identify the stretch relaxation as the mechanism responsible for the anomalous slowness of the overall dynamics, we have not been able to elucidate its origin.

An interesting result of our simulations is that the relaxation time for the self-avoiding walks has the same $\tau \propto N^3$ scaling in one, two, and three dimensions. This fits naturally with the explanation that the stretch relaxation requires a time on the order of N^2. The relaxation time exponent for the ideal case seems to increase from 2.5 in one and two dimensions to 2.75 in three dimensions. This may imply that the stretch relaxation time has a different chain length dependence for ideal chains in different dimensions. It may also be interesting to see if the exponents for the ideal and self-avoiding polymers are identical in four dimensions. We have not checked these points.

In order to compare our algorithm with one involving local dynamics, we performed simulations in which monomers are allowed to make local moves, without altering the connectivity between them. This results in a relaxation time $\tau(N) \propto N^{3.5}$ for two-dimensional polymers, as expected (see section I). The actual relaxation times for this dynamics were approximately 3 times larger than ours for $N = 16$. This ratio increased to 6.3 for $N = 64$. Thus, despite the fact that the scaling behavior of our dynamics is slower than expected, it offers a considerable reduction in computation time in simulations involving large chains.

VI. Conclusion

This work shows that the bead-jump dynamics considered here is an efficient and reliable technique for simulating polymers in situations where reptation dynamics is inappropriate. Further, we have identified a novel relaxation mechanism that appears to be responsible for the peculiar relaxation properties seen in the dynamics. This mechanism is "stretch relaxation" or the relaxation of stored length along the chain. We have not succeeded in explaining the slow decay of such stretches. We believe that the same mechanism may explain the relaxation properties seen by others[6] in previous simulations.

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References and Notes

(1) Baumgärtner, A. In *Applications of Monte Carlo Methods in Statistical Physics*; Binder, K., Ed.; Springer-Verlag: Berlin, 1984; p 145.
(2) Kremer, K.; Binder, K. *Comput. Phys. Rep.* **1988**, *7*, 259.
(3) Grest, G. S.; Kremer, K. *Phys. Rev. A* **1985**, *33*, 3628.
(4) des Cloizeaux, J.; Jannink, G. *Les Polymères en Solution: leur Modélisation et leur Structure*; Les Editions de Physique: Paris, 1987.
(5) Madras, N.; Sokal, A. D. *J. Stat. Phys.* **1988**, *50*, 109.
(6) Caracciolo, S.; Sokal, A. D. *J. Phys. A: Math. Gen.* **1986**, *19*, L797.
(7) Wall, F. T.; Mandel, F. *J. Chem. Phys.* **1975**, *63*, 4592. Mandel, F. *J. Chem. Phys.* **1979**, *70*, 3984.
(8) Kremer, K.; Grest, G. S.; Carmesin, I. *Phys. Rev. Lett.* **1988**, *61*, 566.
(9) Verdier, P. H.; Stockmayer, W. H. *J. Chem. Phys.* **1962**, *36*, 227.
(10) Boots, H.; Deutch, J. M. *J. Chem. Phys.* **1977**, *67*, 4608.
(11) Baumgärtner, A.; Binder, K. *J. Chem. Phys.* **1979**, *71*, 2541.
(12) Lal, M. *Mol. Phys.* **1969**, *17*, 57.
(13) MacDonald, B.; Jan, N.; Hunter, D. L.; Steinitz, M. O. *J. Phys. A: Math. Gen.* **1985**, *18*, 2627.
(14) Pakula, T. *Macromolecules* **1987**, *20*, 679.
(15) Caracciolo, S.; Sokal, A. D. *J. Phys. A: Math. Gen.* **1987**, *20*, 2569.
(16) Another algorithm that utilizes variable bond length was introduced by Carmesin and Kremer: Carmesin, I.; Kremer, K. *Macromolecules* **1988**, *21*, 2819. This algorithm has local moves and reproduces Rouse-like dynamical behavior.
(17) Prentis, J. *J. Chem. Phys.* **1982**, *76*, 1574.
(18) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY 1979.

Evolution of Structure and Viscoelasticity in an Epoxy near the Sol-Gel Transition

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ABSTRACT: The divergences of the average molecular weight, average cluster size, and bulk viscosity as the gel point is approached and the power law behavior of the dynamic shear moduli at the gel point were measured for a cross-linked epoxy. The critical exponents describing the evolution of static structure were found to be significantly different from the predictions of mean-field theory and in reasonable agreement with percolation. The exponents describing the viscoelastic behavior in the critical region were found to be significantly different from the predictions of the de Gennes electrical analogy and in good agreement with our scaling theory.

Introduction

It is difficult to overstate the technological importance of cross-linked elastomers and thermosets, and yet the evolution of structure and viscoelastic properties during cure in these systems is not well understood theoretically nor has it been thoroughly studied experimentally. The general features of structural evolution during gelation such as the divergences of molecular weight and cluster size as the gel point is approached were cap-

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Table I
Critical Exponents for the Evolution of Structure and Viscoelasticity from Various Theories

Static Exponents

	γ	ν	D	τ
percolation	1.76	0.89	2.5	2.2
mean field	1.00	0.50	4.0	2.5

Dynamic Exponents

	k	Δ	z
electrical analogy	0.75 ± 0.04	0.72 ± 0.02	1.94 ± 0.10
dynamic scaling			
general	$(\gamma + \nu)/2$	$6/(7 + \gamma/\nu)$	3ν
using percolation	1.33	0.67	2.67

tured years ago by mean-field theories (e.g., Flory–Stockmayer,[1,2] cascade,[3] and Miller–Macosko[4] theories), and their appeal lies in the simple analytical results obtained. However, all neglect specific correlations (e.g., intracluster circuit formation), which has been shown to be unacceptable at other phase transitions.[5] One expects the same to be true for the sol–gel transition since very large pregel clusters formed by mean-field theories cannot physically fit into three-dimensional space.[6] Mean-field theories may be valid for certain regimes during cure but should crossover to a more physically realistic mechanism of gelation in the critical region.

Recently, it was suggested[7,8] that one such mechanism may be described by percolation where one simply connects bonds (or fills sites) on a lattice of arbitrary dimension and coordination number. As in mean-field theories, percolation offers predictions for the exponents characterizing critical divergences of such quantities as the average molecular weight and cluster size.[6,9] These exponents, which can be related through scaling relationships, are independent of the particular lattice chosen but do depend on the lattice dimension, d. In fact, mean-field theories represent a special case of percolation with the lattice dimension greater than or equal to 6. The most powerful contribution of percolation to an understanding of the sol–gel transition is the concept of complete self-similarity that leads to the so-called hyperscaling relationships. Under this assumption, photographs of the ensemble in the reaction bath at the gel point would be identical regardless of the magnification.

The viscoelastic behavior of near-critical gels is less well understood. Naturally, the bulk viscosity and inverse equilibrium shear modulus diverge at the gel point, but recently it has also been established experimentally that the dynamic shear moduli exhibit power law behavior near the sol–gel transition.[10,11] de Gennes proposed that the viscosity divergence is analogous to the conductance divergence of a superconductor–conductor random mixture[12] and that the shear moduli near the gel point scale as the ac conductivity of a resistor–capacitor random mixture.[13] Recently, we have developed a theory based on a length-scale-dependent viscosity and complete static and dynamic self-similarity.[14,15] Under these assumptions, movies of the ensemble in the reaction bath at the gel point would be identical regardless of the magnification if the speeds were suitably chosen. The predicted critical exponents for the viscoelastic properties in these theories can be expressed in terms of the static exponents describing the evolution of structure in the gel.

It is the purpose of the present study to determine if the static properties near the gel point are correctly predicted by either mean-field or percolation theories and if the previously mentioned viscoelastic theories adequately describe the dynamics. Toward this goal, we have measured a wide range of critical exponents: the critical divergences of the average molecular weight and cluster radius and the bulk viscosity as the gel point is approached and the power law behavior of the dynamic shear moduli near the gel point. While there are several excellent studies in the literature that have investigated either the statics[16,17,18] or dynamics[13,19,20] independently, the present investigation gives a coherent picture of the statics *and* dynamics of one system at the sol–gel transition.

Theory

One can be overwhelmed by the number of exponents predicted by gelation theories. Four of these describe the divergence of a given quantity in the reaction bath and are defined below:

$$M_w \sim \epsilon^{-\gamma} \qquad R_z \sim \epsilon^{-\nu}$$

$$\eta \sim \epsilon^{-k} \qquad G_\infty^{-1} \sim \epsilon^{-z}$$

where M_w is the weight average molecular weight, R_z is the z-average cluster radius (or equivalently the connectivity correlation length, ξ), η is the bulk viscosity, G_∞ is the equilibrium modulus, and $\epsilon = |p_c - p|/p_c$ with p_c being the cross-linking probability at the gel point. The mass of a single cluster is related to its radius by the fractal dimension D such that $M \sim R^D$. In addition, the number distribution at the gel point is described by a power law with $n(M) \sim M^{-\tau}$. D and τ can be related to γ and ν by the scaling relationship $\gamma/\nu = D(3 - \tau)$. Two more exponents, $\bar{\nu}$ and $\bar{D}$, are needed to account for swelling of the clusters when taken from the reaction bath and diluted in a good solvent. Since it is these swollen exponents that are usually measured, we have used the Flory-type arguments for percolation clusters relating swollen exponents to unswollen ones,[21] which result in $\bar{D}/D = \nu/\bar{\nu} = 0.8$. One additional critical exponent, Δ, describes the power law dependence of the dynamic moduli on frequency, $G' \sim G'' \sim \omega^{\Delta}$.

Predictions for these exponents from the various theories are given in Table I. The predictions of Martin et al. for the dynamic exponents k and Δ are those obtained in the limit of complete hydrodynamic screening (Rouse limit). This theory, in general, only sets the limits $0 \leq k \leq \nu(D - 1)$ and $3/(D + 2) \leq \Delta \leq 1$ on these exponents, but, as shown later, our results on epoxies agree with this Rouse limit. We have listed in Table I the dynamic scaling Rouse limit results for three dimensions in terms of arbitrary static exponents and for the specific case of structural evolution by percolation. In addition, all dynamic theories listed obey the scaling relationship $\Delta = z/(z + k)$, which is derived from more fundamental considerations.[22]

Experimental Section

Our gels were made from 89% by weight of the diglycidyl ether of Bisphenol A (Shell Epon 828) cured with 11% by weight diethanolamine (Fisher Scientific). These weight percents give a fully cured material with the highest possible glass transition temperature, 70 °C. Both components were used as received. The components were prereacted at 90 °C while stirring to solubilize the diethanolamine through end capping. Stirring was then stopped, and the reaction bath was held at 90 °C until the gel point. A thorough investigation of the cure kinetics of this system is presented in a separate paper where the extent of reaction (as defined either by the disappearance of epoxy or by the appearance of the ether linkage) was monitored by FTIR.[23]

The divergences of the molecular weight and radius were measured by quenching aliquots taken from the reaction bath at known intervals up to the gel point by dilution in a 60/40 toluene/isopropyl alcohol solution. The gel time, t_c, was taken to be the midpoint between the time at which the first insoluble aliquot was taken (174 min) and the time at which the last soluble aliquot was taken (170 min). From this, we calculated $\epsilon_t = |t_c - t|/t_c$, which was converted to ϵ from FTIR measurements of extent of reaction versus time. The weight average molecular weights were then measured with a commercial Chromatix KMX-6 low-angle light-scattering photometer (at concentrations of 10–50 mg/mL and solid angles of 4–5 and 6–7°) where the specific refractive index had been measured with the accompanying Chromatix KMX-16. The z-averaged hydrodynamic radii were measured using a HeNe laser operating at 633 nm and an Ar ion laser operating at 336 nm. For all samples prior to the gel point, the clusters were small compared to Q^{-1}, so the measured radii for both wavelengths agreed. A scattering angle of 20° was used for all measurements. A cumulant analysis obtained from a 256 channel Langley–Ford digital correlator was used to obtain the relaxation time, and the hydrodynamic radii were obtained using Stokes law and the known solvent viscosity. Both the hydrodynamic radius from quasielastic light scattering and the radius of gyration from static light scattering are z-averaged quantities and have been shown theoretically to diverge with the same critical exponents.[24] This has been shown experimentally for the silica sol–gel in our previous study[16] and for γ-irradiated polystyrene[25] although there may be some dispute in other systems.[26]

The power law behavior of the dynamic shear moduli and the divergence of the bulk viscosity were measured using a Rheometrics RDS-2 with 50-mm-diameter parallel plates. For measurements of G' and G'', dynamic scans spanning frequencies from 5 to 300 rad/s at 90 °C were taken every 2 min until well past the gel point. To measure the bulk viscosity, the transducer torque was monitored continuously at constant shear rate at 90 °C until it exceeded the instrument capabilities. By taking several runs at different shear rates, we determined that the measured viscosity was Newtonian up to roughly 10 000 P at a shear rate of 4×10^{-3} rad/s. Determination of the gel time is difficult in this experiment. We followed the standard procedure of plotting log η against log ϵ for various values of the gel time and used the value that resulted in the most linear relationship. This approximation is the source of the relatively large uncertainties in the stated results. It should be noted that the increase of viscosity as the gel point is approached is in general due not only to the divergent molecular weight but also to the increase in the glass transition temperature of the epoxy with extent of reaction. The glass transition temperature of this system increased only 7 °C from 26 to 33 °C in the experimental range, so corrections to the measured viscosity based on assuming "universal" WLF parameters[27] were found to be small.

Results and Discussion

In Figures 1 and 2, we show the divergences of the weight averaged molecular weight and the z-averaged hydrodynamic radius as the gel point is approached. The slopes show the critical exponents γ and $\tilde{\nu}$ to be 1.7 ± 0.1 and 1.4 ± 0.1, respectively. To relate the divergence of the swollen hydrodynamic radius to the unswollen divergence, we have used the Flory-type arguments, which reduce $\tilde{\nu}$ by a factor of 0.8 such that $\nu = 1.1 \pm 0.1$. These should be compared to the mean-field and percolation predictions in Table I. We see that the measured values are in much better agreement with the percolation predictions; however, the measured ν is approximately 20% larger than predicted. Whether this is due to the actual divergence of the average size or to the Flory-type calculations for the swelling upon dilution cannot be determined from these experiments.

Using the scaling relationship $D = (3 + \gamma/\nu)/2$ and letting $\nu = 1.1 \pm 0.1$, we calculate that the fractal dimension of the clusters formed in this system is 2.25 ± 0.10, which, again turning to Table I, is approximately 10% smaller than predicted by percolation. We also calculate the polydispersity exponent, $\tau = 3 - \gamma/D\nu$, to be 2.3 ± 0.1, which is within experimental error of the percolation predictions.

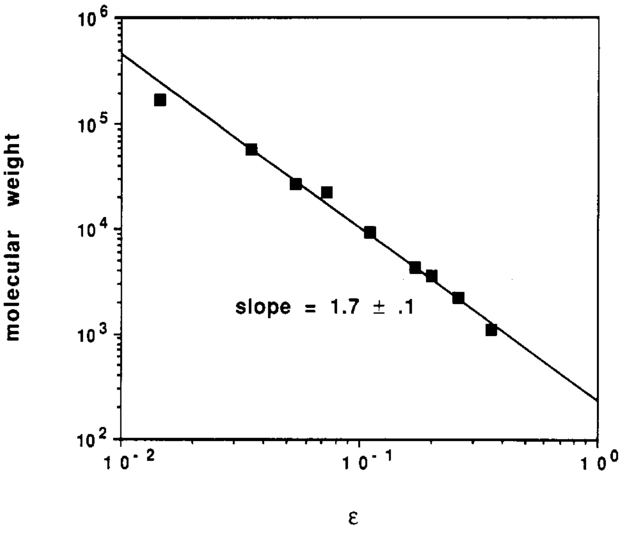

Figure 1. Divergence of the weight averaged molecular weight. The slope, $\gamma = 1.7 \pm 0.1$, agrees well with the percolation prediction of 1.76.

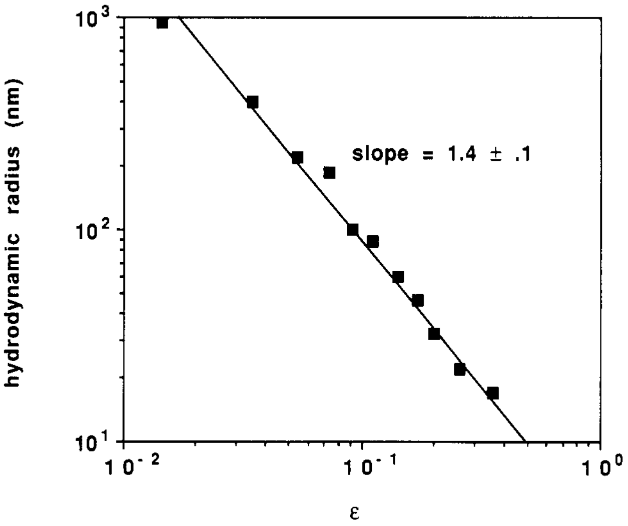

Figure 2. Divergence of the z-averaged cluster radius. The slope, $\nu = 1.4 \pm 0.1$, is somewhat larger than the swollen percolation prediction of 1.1.

In Figures 3 and 4, we show the divergence of the bulk viscosity and the power law behavior of the dynamic shear moduli at the gel point. The critical exponents k and Δ that we measure are 1.4 ± 0.2 and 0.70 ± 0.05, respectively. These are in poor agreement with the predictions of the electrical analogy but are within experimental error of the dynamic scaling theory using percolation as seen in Table I. We can also use the theoretical predictions of Martin et al. to calculate the exponent z describing the increase in the equilibrium modulus after the gel point and see that $z = 3\nu = 3.3 \pm 0.3$, which differs greatly from the de Gennes prediction. Unfortunately, we cannot quench our experimental reaction and therefore cannot measure this divergence due to the exceedingly long relaxation times. Alternatively, we can use the more fundamental arguments stated previously that predict $\Delta = z/(z + k)$. Using the experimental values of k and Δ, we find that $z = 3.3 \pm 1.3$. Even with these huge experimental uncertainties, the predictions of Martin et al. agree with experiment better than those of the electrical analogy.

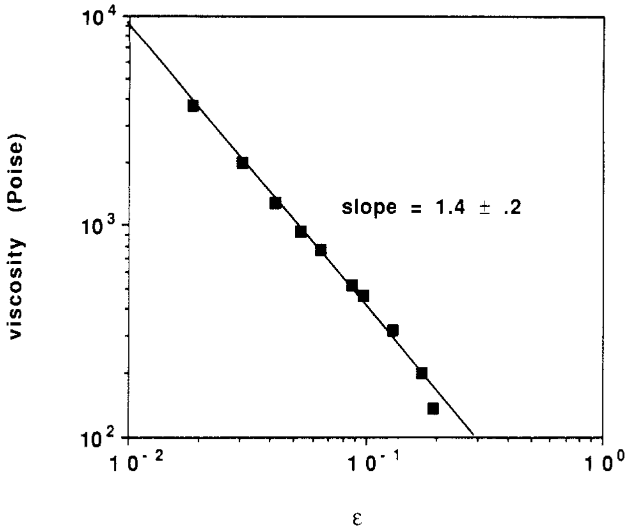

Figure 3. Divergence of the bulk viscosity. The slope, $k = 1.4 \pm 0.2$, agrees well with the predictions of the scaling theory of Martin et al.

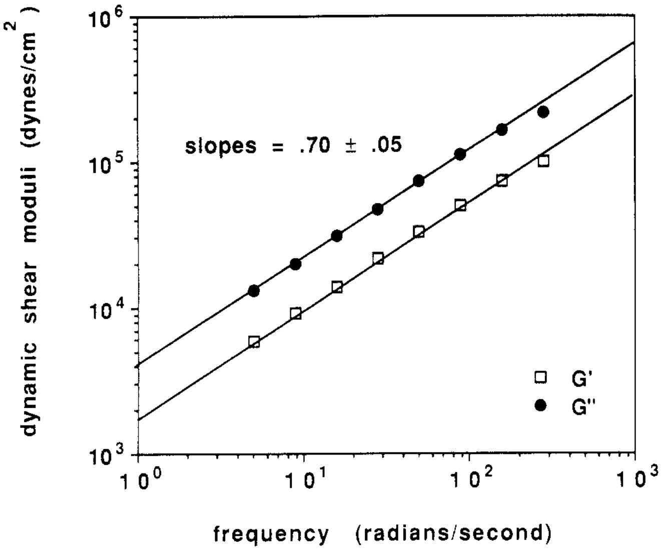

Figure 4. Power law behavior of the dynamic shear moduli at the gel point. The slope, $\Delta = 0.70 \pm 0.05$, agrees well with the predictions of the scaling theory of Martin et al.

Conclusions

One surprising conclusion from this study is that the critical region over which power law divergences are observed is quite large. For example, one exponent k describes the viscosity divergence over the entire accessible range in extent of reaction covering approximately 1/3 of the pregel reaction. In fact, the critical region may be much larger than this but we are not able to resolve the lower molecular weights experimentally.

We can also say with certainty that the mean-field theories (i.e., Flory–Stockmayer) do not *quantitatively* describe the critical divergences of the static structure in this system. The predicted divergences are much weaker than the experimental data. We should note that attempts to account for substitution effects and cyclization in mean-field theories (e.g., cascade theory) do not change any of the predicted exponents. That is, the classes of nonideal structures that can be handled in this formalism change only the prefactors describing the critical divergences. However, the percolation prediction for the critical exponent describing the molecular weight divergence agrees quite well with experiment. The experimental divergence of the average cluster size is somewhat stronger than predicted by percolation but may be due to the assumptions made in accounting for swelling upon dilution.

The dynamics of the critical sol seem to be in excellent agreement with the predictions based on the scaling theory of Martin et al. but not with the electrical analogies. This implies that the reaction bath can be modeled as an unentangled melt of polydisperse clusters with no hydrodynamic interactions, a Rouse melt. This is perfectly reasonable if one accepts that percolation describes the evolution of structure in the melt as seen above. In percolation, the clusters do not overlap but rather fit neatly together as a three-dimensional "jigsaw puzzle", and one would not expect dynamic entanglements. Percolation also predicts that excluded-volume effects are partially screened in the melt; that is, the static screening length is small. One's first guess, then, for the dynamic screening length which controls the hydrodynamic interactions would be that it too is small. We are left, therefore, with the conjecture that a Rouse model for branched polymer would be appropriate for the dynamics in the critical region, and the data seem to support this. Recently, Colby et al. have independently come to the same conclusion.[20]

We must stress that, although this system seems to be consistent with percolation and the dynamical scaling arguments, the same cannot be said for all of the numerous studies on different systems. While some experiments on the evolution of structure in cross-linked systems do seem to agree with percolation, others follow mean-field theory and still others are in poor agreement with both. Likewise for the critical dynamics, some studies find agreement with the dynamic scaling arguments while others agree with the de Gennes electrical analogies. The apparent nonuniversal behavior may be due to measurements that were made outside the true critical regime; however, this should be investigated further.

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References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(3) Good, I. J. *Proc. Cambridge Philos. Soc.* **1960**, *56*, 367.
(4) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(5) Ma, S. K. *Modern Theory of Critical Phenomena*; Benjamin/Cummings: Reading, MA, 1976.
(6) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103.
(7) deGennes, P. G. *J. Phys., Lett.* **1976**, *37*, 61.
(8) Stauffer, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(9) Stauffer, D. *Phys. Rep.* **1979**, *54*, 1.
(10) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
(11) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3*, 297.
(12) Adam, M.; Delsanti, M.; Durand, D.; Hild, G.; Munch, J. *Pure Appl. Chem.* **1981**, *53*, 1489.
(13) Adam, M.; Delsanti, M.; Durand, D. *Macromolecules* **1985**, *18*, 2285.
(14) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. A* **1989**, *39*, 1325.
(15) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 2620.
(16) Martin, J. E.; Wilcoxon, J. P.; Adolf, D. *Phys. Rev. A* **1987**, *36*, 1803.

(17) Schosseler, F.; Leibler, L. *J. Phys., Lett.* **1984**, *45*, L501.
(18) Bouchaud, E.; Delsanti, M.; Adam, M.; Daoud, M.; Durand, D. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 1273.
(19) Plazek, D., private communication.
(20) Colby, R.; Rubenstein, M., private communication.
(21) Isaacson, J.; Lubensky, T. C. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, L469.
(22) Clerc, C. P.; Trembley, A. M. S.; Albinet, G.; Mitescu, C. D. *J. Phys. Lett.* **1864**, *45*, L913.
(23) Keenan, M. R.; Adolf, D. B., to be published.
(24) Martin, J. E.; Ackerson, B. *Phys. Rev. A* **1985**, *31*, 1180.
(25) Karjiwara, K.; Burchard, W. In *Characterization of Highly Cross-linked Polymers*; Labanna, S. S., Dickie, R. A., Eds.; American Chemical Society: Washington DC 1984; p 55.
(26) Scmidt, M.; Nerger, D.; Burchard, W. *Polymer* **1979**, *20*, 582.
(27) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

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Nematic to Isotropic Transition in Chemically Disordered or Multicomponent Liquid-Crystalline Polymers

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ABSTRACT: A Landau theory is presented for the nematic to isotropic (N–I) transition of main-chain liquid-crystalline polymers that are chemically disordered, i.e., statistical copolymers. The two constituent monomers are assumed to differ in flexibility but could be otherwise identical. For such a system, the chemical disorder contributes a random component to the local bending elastic constant of each chain. We find a coupling between the conventional nematic (orientational) order parameter and a compositional order parameter that expresses nonuniformity in the density of flexible monomers. This coupling leads to a biphasic region at the N–I transition in accordance with the recent experiments of Stupp et al. (*Macromolecules* **1988**, *21*, 1217–1234). In the limit of high molecular weight, the width of the biphasic window is proportional to the difference between the elastic constants of the two monomers and is inversely proportional to the square root of the molecular weight. Segregation by flexibility at the N–I transition is also analyzed for binary blends of thermotropic homopolymers.

I. Introduction

Thermotropic liquid-crystalline polymers are materials with remarkable mechanical, optical, and electrical properties. Recent advances in synthetic methods, purification, and processing techniques are stimulating new commercial applications of these materials, as well as careful scientific studies.[1,2]

While the myriad of phase transitions exhibited by low molecular weight liquid crystals have been exhaustively studied for decades, the corresponding transitions in liquid-crystalline polymers have received much less attention. Experimental and theoretical investigations of phase transitions in flexible macromolecular systems have revealed interesting physics that are not realized in low molecular weight systems. Hence, it is natural to expect new phenomena in liquid-crystalline polymers. Indeed, such phenomena have been evidenced in a number of recent studies.[3-8]

Of particular relevance to the present paper are a set of experiments by S. I. Stupp and colleagues.[6-8] These authors synthesized two thermotropic copolymers, both containing (on average) equal amounts of three types of monomers (A–C). Two of the monomers (A and B) were rigid (mesogenic), while the third (C) was flexible. The first polymer was an *ordered* copolymer with repeat unit (CABCBA) and was found to exhibit a sharp nematic to isotropic (N–I) transition at 275 °C. The second polymer was a *disordered* statistical copolymer of the same average composition but, in contrast to its ordered isomer, exhibited a broad biphasic region over the temperature range 250–400 °C. In this temperature range, an isotropic fluid phase was observed to coexist in varying proportions with a nematic, birefringent phase. Pure nematic and isotropic phases, respectively, were observed at temperatures below and above the biphasic region.

Stupp et al.[8] provided a very plausible explanation for the curious behavior of the disordered copolymer. Because of statistical fluctuations in the composition of each chain, the various polymers in the sample differ in their effective flexibility. Here, "effective flexibility" refers to an average persistence length or bending elastic constant that characterizes each copolymer molecule in the sample (see, e.g., eq 3.8). Stupp et al. coined the term "polyflexibility" to describe the distribution of effective flexibilities present in a random copolymer sample. This multicomponent character of a statistical copolymer melt opens the possibility that it could segregate into two or more phases (each differing in effective flexibility) at the N–I transition. In order to test this hypothesis, the authors of ref 8 numerically sampled a large number of copolymer sequences that were representative of their sample. For each generated chain, an effective flexibility was computed and a theory for the N–I transition of a homopolymer[9] (with that flexibility) was used to estimate the corresponding N–I transition temperature. The spread in calculated transition temperatures was consistent with the width of the experimentally observed biphasic region.[10] The authors also provided convincing evidence

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