respectively. Results of calculations from these equations are compared in Figure 7 for $\zeta = 0.3$, $\phi = 4$, and $\kappa = 10$ and 100. The fluctuations represented by the ratio $\langle(\Delta X_i)^2\rangle/\langle x^2\rangle_0$ along the ordinate are linear in λ^2 for the affine and the phantom models. Results for these two are shown with dashed curves. It is interesting to note that the two lines intersect around $\lambda^2 = 3.5$, due to the strain dependence of the fluctuations of point i in the phantom network. At low values of λ, the fluctuations in the phantom network are larger than those in the affine network due to the freedom of the junction points. However, as λ is increased the affine behavior results in larger fluctuations, as seen in Figure 7. The fluctuations in the real network are very close to the affine limit at low values of λ for $\kappa = 10$ and 100. Phantomlike behavior at low λ is obtained only when κ is less than unity. At higher extensions the curve for $\kappa = 10$ is substantially closer to the phantom result. Similarly, the one with $\kappa = 100$ is close to the affine limit.

Results of calculations for the fluctuations of the mean-square length $\langle(\Delta x_{ij})^2\rangle/\langle x^2\rangle_0$ of a portion of a chain between points i ($\zeta = 0.3$) and j ($\theta = 0.7$) are presented in Figure 8. Trends in the curves are similar to those shown in Figure 7.

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Comparison of Experiment and the Proposed General Linear Viscoelastic Theory. 5. Zero Shear Viscosity of Polybutadiene over a Wide Molecular Weight Range

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ABSTRACT: The viscosity data of nearly monodisperse polybutadiene samples recently obtained by Graessley et al. over a wide molecular weight (MW) range have been analyzed in terms of the proposed general linear viscoelastic theory. The transition from the $\eta_0 \propto M^{3.4}$ region to the $\eta_0 \propto M^3$ region with increasing MW as predicted by the theory is supported by the experimental results. This supports the validity of the chain length fluctuation mechanism as incorporated into the general theory. Over more than 3 decades of MW above M_c, good agreement between theory and experiment is obtained. The present result of analysis is consistent with the previous conclusion that the tube renewal process is negligible in a monodisperse system. It is proposed that the approximate 35% higher values of the experimental results in the low MW region, $M_e < M < M_c$, related to the abnormal higher M_c/M_e ratio of polybutadiene. This seems to occur to polymers of high plateau modulus.

I. Introduction

In the molecular weight (MW) region, where most viscosity measurements for various polymers have been done, the zero shear viscosity η_0 varies with MW as $\eta_0 \propto M^{3.4}$.[1,2] The *pure* reptation model (originally proposed by de Gennes[3] and further developed by Doi and Edwards[4–7] into a constitutive equation) predicts $\eta_0 \propto M^3$. Models including the chain length fluctuation effect[8–10] have been proposed to account for the discrepancy. The chain length fluctuation relaxes the "tube" stress at chain ends and its effect theoretically becomes negligible at very high MWs. Thus, in the very high MW region, one would expect that $\eta_0 \propto M^{3.4}$ transits into $\eta_0 \propto M^3$. Whether this will occur is an important test to the chain length fluctuation mechanism.[8–11]

For this purpose, Graessley et al.[12] recently measured the melt viscosity of polybutadiene over a wide range of MW to as high as 1.65×10^7. The entanglement MW (M_e) of polybutadiene is relatively small compared to most other polymers. This helps reach the M/M_e region sufficiently high to see if the $\eta_0 \propto M^3$ asymptote indeed occurs. Theoretical estimation[8–10] indicates that M/M_e needs to be much larger than ~100 to see the transition.

Graessley et al. analyzed their results in terms of Doi's equation[9]

$$\eta_0 = \text{const}\ M^3[1 - \mu(M_e/M)^{0.5}]^3 \quad (1)$$

with $\mu = 1.7$ (an adjustable parameter) and $M_e = 1850$ (calculated by using $M_e = \rho RT/G_N$ with $G_N = 1.2 \times 10^7$ dyn/cm^2). The analysis suggested an asymptotic limit of $\eta_0/M^3 \approx 1 \times 10^{-9}$. On the other hand, using the viscosity–molecular weight ratio (η_0/M) for Rouse chains (value obtained in the MW region: $M < M_c$ and corrected to constant free volume), they obtained $\eta_0/M^3 = 6.4 \times 10^{-9}$ for pure reptation. They attributed the difference of the two η_0/M^3 values to the tube renewal process.

The validity of the tube renewal model,[13,14] which Graessley et al. have used to interpret the viscosity data of polybutadiene, was recently questioned on a theoretical ground.[15] Furthermore, extensive comparisons of the proposed general linear viscoelastic theory and the viscoelastic[10,16–18] and diffusional data[19] of (nearly) monodisperse polystyrene samples have consistently led us to reach a conclusion that the tube renewal process is negligible in a monodisperse sample.

Here the melt viscosity data obtained by Graessley et al. and by Roovers[12a–c] are compared with the proposed general linear viscoelastic theory.[10] The transition from the $\eta_0 \propto M^{3.4}$ region to the $\eta_0 \propto M^3$ region with increasing MW as predicted by the theory is in agreement with the

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experimental results within the experimental error. The agreement between theory and experiment supports the validity of the chain length fluctuation mechanism as incorporated into the proposed general theory. It also shows the great improvement of the general theory over eq 1. Furthermore, only the vertical shift factor (which is a function of temperature) is used as a fitting parameter here, while μ is used as an additional fitting parameter in the analysis of Graessley et al. using eq 1. The present result of analysis is consistent with the previous conclusion that the tube renewal process is negligible in a (nearly) monodisperse sample.

II. A Brief Review of Theory

A general stress relaxation function containing four dynamic processes has been obtained as[10,16]

$$G(t) = \frac{4\rho RT}{5M_e}[1 + \mu_A(t/\tau_A)][1 + \tfrac{1}{4}\exp(-t/\tau_X)] \times [B\mu_B(t/\tau_B) + C\mu_C(t/\tau_C)] \quad (2)$$

where $\mu_A(t/\tau_A)$ is the Rouse motion of an entanglement strand (assuming entanglement points being fixed in the short time region), $\mu_X(t/\tau_X)$ the chain slippage through entanglement links, $\mu_B(t/\tau_B)$ the primitive chain length fluctuation, and $\mu_C(t/\tau_C)$ the reptational motion corrected for the chain length fluctuation effect. The theoretical forms of the different relaxation processes and the MW dependence of their relaxation times are referred to the previous papers.[10,16]

If the MW is sufficiently high, the contribution of the $\mu_A(t/\tau_A)$ and $\mu_X(t/\tau_X)$ processes to the zero shear viscosity is negligible and the MW dependence of η_0 can be obtained as[10,17]

$$\eta_0 = \frac{\rho RT\pi^2}{15}K\frac{M^3}{M_e^2}[(1 - (M_e/M)^{0.5})^3 + (\tfrac{1}{3})(M_e/M)^{1.5}] \quad (3)$$

with

$$K = \zeta b^2 N_0^2/kT\pi^2M^2 \quad (4)$$

where ζ, b, and M/N_0 are the friction constant, length, and mass associated with each Kuhn segment. Each relaxation time (τ_A, τ_X, τ_B, and τ_C) is given by a product of the friction factor (K) and a structural factor.[10,16]

In the low MW region, the $\mu_A(t/\tau_A)$ and $\mu_X(t/\tau_X)$ processes contribute appreciably to the zero shear viscosity. The viscosity values including these two processes can only be calculated by integrating numerically eq 2. It has been shown that the K value in the $\mu_X(t/\tau_X)$, $\mu_B(t/\tau_B)$, and $\mu_C(t/\tau_C)$ processes is independent of MW and that the K value in the $\mu_A(t/\tau_A)$ process (denoted as K') decreases from a plateau value of $K' \simeq 3.3K$ in the high MW region to a limiting value of $K' = K$ at $M \sim M_e$.[16] The MW dependence of K' was explained as due to the extra free volume associated with the polymer chain ends.[10,16,17]

The MW dependence of K'/K can be described by the following emperical equation

$$\frac{K'}{K} = \frac{2.525}{\exp[-0.6432(M/M_e - 4.5676)] + 1} + 0.76885 \quad (5)$$

The comparison of experimental values and those calculated from eq 5 is shown in Figure 1.

III. Viscosity Data

In Figure 2, we show the theoretical curves of η_0/M^3 calculated from eq 3 (curve 1) and from integrating numerically eq 2 in combination with eq 5 (curve 2). The line shapes of both η_0 and η_0/M^3 are universal functions

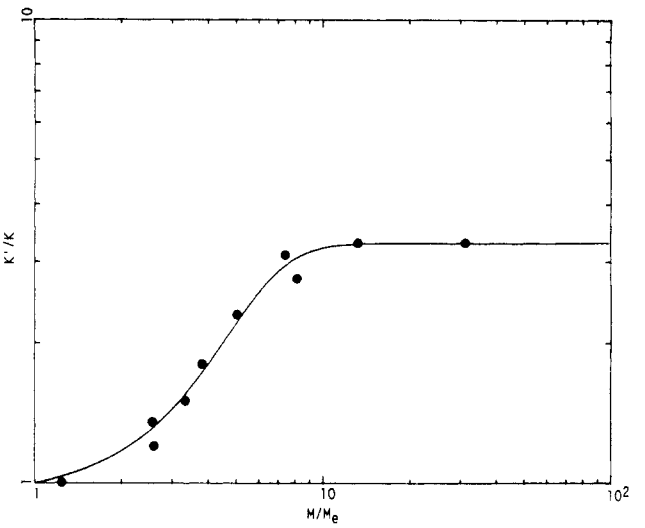

Figure 1. The molecular weight dependence of the K'/K ratio: experimental data (●) and the values (the solid line) calculated from eq 5. The K'/K experimental values (~3.3) in the high MW plateau region have been obtained after an ~30% correction for an effect related to molecular weight distribution (see ref 16 for details).

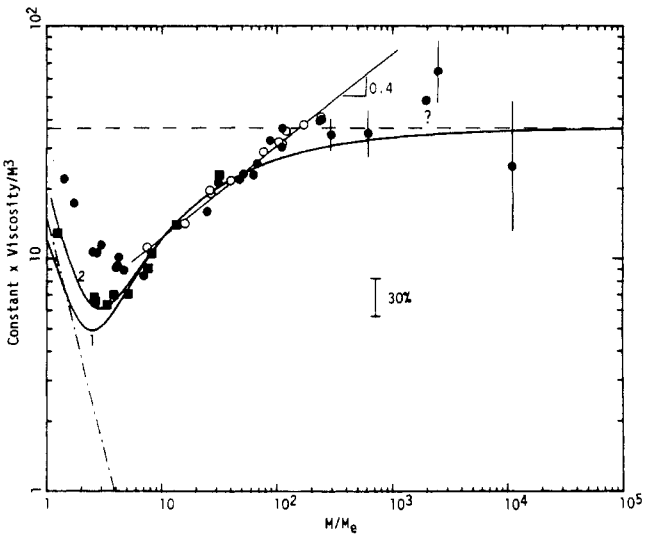

Figure 2. Comparison of the zero shear viscosity data of nearly monodisperse polybutadiene (● from Table XI of ref 12a, which includes data in ref 12b; ○ from ref 12c) and polystyrene (□ from ref 17) samples with the values calculated from eq 3 (curve 1) and the values numerically calculated from the general linear viscoelastic theory (including the $\mu_A(t)$ and $\mu_X(t)$ processes) in combination with eq 5 (curve 2). Also shown is the line of slope 0.4. The M_e values used for normalizing MW (for the horizontal coordinate) in plotting the experimental data are 1480 and 13500 for polybutadiene and polystyrene, respectively. The asymptotic η_0/M^3 value corresponding to the data of Graessley et al. at 25 °C is 6×10^{-10}. For comparison, the values calculated by using the same K value from the Rouse theory (-·-) and the Doi–Edwards theory (---) are also shown. As shown in ref 18, the general linear viscoelastic theory has bridged the gap between the Rouse theory and the Doi–Edwards theory.

of M/M_e.[25] Plotting η_0/M^3 vs M/M_e allows one to see the subtle change of η_0 with MW with a better sensitivity. Also shown in Figure 2 are the experimental results of polystyrene and polybutadiene samples, which are only allowed to shift along the η_0/M^3 coordinate to superpose on the theoretical curve (curve 2). The M_e values used for plotting the viscosity data (for the M/M_e coordinate) are 13500 and 1480 for polystyrene and polybutadiene, respectively. The M_e values are calculated from the plateau modulus values using $M_e = 4\rho RT/5G_N$.[5,10,16] Thus, the M_e value of poly-

butadiene is smaller than that in the paper of Graessley et al.[12a] by a factor of $^4/_5$.

The good agreement between experiment and theory for the polystyrene samples is expected from the successful quantitative viscoelastic relaxation spectrum line-shape analyses to MW as low as 1.24 M_e, which were reported previously.[10,16] This was explained in detail in paper 3,[17] although η_0 vs M instead of η_0/M^3 vs M/M_e was shown. Again, the comparison of curve 1 and curve 2 with the experimental data in Figure 2 shows the importance of the $\mu_A(t)$ and $\mu_X(t)$ processes in contributing to the viscosity values in the low MW region.

In the case of polybutadiene, there is a good overall agreement between theory and experiment. The theoretical prediction of the bending over of η_0/M^3 around $M/M_e = 100$ to become basically independent of MW is in agreement with the experimental results within experimental error. A possibility that the sample of the highest MW might not have reached an equilibrium state was raised by Professor Plazek. However, by comparing the terminal relaxation time and the time between sample molding and testing, Graessley et al. think that the nonequilibrium effects should be small. The third highest MW sample has somewhat higher vinyl content than others; its error is difficult to estimate. As indicated in ref 12a, the experimental error is about 3% in both viscosity and molecular weight for MW smaller than 5×10^5. Obtained through private communication with Graessley, the estimated experimental errors beyond this point are indicated by the error bars in Figure 2. In their paper Graessley et al. stated that the errors from all sources seemed too small to compromise their main conclusion of significant departure from the 3.4 power law at large MW. Above $M/M_e = 100$ the experimental values tend to be larger than the calculated values by about 20% in average. This can be attributed to broader molecular weight distribution (MWD) that often occurs in high MW samples. It has been observed[20] that at the same weight average MW, samples of broader MWDs have higher zero shear viscosity values. In the case of nearly monodisperse samples, where the linear additivity law is applicable, it can be shown that $\eta_0 \propto M_w M_z M_{z+1}$ if mainly pure reptation is involved (applicable in the very high MW region, where the chain end effect is negligible).[16,31] Although there is no information about the MWD characterization in ref 12a, a 20% larger viscosity value is of the right order of magnitude that can be expected to arise from the samples made by anionic polymerization. In view of this, the agreement between theory and experiment as shown in Figure 2 is quite good over more than 3 decades of MW above M_c.

In the low MW region ($M/M_e < 4$) the theoretical values (curve 2) are smaller than the experimental results by about 30–40%. M_c occurs at about the minimum of η_0/M^3. The deviation of experimental results from the theory begins around M_c and appears closely related to the higher M_c/M_e ratio (~4.3) associated with polybutadiene. Most polymers (e.g. polystyrene, poly(α-methylstyrene), poly(vinyl acetate), polyisobutylene, polyisoprene) have $M_c/M_e \sim 2.4$, while some polymers, especially those with high values of plateau modulus (such as polyethylene and polybutadiene), have significantly larger M_c/M_e ratios.[2,15,21a,b] Thus, M_c/M_e is not that constant among polymers, although the experimental relation of $\eta_0 \propto M^{3.4}$ in the MW region, where most experimental data have been measured, is quite universal. This strongly suggests that we can not expect to have an absolutely universal theory that can explain *all* the viscoelastic data of different polymers. This does not mean that the universality of the topological constraint effect of chain entanglement is not valid. In fact, on the basis of the topological universality, we have predicted that the number of entanglement strands per cubed tube diameter be a constant,[15] which is very well supported by data of a large assembly of polymers. We may consider $M_c/M_e \sim 2.4$ as a "normal" case. The proposed general theory should explain very well the viscoelastic data of the polymers in this category as it has been demonstrated in the case of polystyrene. The higher M_c/M_e values of the polymers in the "abnormal" category can be caused by (perturbation) effects additional to those considered in the proposed general theory. One likely explanation is the interaction among the chain end segments. The chain end segments might behave *thermodynamically* differently from the internal segments of the chain. As a result, if the concentration of the chain end segments is sufficiently high, they would tend to aggregate and the viscoelastic behavior of the medium would be affected. Polymers of low M_e values would be more likely to have sufficiently high concentrations of chain end segments in the MW region $M_e < M < M_c$. This might explain the abnormality typically occurring to polymers of high plateau modulus.

The iso-free-volume correction to the viscosity data in the low MW region should be more complicated than commonly done.[1,2,12a,26] We have observed that free volume change with MW only affects the K' value, while K is independent of MW. This is related to what has been observed by Plazek[27] in the creep measurements of nearly monodisperse polystyrene samples and poly(vinyl acetate) samples. He reported that between T_g and $T_g + 25$ °C the time scale shift factor varied more rapidly with temperature in the glass–rubber transition region (the $\mu_A(t)$ process, where K' is applicable) than in the terminal region (the $\mu_B(t)$ and $\mu_C(t)$ processes, where K is applicable). Plazek's observation implies that K' be greater than K in agreement with our results. Plazek's results also suggest that K'/K is basically independent of temperature above $T_g + 25$ °C. Our K'/K values were obtained at 127.5 °C for polystyrene ($T_g = 100$ °C). As shown previously[10,16–18] and above, the $\mu_A(t)$ process contributes significantly to the viscosity values in the low MW region. The MW dependence of K' is the one that needs to be considered for the iso-free-volume correction in the low MW region. In the case of polybutadiene, the iso-free-volume correction may be particularly complicated. In their common way of free volume analysis,[28] Graessley et al. found that the values of several coefficients were quite different from the more common values. Thus, we think that it is better to compare theoretical and experimental results, both without iso-free-volume correction. The theoretical curve (curve 2 in Figure 2) calculated with K' being dependent on MW (eq 5) corresponds to the values without correction to iso-free-volume. The experimental points compared with the theoretical curve in Figure 2 are also without iso-free-volume correction. The 30–40% difference between theory and experiment in the low MW region ($<M_c$) of polybutadiene while being related to its high M_c/M_e ratio is far less than the difference of the two asymptotic η_0/M^3 values obtained by Graessley et al. (see above).

In terms of the free Rouse chain theory and the Doi–Edwards theory, Graessley et al. calculate $\eta_0/M^3 = 6.4 \times 10^{-9}$ for pure reptation using the η_0/M value obtained (after the iso-free-volume correction) in the low MW region ($M_c > M > M_e$). We have shown from the viscoelastic relaxation spectrum line-shape analysis that polymer dynamics in the MW region between M_e and M_c is not described by the *free* Rouse chain motion but well described by the

proposed general theory (see Figure 5 of ref 17). As a result, the viscosity value at $M \sim M_e(+)$ calculated from the general theory (including the iso-free-volume correction which corresponds to calculation using constant K'/K ratio ($\sim$3.3) over the entire MW region) is about 3 times greater (due to chain entanglement) than that of the free Rouse chain theory (see Figure 1 of ref 17). Thus an asymptotic η_0/M^3 value too large by a factor of three will result, if, as Graessley et al. have done, the free Rouse chain theory is used to calculate η_0/M in the low MW region. A great part of the large difference (a factor of 6) between the two η_0/M^3 values obtained by Graessley et al. should be due to this reason. If the iso-free-volume correction to the viscosity values were not as complicated as pointed out above, what causes the M_c/M_e ratio of polybutadiene to be higher than the normal value, should account for the remaining difference. The tube renewal process, which Graessley et al.[12a] have used to explain the whole difference, should not be the reason. Extensive comparisons of the proposed general linear viscoelastic theory and the viscoelastic[10,16-18] and diffusion data[19,22] of nearly monodisperse polystyrene samples have consistently led us to conclude that the tube renewal process is negligible in a monodisperse sample. It is hard to think that the tube renewal process is effective in one polymer but not in another. Furthermore, if the tube renewal process had an effect on the viscosity value, it would be most noticeable in the low MW region, and one would expect that the experimental viscosity values be smaller than the theoretical values in the low MW region (with experimental and theoretical values matched in the region of higher MW). On the contrary, at $M < 5M_e$, the measured values deviate from the theoretical curve on the high side.

IV. Viscosity Shift Factor and the Frictional Factors K' and K

Responding to a comment by a reviewer, we would like to elaborate on a significant effect associated with the two frictional factors K' and K here. In the case of polystyrene (considered as a normal case), the obtained invariance of K to MW and the MW dependence of K'/K allow us to explain the behavior of the viscosity shift factor (the ratio of viscosity values measured at two different temperatures). Using the viscosity values at 217 °C as reference, Allen and Fox[26,29] showed the viscosity ratios η_T/η_{217} (T = 140, 155, and 190) as a function of MW. The results indicate that above M_e η_T/η_{217} is insensitive to the change of MW and at M_e it begins a precipitous drop with decreasing MW. The explanation is as follows. Above M_e, the $\mu_B(t)$ and $\mu_C(t)$ processes (the terminal region where K is applicable) contribute a great deal to the zero shear viscosity. Because K is independent of MW, it has a *buffering* effect (also see Ref 17) to the change of η_T/η_{217} with MW. Furthermore, as pointed out above, Plazek's results suggest that K'/K is basically independent of temperature above T_g + 25 °C. This minimizes the change of $\eta_T-\eta_{217}$ with MW above M_e. Below M_e, there is the Rouse process only, which contains a single K. Any free volume change (as caused by the change of MW or temperature) has a direct effect on the K value and therefore the viscosity value. Thus, at M_e η_T/η_{217} goes through a transition and begins to decline sharply with decreasing MW.

In addition, the results of our line-shape analyses of the linear viscoelastic spectra just above M_e and just below M_e[17] indicate that as far as the free volume distribution on the polymer chain is concerned, there is a "phase" transition point at MW $\sim M_e(+)$, i.e., from "anisotropic" to "isotropic" as the MW decreases in passing through M_e.

The small MW dependence of the η_T/η_{217} data obtained by Allen and Fox in the region between M_c and M_e can be attributed mainly to some low MW tail (the MWs of the tail components are smaller than M_e) in the MWD of their samples, which did not appear to be extremely narrow ($M_w/M_n \approx 1.1$;[26] M_w/M_n needs to be below 1.05 to be free of such a low MW tail at $M_w = M_c$).

Consistent with the above explanation for the MW dependence of η_T/η_{217} above and below M_e is the recent observation made by McKenna et al.[30] They reported that the superposability of log η_0 curves (plotted as a function of temperature) could be qualified as excellent for the linear polystyrene fractions, provided that their MW was larger than 40 000 (M_c = 33 000).

V. Conclusion

Graessley et al. used Doi's equation (eq 1) to analyze the viscosity data of polybutadiene. As pointed out previously,[10] Doi's equation has a too drastic decline of the viscosity value with decreasing MW below $M \approx 20M_e$. This is also clearly noticeable in Figure 12 of the paper by Graessley et al.[12a] In this report, the analysis of the same experimental data in terms of the proposed general linear viscoelastic theory is extended to M_e. The theoretically predicted transition from the $\eta_0 \propto M^{3.4}$ region to the $\eta_0 \propto M^3$ region is supported by the experimental results. Over more than 3 decades of MW above M_c, agreement between theory and experiment is obtained within the experimental error. Thus, the validity of the chain length fluctuation mechanism as incorporated into the general linear viscoelastic theory is supported by this comparison. It is proposed that the approximate 35% higher values of the experimental results in the low MW region: $M_e < M < M_c$ is related to the abnormal higher M_c/M_e ratio of polybutadiene. This seems to occur typically to polymers of high plateau modulus. The present result of analyzing the viscosity data of polybutadiene is consistent with the previous conclusion[10,15-19,23,24] that the tube renewal process is negligible in a monodisperse system.

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Registry No. Polybutadiene, 9003-17-2.

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Computer Simulation of End-Linked Networks: Telechelic Poly(oxyethylene) Cross-Linked with Plurifunctional Isocyanates

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ABSTRACT: Networks formed from α,ω-dihydroxypoly(oxyethylene) (POE) with plurifunctional isocyanate at various initial polymer volume fractions v_{2c} have been simulated with a computer. Monte Carlo samples of chains based on RIS statistics have been constructed, which yield networks comparable to those based on Gaussian statistics. A detailed study of various types of network imperfections and cycle ranks of the networks is reported. Computer simulation shows that, at a given sol fraction w_s, the Miller–Macosko theory underestimates the extent of reaction by as much as 3.2–8.5%. Moduli are calculated according to the phantom network model, and very good agreement with experiment is found for networks prepared with low molecular weight polymer and with high molecular weight polymer cross-linked at high dilution.

Introduction

The structures of network polymers are important, since the nature of these structures determines the final mechanical properties, such as modulus, dynamical behavior, and ultimate strength. Since techniques for direct investigation of network structures are absent, many efforts have focused on theoretical predictions. Among these are the gelation theory of Flory[1] and Stockmayer,[2] the cascade (stochastic branching) theory,[3] the Miller–Macosko (recursive branching) theory,[4,5] and the rate theory.[6]

The assumptions[1,2] of equal and independent reactivity of like functional groups and no loop formation are not always correct. At high extents of reaction, the remaining unreacted groups in the gel can become isolated from one another. One must also consider intramolecular reactions that lead to the formation of cyclic species in both the sol and the gel portions. Beyond the gel point, the problem of the sol–gel distribution becomes complicated because of the strong competition between intramolecular and intermolecular reactions. The assumption that the sol fraction is acyclic leads to inaccurate gel conditions and distorted distributions, and one must expect that these inaccuracies will persist beyond the gel point. Even in the limit of acyclic pregel systems, postgel intramolecular reactions are found to be important.[7,8] The complexity of postgel reactions renders a comprehensive theoretical treatment rather difficult.

On the other hand, computer simulation can provide valuable information on these reactions. The algorithm that simulates random polycondensation has been well developed in previous work.[9] The advantage of our computer algorithm is the fact that we are able to probe the internal structures of the simulated molecules. Subsequently, the information obtained can give us details of the extent of cyclization, cycle rank, and sol–gel distributions.[9] The algorithm has been adapted to simulate critical gel points[10] and mechanical properties.[11] Another advantage of the algorithm is that it is easily modified to simulate other types of reactions, such as the end-linking of polyol stars[12] with bifunctional groups or the radiation cure of clastomer networks.[13,14]

The system that is simulated here was studied experimentally by Gnanou, Hild, and Rempp.[15] It is described chemically as $A_2 + B_f$ (ref 15 defines their system as $A_f + B_2$), where A_2 is a telechelic prepolymer with α and ω reactive end groups and B_f (f = 2, 3, 5, 7, 9)[15] is a cross-linker with a distribution of functionalities: the mole fractions of the B_f are 0.055, 0.55, 0.17, 0.11, and 0.115, respectively. A code which generates Monte Carlo samples of polymer chains[16–21] based on the rotational isomeric state theory[22] has been written. In these simulations, prepolymers having n skeletal bonds were generated by using both the RIS and the Gaussian distribution of end-to-end distances. Results from the two distributions are compared.

Simulation Procedure

Generation of Reaction Container. The details of end-linking algorithm have been described in a previous work.[9] In the model, prepolymer chains and cross-linkers are randomly distributed in a cubical box whose length L is determined by the equation

$$L = (nM_0N_p/\rho N_a v_{2c})^{1/3} \quad (1)$$

where n is the number of skeletal bonds, M_0 is the average molecular weight of one bond unit, N_p is the number of prepolymer chains, ρ is the density of the prepolymer, N_a is Avogadro's number, and v_{2c} is the volume fraction of polymer during the cross-linking process. The sample chain configurations are generated either by use of a

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