$ and a temperature T_1 is identical, within experimental uncertainty, with that obtained at a temperature T_2 and a strain rate $\dot{\epsilon}_2$ such that $\dot{\epsilon}_2 = \dot{\epsilon}_1/a_{T_2/T_1}$ where a_{T_2/T_1} is the shift factor between temperatures T_2 and T_1. It is given by the WLF equation

$$\log a_{T_2/T_1} = \frac{-A(T_2 - T_1)}{B + (T_2 - T_1)} \tag{2}$$

The coefficients obtained by Plazeck[18] have been used here since the accuracy of orientation measurements is too low and the data not numerous enough to determine the coefficients of the WLF equation corresponding to our polymers.

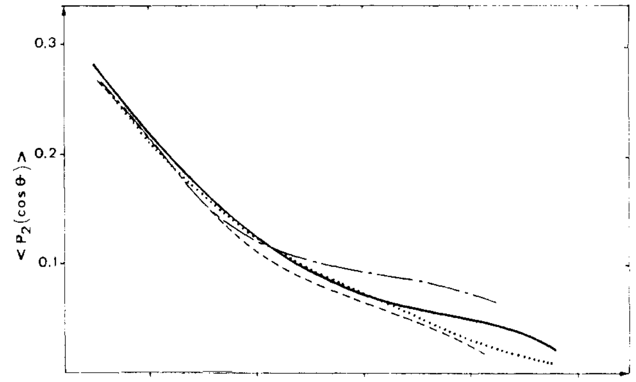

Figure 2. Master curve of the relaxation of orientation for the narrow distribution polystyrenes at a reference temperature of 120 °C: (---) PS 100; (···) PS 180; (—) PS 500; (-·-) PS 900.

This is illustrated in Figure 1, where the orientation measured at $\lambda = 4$, for the polydisperse sample and for different pairs ($\dot{\epsilon}$, T) is plotted versus the parameter $-\log \dot{\epsilon} a_T$ by using eq 2 with $A = 9.06$, $B = 69.8$, and a reference temperature T_1 of 120 °C. In such a representation, the short times appear on the left part of the plot.

The data obtained under different conditions of temperature and strain rate superimpose rather well on a single master curve for the relaxation of orientation. This result means that the time–temperature superposition principle, usually verified in the linear domain, also applies in the field of large deformations as has been noted for the stress.[19]

Influence of the Molecular Weight. The master curves for all the molecular weights investigated are given in Figure 2, for a reference temperature of 120 °C. As usual, the same shift factors have been used for all the polymers. This plot emphasizes two important points:

(i) In the short time domain, the orientation is independent of the molecular weight. The splitting between the different curves gives an estimate of the experimental uncertainty.

(ii) At longer times, the orientation increases with the length of the chains.

These experiments appear sensitive to at least two different relaxation processes on the investigated time scale. At short times, the characteristic relaxation time seems independent of the molecular weight, whereas at long times the relaxation time increases with the molecular weight. This behavior is in qualitative agreement with the predictions of the DE model. On the basis of molecular weight effects, the short-time behavior can be associated with the local relaxation process (A). At longer times, retraction and perhaps reptative motion can be evoked. Nevertheless, since the initial length of the sample can be recovered with an annealing treatment above T_g, the participation of reptation during the deformation is probably minimal. It is now interesting to go further and to try a quantitative comparison with the model.

Theoretical Calculation of Orientation

The second moment of the orientation distribution function $\langle P_2(\cos\theta)\rangle$, which can be measured by infrared dichroism or birefringence, can be derived from the theoretical distribution of the orientation of the chain segments. Such a distribution function has been calculated by Doi–Edwards (ref 2, eq 3.10) and Curtiss–Bird (ref 20, eq 6.18) for purely reptative motion of a deformed chain.

This expression has been used to calculate the evolution of $\langle P_2(\cos\theta)\rangle$ for a reptating chain.[21]

As previously mentioned, we believe that reptation is not the main process which occurs at these experimental conditions but that shorter time motions must be taken into account. We therefore return to the idea of a slip-link network model for the system as proposed by Doi and Edwards. The time evolution of $\langle P_2(\cos\theta)\rangle$ is related to the evolution of the quantities $a(t)$ (the average distance between slip-links) and $n(t)$ (the average number of segments between slip-links) by the proportionality[8,22]

$$P_2(t) = \frac{\overline{a^2(t)}}{\overline{n^2(t)}} \qquad (3)$$

At the end of stage A, the slip-link network is temporarily at equilibrium and the classical expression, derived from the rubber elasticity theory, should apply.[23] Therefore, eq 3 becomes

$$P_2(\tau_A < t < \tau_B) = P_2^{\text{network}} = \frac{1}{5n_K}(\lambda^2 - \lambda^{-1}) \qquad (4)$$

where n_K is the average number of statistical Kuhn segments between slip-links.

The various expressions for the relaxation of orientation during the different processes of the DE model are given in the appendix. In the following section, we discuss their influence on the orientation.

Effects of the Various Improvements of the DE Model. In order to observe the practical consequences of these different treatments, we have computed the relaxation of orientation in three cases: free chain in a network; self-consistent treatment of the relaxation; self-consistent treatment including the diffusion of monomers through entanglements.

A chain containing 20 entanglements has been considered at three extension ratios (λ = 1.5, 2.5, 4). Calculations of P_2 from eq 14, 15, and 18 requires a numerical value of n_K (the number of Rouse subchains between entanglements). In order to avoid such a choice at this stage, the results are presented in terms of the product ($P_2^{\text{theo}}n_K$) in Figure 3. The orientation appears to be independent of the chosen model at short times. At longer times the orientation predicted by the free chain in a network model is higher than predicted by the self-consistent treatment, and still higher than predicted by the other more complete model.

The equilibration of the curvilinear monomer density achieved by the diffusion through entanglements yields a smoother decrease of the orientation between τ_A and τ_B than the other models. The acceleration of the relaxation due to the motion of the surrounding chains appears beyond τ_B. The nonlinear character of the retraction motion can be discerned by comparing the three extension ratios.

The curves of Figure 3 show that the differences between the models are rather small. When the experimental precision and the proportionality factor between calculated and measured orientation are considered, the resulting experimental error bars reported on the plots show that the splitting between the models is less than the experimental uncertainty for extension ratios of 1.5 and 2.5. At λ = 4, one can expect to see the influence of the diffusion of monomers through entanglements but not the effects of the self-consistent treatment.

Comparison between Theory and Experiment

These experiments deal with constant strain rate extensions whereas theoretical predictions have been made in the case of step strains. A method to derive a constitutive equation for the response to a step deformation has been proposed,[12] and applied to stress–strain curves.[13] It could be extended to calculate the growth of orientation in a constant strain rate extension. However, since the precision of the orientation measurements is much less than that of the stress, the use of a constitutive equation has been avoided. It is interesting to compare the relaxation after a step deformation of amplitude λ with the relaxation of orientation measured at the same draw ratio λ obtained by varing either the strain rate or the relaxation time (practically the temperature). The time scales in these two types of experiment can be related by choosing $t = \dot\varepsilon^{-1}$. We have plotted in Figure 4 the orientation calculated at λ = 4 versus $-\log \dot\varepsilon\tau_A$ in a continuous extension and the relaxation of orientation after an extension of λ = 4 versus $\log t/\tau_A$. The curves appear to be similar and the orientations, for a given t/τ_A or $(\dot\varepsilon\tau_A)^{-1}$ are rather close; the differences are less than the experimental accuracy. One can still notice that the constant strain rate deformation is sensitive to relaxation processes at earlier stages than the step deformation. Hereafter, the experimental

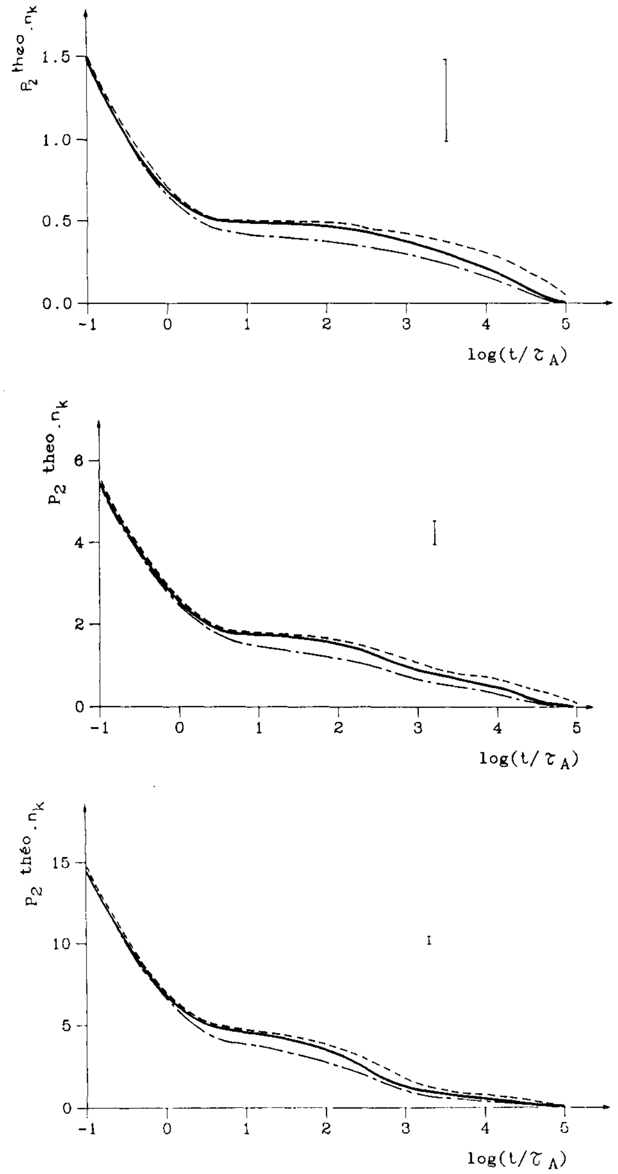

Figure 3. Comparison of the relaxation of orientation for the different models for a chain containing 20 entanglements: (- - -) free chain in a network; (—) self-consistent treatment; (–·–) self-consistent treatment including A′ process for λ = 1.5 (top), λ = 2.5 (middle), and λ = 4 (bottom). The error bar represents the experimental uncertainty in P_2 measurements.

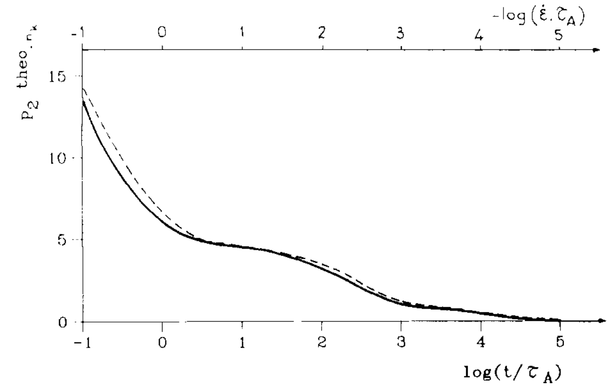

Figure 4. Comparison between the relaxation of orientation following a step deformation of amplitude $\lambda = 4$ plotted as a function of t/τ_A (- - -) and the orientation at $\lambda = 4$ in a constant strain rate experiment plotted as a function of $(\dot{\epsilon}\tau_A)^{-1}$ (—) for a chain containing 20 entanglements.

relaxation of orientation measured at $\lambda = 4$ will be compared with the theoretical predictions calculated for a step deformation of amplitude $\lambda = 4$.

Influence of the Number of Subchains between Entanglements. Before going further into a comparison between theory and experiment, it is interesting to examine the influence of the number of Rouse subchains between entanglements on the relaxation of orientation at short times.

Indeed the distribution of the relaxation times in step A, $\tau_k = \tau_A/k^2$ for $1 \leqslant k \leqslant N_R$ as used in eq 7, is valid if $N_R \gg 1$. If a Gaussian subchain is assumed to contain around 50 monomer units, then the number of subchains between entanglements is on the order of 3 since the molecular weight between entanglements is around 18 000 for polystyrene. Therefore the relaxation times must be expressed as[24]

$$\tau_k = \tau_1 \sin^2 \frac{\pi}{2(N_R + 1)} \sin^{-2} \frac{k\pi}{2(N_R + 1)} \qquad (5)$$

where τ_1 is the longest one, related to τ_A in the limit $N_R \gg 1$ by

$$\frac{\tau_A}{\tau_1} = \frac{4{N_R}^2}{\pi^2} \sin^2 \frac{\pi}{2(N_R + 1)} \qquad (6)$$

The main effect of using the exact formulation instead of the approximation is an increase in the absolute value of the longest relaxation time with respect to τ_A. The prefactor of the scaling law between τ_A and τ_B is therefore modified: $\tau_B = N^2\tau_A$ for $N_R = 3$ and $\tau_B = 0.8N^2\tau_A$ for $N_R = 2$ instead of $\tau_B = 2N^2\tau_A$. This can be seen in Figure 5 where the orientation has been calculated for different values of N_R. Furthermore, as a result of eq 7, the maximum orientation that can be achieved at very short times decreases with the number of subchains.

Later in this paper, for the comparison with experimental results, the calculations will be done with 2 and 3 subchains between entanglements.

Comparison with Experiment. Two models have been considered here: the free chain in a network and a self-consistent treatment which includes the slippage of monomers through entanglements. Since the parameters τ_B and τ_C are related to τ_A by theoretical scaling laws, there is no adjustable parameter for a given chain length.

The theoretical relaxation of orientation for the two models and for chain lengths considered here is plotted in Figure 6. A great similarity with the experimental data can be seen. Regardless of which model is considered, theoretical and experimental curves show both a short time behavior that is independent of the molecular weight of the chain and molecular weight effects at long times. Quantitative comparison involves rescaling the two types of curves in both time and orientation.

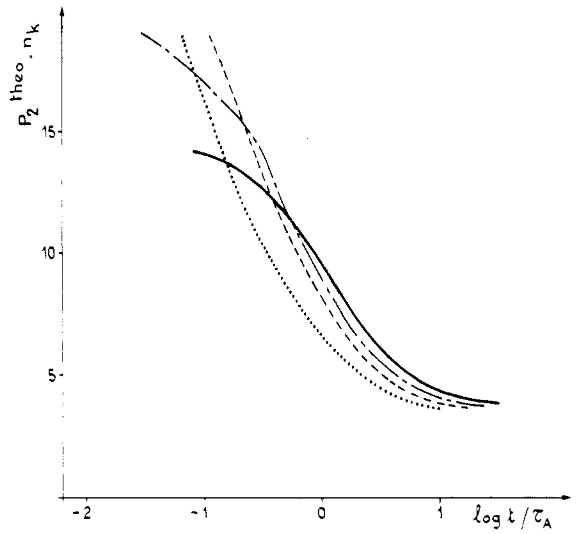

Figure 5. Influence of the number of Rouse subchains between entanglements on the relaxation of orientation at short times. Differences between τ_A and τ_1 for the different values of N_R have been taken into account: (···) limit $N_R \gg 1$; (—) $N_R = 2$; (-·-) $N_R = 3$; (- - -) $N_R = 4$.

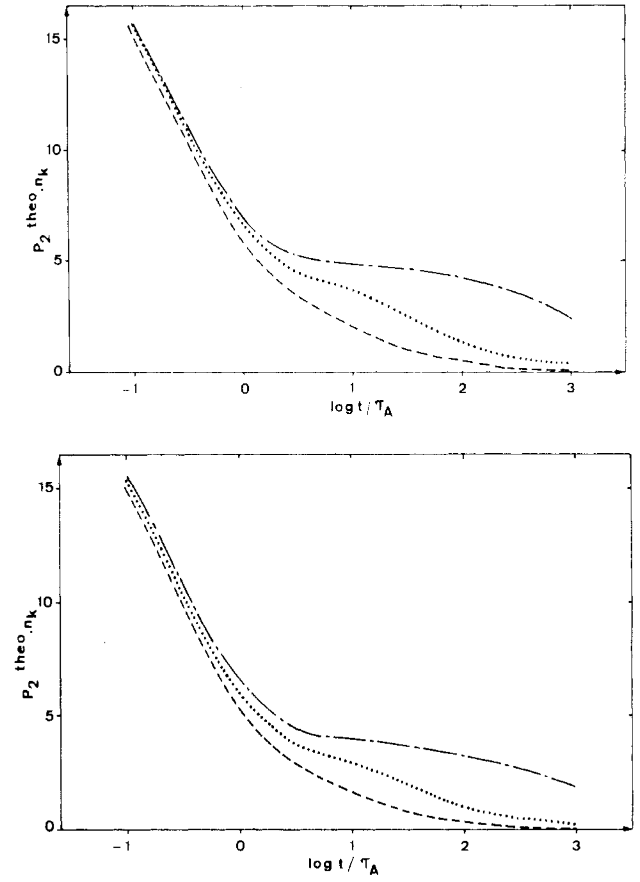

Figure 6. Theoretical relaxation of orientation for a free chain in a network model (top) and the self-consistent treatment including the A′ process (bottom) for a chain containing (- - -) 5 entanglements, (···) 10 entanglements, and (-·-) 50 entanglements.

The theoretical curves show a significant change in slope for times around log $t/\tau_A = 0.25$, especially for the longest chains. This is due to the end of the A process, where the orientation is on the order of 5 theoretical P_2n_K units. For

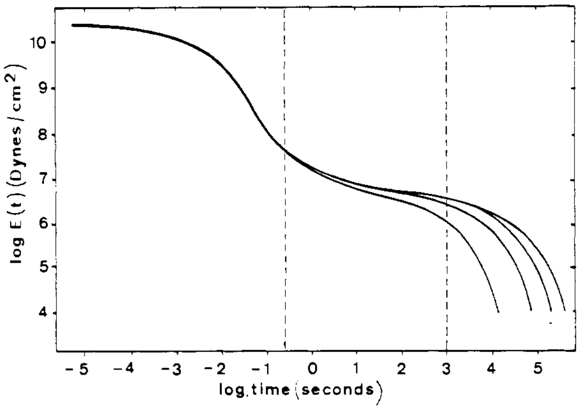

Figure 7. Master curve of the relaxation modulus at a reference temperature of 120 °C (the different curves correspond to different molecular weights), from ref 28. The time domain covered by our experiments is located between the dashed lines.

the rescaling, it is necessary to select the part of the experimental curves similar to this theoretical behavior. We have decided to choose, in a somewhat arbitrary way, the point corresponding to $-\log \dot{\epsilon} a_T = 1$ for which the average value of the orientation is $P_2 = 0.12$.

This rescaling leads to reasonable values of physical parameters. Since the rescaling point is expected to be associated with the end of the A process, the orientation is similar to that of a network at equilibrium and so eq 4 should apply. From the experimental value of P_2 and the average molecular weight between entanglements (M_e = 18 000) the number of statistical segments between entanglements can be calculated and yields a value of 7 monomeric units per statistical segment. This value is in agreement with literature data.[25] Moreover, the rescaling in time is also consistent with the values of the parameter τ_A. The correspondence between $\log t/\tau_A$ and $-\log \dot{\epsilon} a_T$ leads to τ_A = 5.6 s at a temperature of 120 °C. Various determinations of the parameters τ_B and τ_C have been proposed[26,27] from which τ_A can be roughly estimated by using theoretical scaling laws. From ref 26, τ_A at 120 °C should range between 0.8 and 11 s.

The relaxation of the modulus for different molecular weight polystyrenes has been studied by Tobolsky et al.[28] over a very broad time domain (10 decades). Figure 7 shows the time domain covered by the present experimental conditions at the reference temperature of 120 °C. It can be seen that the shortest times correspond to the end of the transition zone, the longer times being characteristic of the plateau region. This remark also substantiates our rescaling in time.

Under these conditions, theoretical curves with N_R = 2 and 3 and experimental ones can be directly compared. The theoretical curves for the two models investigated, superimposed on the experimental ones, are depicted in Figure 8 for the free chain in a network model and in Figure 9 for the self-consistent treatment including the A′ process. The discussion of the comparison will be divided into two parts dealing with the behavior at times shorter or longer than τ_A.

Short-Time Behavior. The theoretical behavior corresponds to a rapid decrease of the orientation, identical for all the molecular weights and independent of the chosen model. Qualitatively, the experimental observations agree with this behavior. Quantitatively, some differences can be discerned. The experimental orientation is lower than predicted by the theory and the kinetics of the relaxation appear more rapid theoretically than experimentally. The theoretical orientation is closer to the experimental one if two subchains instead of three are

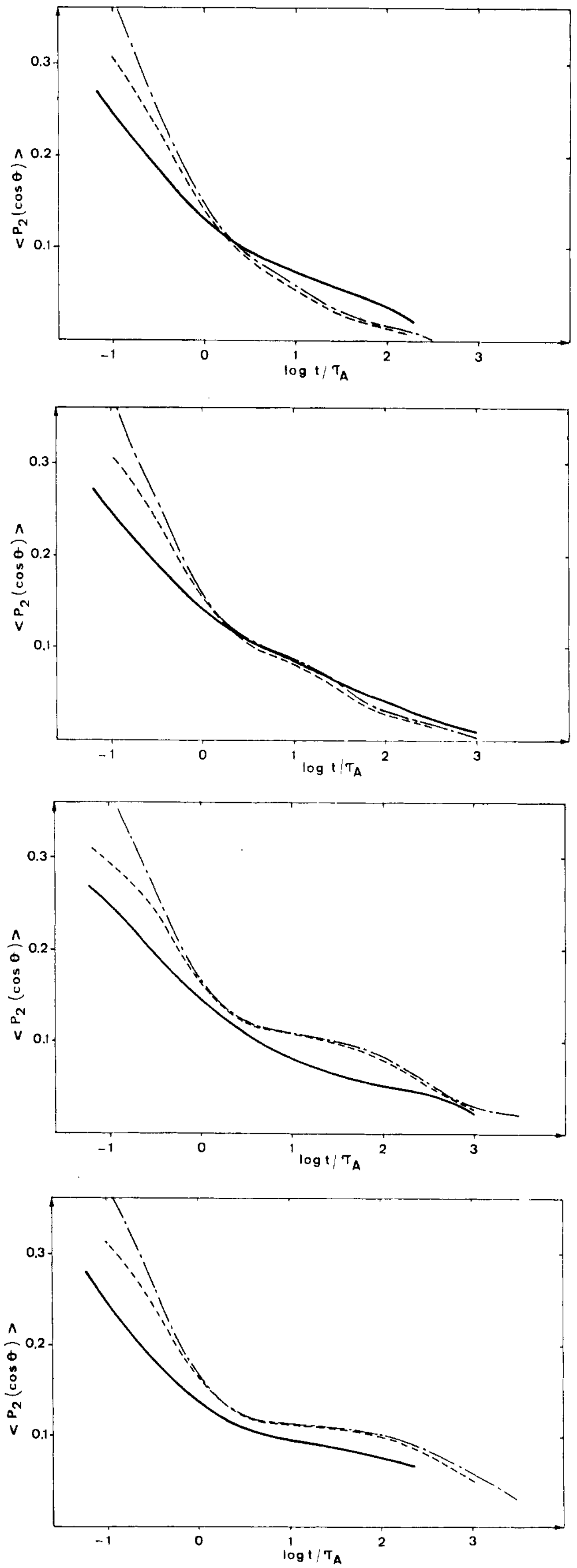

Figure 8. Comparison between the experimental relaxation of orientation and theoretical predictions of the free chain in a network model for the different polymers: (a) for PS 100; (b) for PS 180; (c) for PS 500; (d) for PS 900. (—) Experimental curve; (- - -) theory with N_R = 2; (-·-) theory with N_R = 3.

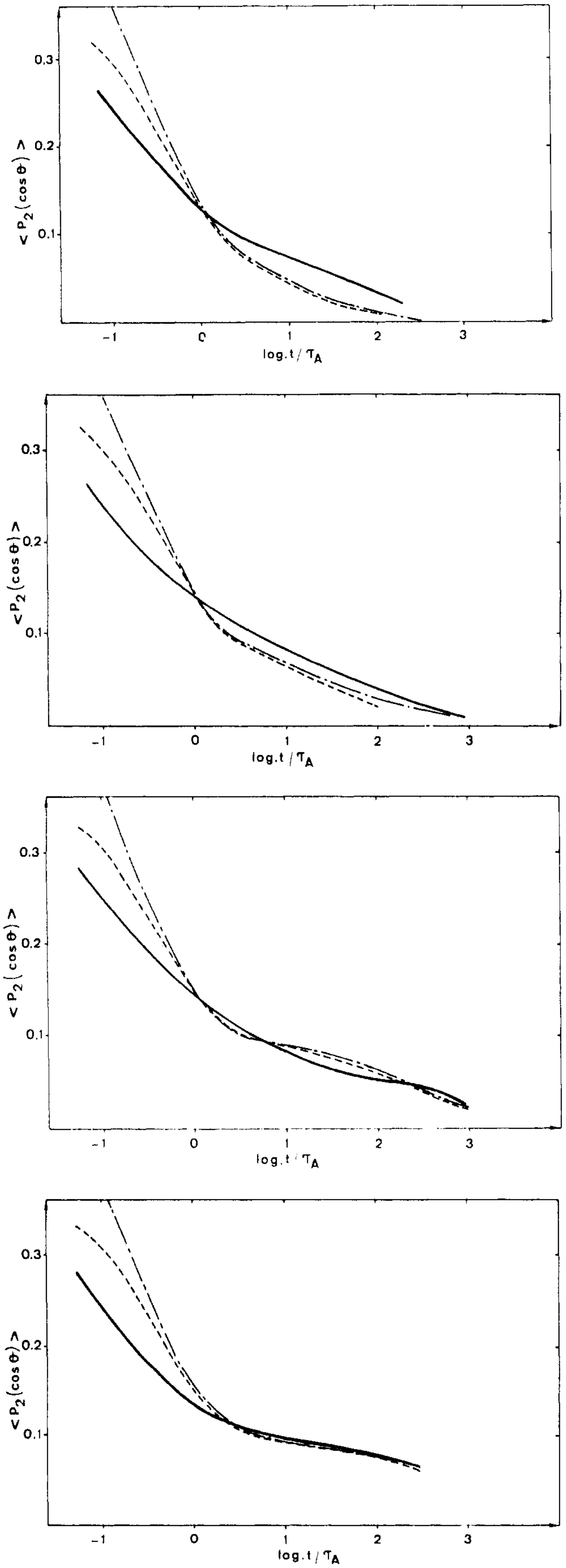

Figure 9. Comparison between the experimental relaxation of orientation and theoretical predictions of a self-consistent model including the A′ process for the different polymers. (Same conventions as in Figure 8.)

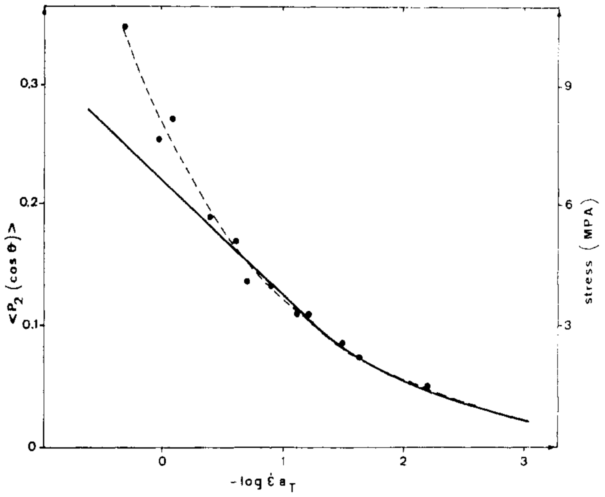

Figure 10. Comparison between the relaxation of the true stress and of the orientation for the PSP polymer at a reference temperature of 120 °C.

taken into account in the calculations. This is not, however, sufficient to explain the discrepancy.

For a better understanding, the behavior of the stress and of the orientation were compared. The relaxation of these quantities is plotted in Figure 10 for the polydisperse polystyrene. Their behavior appears to be identical except at short times where the stress increases more rapidly than the orientation. Thus the stress optical law does not seem to hold for temperatures close to the glass transition temperature. Such a behavior has already been noted by several authors[19,29,30] especially when the stress exceeds a critical value around 2 MPa. The physical origin is not clear.[30] This experiment shows that the stress is predicted more closely than the orientation. Recent experiments performed in the linear domain by Lin[5] confirm that the relaxation of the shear modulus can be described by the DE model in the short-time range. In a log–log representation of the modulus versus time, a slope of $-^1/_2$ is predicted and observed,[31-33] whereas the present orientation data lead to a $-^1/_4$ slope.

The origin of this discrepancy is not clear at the present time. It has been shown that the relaxation behavior is not universal in the transition zone but depends on the chemical nature of the polymer.[33] However, this is usually observed at temperatures very close to T_g, not under investigation here.

Nonlinear effects due to the magnitude of the deformation can also be invoked. In fact, good agreement with the DE model has been noted for small strains. Unfortunately, orientation cannot be studied under these conditions because the accuracy of the measurements is too low. From a theoretical point of view, the expression of the relaxation in step A implies an affine deformation on the spatial scale of the Rouse subchain. Recent studies on the deformation of polymer melts and gels performed by neutron scattering[34] indicate the nonaffinity of the deformation at small spatial scales. The effective deformation is less than predicted by the affine model, therefore the orientation should be lower, as experimentally observed.

Longer Time Behavior. For times larger than τ_A, a smooth decrease of the orientation is predicted by the theory. As can be seen in Figures 8 and 9, the smoother relaxation induced by the mechanism of diffusion of monomers through slip-links represents the experimental results well. In view of the accuracy of the orientation measurements, a good fit is obtained for the highest molecular weight polystyrenes (PS 500 and PS 900) whereas the relaxation is experimentally slower than predicted by the model for PS 100. This may be an effect of the polydispersity of the samples. Polydispersity effects would be more important at the lowest molecular weights, where the retraction process is more complete. With increasing chain length, more local processes are observed at the same experimental relaxation time, and therefore polydispersity effects are less important. Even in the absence of such effects, the retraction and the reptation processes are not clearly apparent on the theoretical curves. Hence, these experiments are not sufficiently discriminative to decide whether such motions exist or not.

Conclusion

Infrared dichroism has been used to study the relaxation of orientation at a molecular scale over 4 decades of time and for four different molecular weights. It has been shown that the time–temperature superposition principle can be used, even for large deformations, to obtain the master curve of the relaxation of orientation.

In these curves, the short-time behavior appears to be independent of the molecular weight. This is in agreement qualitatively and semiquantitatively with the predictions of the Doi–Edwards model. The kinetics of the relaxation at longer times are slowed down when the molecular weight is increased as expected from the model. The retraction and reptation motions both involve a more rapid relaxation of the chain ends, which can be studied with the isotopically labeled block copolymers. Such studies can afford a more direct proof of the existence of these motions. Preliminary results have already been published[15] and a complete comparison with models will be reported soon.

Acknowledgment. It is a pleasure to thank Dr. L. J. Fetters for kindly providing us with the isotopically labeled block copolymers.

Appendix

Orientation Relaxation during A. The relaxation arises from the Rouse motion of the Rouse segments between entanglement points. As proposed by Doi the stress is directly related to the orientation of the segments, so that orientation should relax with the same kinetics

$$P_2(t) = P_2^{\text{network}}\mu_A(t) = P_2^{\text{network}}\left(1 + \sum_{p=1}^{N_R}\exp\left(-\frac{tp^2}{\tau_A}\right)\right) \tag{7}$$

where N_R is the average number of Rouse subchains between entanglements.

Orientation Relaxation during Step B. In the case of the basic DE model, the relaxation of orientation during step B has already been derived (ref 8, eq 25). The following expression has been proposed:

$$P_2(t) = \frac{P_2^{\text{network}}}{\alpha^2(\lambda)}g^2(t/\tau_B) \tag{8}$$

where

$$g(t/\tau_B) = 1 + (\alpha(\lambda) - 1)\mu_B(t) \tag{9}$$

and

$$\mu_B(t) = \sum_{p\,\text{odd}}\frac{8}{p^2\pi^2}\exp\left(-\frac{tp^2}{\tau_B}\right) \tag{10}$$

$$\alpha(\lambda) = \langle|\mathbf{E}\cdot\mathbf{u}|\rangle_{\mathbf{u}} \tag{11}$$

where **U** is a random unit vector and **E** the strain tensor.

Orientation during Step C. The orientation remains proportional to the number of segments still trapped in the initial anisotropic tube.[1] At time t,

$$P_2(t) = \frac{P_2^{\text{network}}}{\alpha^2(\lambda)}\mu_C(t) \tag{12}$$

where

$$\mu_C(t) = \sum_{p\,\text{odd}}\frac{8}{p^2\pi^2}\exp\left(-\frac{tp^2}{\tau_C}\right) \tag{13}$$

Expressions 7, 8, and 12 can be combined to yield the relaxation of orientation following a step deformation of amplitude λ:

$$P_2(t) = \frac{P_2^{\text{network}}}{\alpha^2(\lambda)}\mu_A(t)g^2(t/\tau_B)\mu_C(t) \tag{14}$$

This expression should describe the behavior of a free chain in a deformed network. It can be modified to take into account the slipping of monomers through slip links and the simultaneous relaxation of all the chains.

Influence of the Diffusion of Monomers through Entanglements. The expression proposed by Viovy in ref 4 for the stress can be directly transposed to the orientation, leading to the following expression:

$$P_2(t) = \frac{P_2^{\text{network}}}{\alpha^2(\lambda)}\mu_A(t)\left[\frac{A(\lambda)\alpha(\lambda)}{P_2^{\text{network}}} + 1 - \frac{A(\lambda)\alpha(\lambda)}{P_2^{\text{network}}}\psi(\epsilon/\tau_B)\right]g^2(t/\tau_B)\mu_C(t) \tag{15}$$

where $A(\lambda)$ is the tensorial average defined as

$$A(\lambda) = \left\langle\frac{(\mathbf{E}\cdot\mathbf{u})_z^2 - (\mathbf{E}\cdot\mathbf{u})_x^2}{|\mathbf{E}\cdot\mathbf{u}|}\right\rangle_{\mathbf{u}} \tag{16}$$

and

$$\psi(t/\tau_B) = \frac{1}{N}\sum_{p=1}^{N}\exp\left(-\frac{tp^2}{\tau_B}\right) \tag{17}$$

N being the number of entanglements per chain.

Self-Consistent Treatment. The simultaneous relaxation of the polymer chains does not modify the tensorial averages but only accelerates the kinetics of the relaxation processes.

Precisely, the function $g(t/\tau_B)$ should be replaced by $g'(t/\tau_B)$ where

$$g'(t/\tau_B) = 1 + (\alpha(\lambda) - 1)\mu_B(t)\mu_B'(t) \tag{18}$$

$$\mu_B'(t) = \exp\left(-\frac{0.5t}{\tau_B}\right) \tag{19}$$

and in the reptation stage $\mu_C(t)$ must be changed in $\mu_C^{1+\gamma}(t)$ with $1 \leqslant \gamma \leqslant 1.3$.

Registry No. Polystyrene, 9003-53-6.

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Statistical Thermodynamics of Mixtures of Rodlike Particles. Surface Tension and the Most Probable Distribution

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ABSTRACT: The surface tension in an anisotropic monolayer is investigated for athermal mixtures in which the solute comprises rodlike molecules having the familiar most probable, or Flory, distribution $v_x{}^0 = v_2{}^0(1 - p)^2 x p^{x-1}$, x being both the number of units and the axis ratio. Preferential partitioning of lower and higher species between isotropic and anisotropic phases, respectively, may favor the formation of an anisotropic surface layer of solute particles with considerable lowering of surface tension. Over the range that the undiluted polydisperse solute is biphasic, however, self-ordering of the rods in the surface layer cannot in itself bring about a lowering of surface tension. We also find that the alteration of surface tension due to the formation of a surface layer of anisotropic material that has separated out of a parent isotropic phase (in which the solute retains the foregoing distribution) does not occur spontaneously but rather depends on the presence of a finite amount of ordered material in the mixture. In the limit that the anisotropic phase retains the parent distribution, there exists a range of $(1 - p)^{-1}$ between ~18 and 42 over which theory predicts the formation of an incipient isotropic phase at the surface; at larger values of $(1 - p)^{-1}$ theory favors the presence of an anisotropic layer at the surface.

Introduction

This paper treats the surface tension of an athermal mixture of rodlike particles having a most probable, or Flory, distribution of axial ratios and partitioned into isotropic and anisotropic phases. As in the previously published papers,[1-3] exchange interactions between solute particles are assumed to be null, and only spaciogeometric requirements are considered.

A theory first proposed in 1941 by Flory[4] introduced the quasicrystalline lattice theory to describe the statistical thermodynamics of macromolecules and solvent molecules in equilibrium. According to the theory, solvent molecules (type 1) occupy one lattice site, while macromolecules (type 2) occupy x contiguous lattice sites (x-mers). Finding the number of ways of arranging the molecules in space, by taking into account molecular volumes and shapes and calculating the entropy of mixing, is found by counting the number of geometrical configurations accessible to each type of molecule on the lattice. Then, by determining the average number of contacts between molecular species, one can obtain the configurational energy and, finally, formulate the statistical mechanics of the solution.

In the limit that the volume fractions of solvent and solute molecules in a monolayer parallel to a surface in the liquid are nearly the same as their respective volume fractions in the liquid, it can be shown from the theoretical work of Prigogine,[5] which in turn was based upon Flory's pioneering quasilattice studies, that the surface tension s may be formulated as follows:

$$s = (s_1 v_1{}^{\mathrm{l}} + s_x v_2{}^{\mathrm{l}}) + (RT/a)[v_1{}^{\mathrm{l}} \ln (v_1{}^{\mathrm{m}}/v_1{}^{\mathrm{l}}) + v_2{}^{\mathrm{l}} x^{-1} \ln (v_2{}^{\mathrm{m}}/v_2{}^{\mathrm{l}}) + (x - 1)(v_2{}^{\mathrm{m}} - v_2{}^{\mathrm{l}})/x] \quad (1)$$

Or, to the degree of approximation assumed in this paper (cf. eq 10–17)

$$s \approx s_1 v_1 + s_x v_2 - a x v_1 v_2 (s_x - s_1)^2 / 2RT(v_1 + x v_2) \quad (2)$$

where superscripts l and m denote liquid and monolayer, respectively. Here, s_1 and s_x are the surface tensions of undiluted solvent and solute, respectively, v_1 and v_2 are the volume fractions of solvent and solute in the liquid, the parameter a is a constant corresponding to the molar surface area of a solvent molecule, and RT is the product of the gas constant and the absolute temperature.

Monodisperse Case

Although Prigogine[6] attempted to calculate the surface tension of rigid *rodlike* molecules as early as 1950 using Flory's quasilattice model, his approach was limited by the inability of the quasilattice model, as originally formulated, to adequately represent the geometric constraints imposed

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