Gelation in Physically Associating Polymer Solutions

Sanat K. Kumar*
Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania

Jack F. Douglas
Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland
(Received 9 October 2000; revised manuscript received 9 February 2001; published 10 October 2001)

Simulations were performed on solutions of associating polymers, where the pairing energy between "stickers" is comparable to thermal energy, to gain insights into the nature of reversible gelation. At high temperatures, interchain associations relax over microscopic time scales, so that geometrical percolation is unrelated to macroscopic gelation. However, with decreasing temperature, the stickers undergo a clustering "transition," resulting in a transient localization of stickers and hence the chains. These findings imply a close similarity between the dynamics of associating polymer solutions and vitrification of glass-forming liquids, in agreement with many experimental results.

DOI: 10.1103/PhysRevLett.87.188301 PACS numbers: 82.70.Gg, 61.41.+e

Solutions of macromolecules with moieties capable of physical association commonly form thermoreversible gels either on heating or cooling [1–4]. This poorly understood state of matter, which exhibits elasticity for small and rapid deformations and flow over long times, is ubiquitous in contexts ranging from colloids, emulsions, foods, viscosity modifiers and to the cytoskeleton of living organisms [5,6]. There are two extreme types of gels formed by physically associating polymer solutions. When the sticker pairing energy is large (i.e., $\epsilon_{ss} \gg k_B T$) the sticker cluster lifetimes are effectively infinite. In these well-studied examples, geometrical percolation closely corresponds to gelation, i.e., the point where the solution acquires solidlike character [7–16]. In the other extreme, when $\epsilon_{ss} \sim k_B T$, the stickers pair and unpair rapidly. Since the clustering times are comparable to the time scales for monomer size displacements, percolation does not guarantee solidlike behavior at long times. Indeed, recent experimental [17] and theoretical [18] studies of gelation in colloid solutions have suggested that gelation is not synonymous with percolation, but rather is a dynamic, ergodicity breaking transition, similar to vitrification. While these ideas accord with many recent experiments on polymer solutions (see, for example, [19–21]), the molecular origins of this behavior have not been established.

Here we present computer simulation results on the onset of thermoreversible gelation in solutions of associating polymers. We begin by determining the phase boundary for liquid-liquid coexistence for these solutions. Next, we locate the geometrical percolation line, and find hardly any changes in chain dynamics when this line is crossed [22]. Instead, stickers cluster into multiplets on further cooling ("clustering transition"), leading to an abrupt increase in cluster lifetimes over a small temperature range. Analysis of the diffusivity of the chains, their mean squared displacement, and the non-Gaussian parameter [see Eq. (1)] show that the dynamics of these associating polymer solutions is phenomenologically similar to vitrification [23]. The surprising aspect of our findings is that, in contrast to traditional glass formers, such glasslike behavior occurs even though the polymer concentrations are low.

We consider polymer chains on a cubic lattice with periodic boundary conditions in all directions. Chain lengths of $N = 100$ are considered, where stickers are regularly placed 10 monomers apart. Each chain thus contains $r = 10$ stickers. The lattice consists of chains and holes, a system which is isomorphic with an incompressible polymer solution. Nearest neighbor pairs of chain monomers have interaction energies as follows: $-\epsilon_{\rm ss} \neq 0$ and $\epsilon_{sm} = \epsilon_{mm} = 0$, where the subscript s stands for a sticker, while m denotes a nonsticky monomer. The energy of interaction of any species with a hole is zero. Thus, the "sticking" energy $-\epsilon_{ss}$ represents the only attractive interaction, and the chain backbone is in an athermal solvent (the "holes"). The reduced temperature is defined as $T^\star = k_B T/\epsilon_{ss}$. We determined the phase coexistence of these solutions by the histogram reweighting method as in [24]. Figure 1 shows the phase boundary where the solution separates into polymer-rich and solvent-rich phases.

Next, we focus on locating the geometrical percolation line. We consider systems in the *canonical* ensemble, i.e., fixed N_p, V, T, and consider equilibrium snapshots. We define two chains to be "clustered" in a snapshot if a pair of nearest neighbors corresponds to an intermolecular sticker-sticker contact. For polymer volume fractions, ϕ, beyond the percolation threshold, the probability distribution function for cluster sizes is bimodal, with one peak corresponding to the "sol" and the other to the "percolated component." (This distribution has been illustrated in [24].) The volume fraction of monomers that span the system, ϕ_{sl}, is an "order parameter" for the percolation transition. We plot ϕ_{sl} as a function of ϕ, and identify the percolation transition as the extrapolated point where $\phi_{sl} = 0$ [24]. Figure 1 shows that the geometrical

 © 2001 The American Physical Society

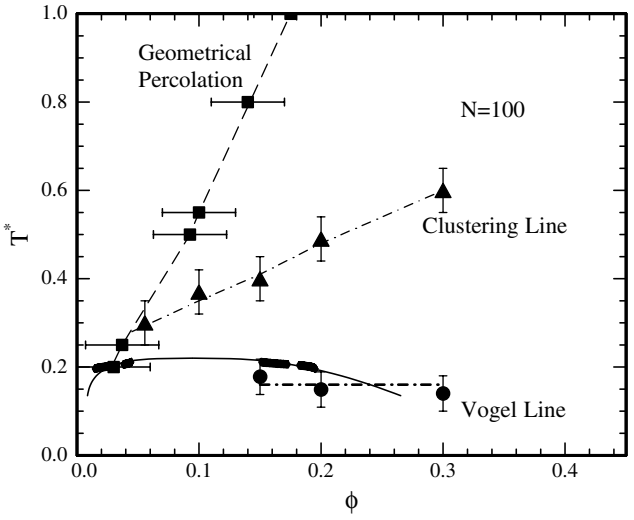


FIG. 1. Behavior of chains of length $N = 100$. The closely spaced symbols (diamonds) represent phase equilibria between a polymer rich and a polymer lean phase, and the dark full line is a fit to the data using an Ising model scaling function [25]. The phase equilibria were enumerated for three box sizes 25^3, 30^3, and 36^3 and found to be independent of system size. The squares are the geometrical percolation transition line, the triangles the clustering line, and circles the Vogel line. All dotted and dashed lines are guides to the eye.

percolation line determined in this fashion rises sharply when plotted as $T^\star$ vs ϕ [26].

Since gelation is experimentally defined in connection with transport properties [17,27], we consider the dynamical properties of these systems. Kovacs and others [28,29] have shown that Monte Carlo simulations with local flip elementary moves allows for the simulation of the dynamics of these systems. However, it must be noted that momentum is not conserved during each Monte Carlo move. Since hydrodynamic interactions are ignored, the dynamics of the chains will follow the Rouse model. We have utilized this method to simulate the mean squared displacement of the centers of mass of the chains, $\langle r^2 \rangle$, as a function of t, the number of Monte Carlo cycles. We obtain linear plots of $\langle r^2 \rangle$ vs t at long times (see Fig. 2a), except at the lowest temperature. For the $\phi = 0.2$ systems considered in Fig. 2, geometrical percolation occurs for $T^* \sim 1$ (see Fig. 1). However, Fig. 2a shows that the chain dynamics hardly change between $T^* = \infty$ and $T^* = 0.4$. Consequently, the stickers do not significantly affect chain dynamics near the geometrical percolation transition [22,30]. Thus, the geometrical percolation line is *not* synonymous with gelation in our model of associating polymers.

To understand the reversible gelation in these systems, we consider if a thermodynamic signature of the onset of this transition can be located. We calculated $U^\star$ ($\equiv U/\epsilon_{ss}$), the dimensionless mean energy per monomer, and the dimensionless heat capacity $C_v^\star = (\partial U^\star/\partial T^\star)_{V,N_p}$ as a function of $T^\star$. While the $U^\star$ data (not shown) are relatively featureless, Fig. 3 suggests a change in the variation of $C_v^\star$ in the vicinity of $T^\star = 0.37$ for $\phi = 0.1$. At high temperatures, entropy dominates and stickers do not tend to cluster. For $T^\star \leq 0.37$, however, the stickers have a strong propensity to associate, and, consequently, the average size of the clusters grows upon cooling. We define the "clustering onset temperature," $T^\star_{\text{cluster}}$, as the point where $C_v^\star$ shows a strong increase, and a plot of its locus as a function of ϕ is given in Fig. 1. Notably, the clustering temperature is generally below the geometrical percolation temperature at any given ϕ (Fig. 1). We do not calculate the clustering line for concentrations below percolation, i.e., at lower ϕ, since the resulting chain clusters, which do not percolate the system, cannot yield gel-like structures which are of interest to this work.

Since the average size of sticker clusters, n, increases below $T^\star_{\text{cluster}}$, we expect that the effective monomer flip time, $\tau = \tau_0 \exp(n/T^*)$ increases dramatically on cooling. Here τ_0 is the microscopic attempt time, and n is the average number of stickers that neighbor the sticker of interest. Consistent with these ideas, Figs. 2a and 4 show that the sticker dynamics and hence chain dynamics noticeably slow on cooling. Figure 4a plots the waiting time distribution, i.e., the probability that a sticker moves at time t after not having moved from time $t = 0$ to $t = t$ [31]. It is clear that, for the lowest two temperatures, the sticker dynamics are dramatically slowed, as evidenced by this probability distribution function showing a long time tail. Figure 4b plots the cluster survival probability, $P_{\text{cluster}}(t)$, which is the fraction of the largest cluster that does not break off after t time steps. This quantity clearly illustrates the dramatic increase in the lifetime of the percolating cluster on cooling. Consistent with these ideas, Figure 2a shows that, as temperature is lowered, the chain displacements show an increasing tendency towards localization, as indicated by a flattening of the $\langle r^2 \rangle$ vs t plots at intermediate times. Similarly, the diffusion constant, D, which is extracted from the long-time Brownian limit following the Einstein equation, $\langle r^2 \rangle = 6Dt$, rapidly drops with decreasing temperature, especially below $T^* \sim 0.4$ (see Fig. 2b) [32]. This dramatic slowing down is a consequence of the stickers: athermal chain systems ($T^* = \infty$) at these low volume fractions show no sign of glass formation. Notably, these results are not a manifestation of slowing down in the vicinity of the critical point for polymer-solvent phase separation, since much of our data are far from the estimated critical composition of $\phi \approx 0.1$ (see Fig. 1).

We estimate the characteristic time of the crossover between chain localization and Brownian motion by employing the non-Gaussian parameter α,

$$\alpha = \frac{3\langle r^4 \rangle}{5\langle r^2 \rangle^2} - 1, \tag{1}$$

which is 0 for Brownian motion. Figure 2c shows that α vs t has a maximum whose magnitude increases with

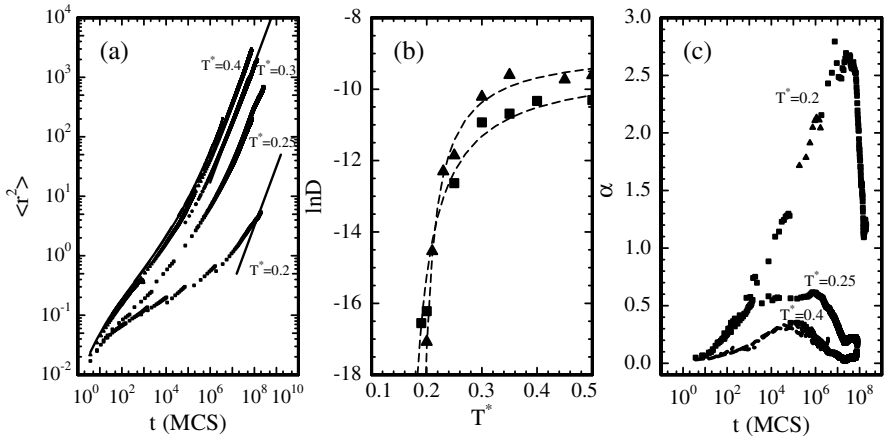


FIG. 2. (a) Plots of the mean squared center of mass displacement of the chains of length $N = 100$ as a function of time (in units of Monte Carlo cycles) at $\phi = 0.2$ at various temperatures as indicated. The dashed line which effectively overlaps the data at $T^* = 0.4$ corresponds to $T^* = \infty$. The lines shown for $T^* = 0.3$ and 0.2 correspond to slopes of 1, which is expected for chains undergoing Brownian diffusion. (b) Plot of ln$D$ obtained from the Brownian regime in (a) for $\phi = 0.2$ (squares) and 0.15 (triangles) as a function of $T^\star$. Lines are fits to the VF equation. There is considerable uncertainty in the low temperature data points [32]. (c) Plot of the non-Gaussian parameter α as a function of time for $\phi = 0.2$. Again the dashed line corresponds to $T^* = \infty$. Data at $T^* = 0.3$, which overlap the data at $T^* = 0.4$ and ∞ are not shown for convenience.

decreasing temperature, especially below $T^* = 0.4$. This trend is consistent with an increased tendency for chain localization with decreasing temperature. The time corresponding to the maximum in α, t^*, which determines the crossover from localization to diffusive motion, is directly related to the structural relaxation of the fluid as determined from viscoelastic measurements or from inelastic scattering [33]. We find that t^* increases with decreasing temperature, and in particular, t^* increases from $\sim 10^5$ for $T^* \sim 0.4$ to $\sim 10^8$ for $T^* = 0.2$, which is in accord with the reduction of D in the same temperature range. Thus, although there is no dramatic slowing down of chain diffusion near the geometrical percolation line, there is a striking resemblance between chain dynamics at low temperatures and diffusion in supercooled liquids [33]. While there are recent suggestions that gelation should have similarities to vitrification [18,34], the evidence supporting this hypothesis has been limited. The data presented in Fig. 2 establish this connection directly.

Glass-forming liquids exhibit a universal phenomenology in the temperature dependence of viscosity and diffusivity, and it is interesting to examine if these ideas also apply to our gelation data. We find that the D data can be approximately described by the Vogel-Fulcher (VF) form, $\ln\frac{D}{D_0} = \frac{CT_0}{T-T_0}$, where D_0 and C (the "fragility" parameter) are constants, and T_0 represents an extrapolated temperature at which the diffusion constant goes to zero (Vogel temperature in glass forming liquids). For this VF form to be an appropriate descriptor of the diffusion data requires that the fit values of $C < 5$ [23]. For larger C values an Arrhenius dependence of D on temperature is more

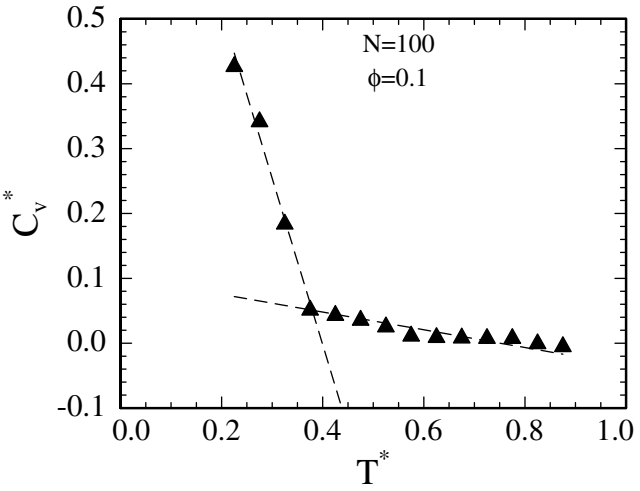


FIG. 3. Plot of the dimensionless heat capacity, $C_v^\star$, as a function of $T^\star$ for a system with $\phi = 0.1$.

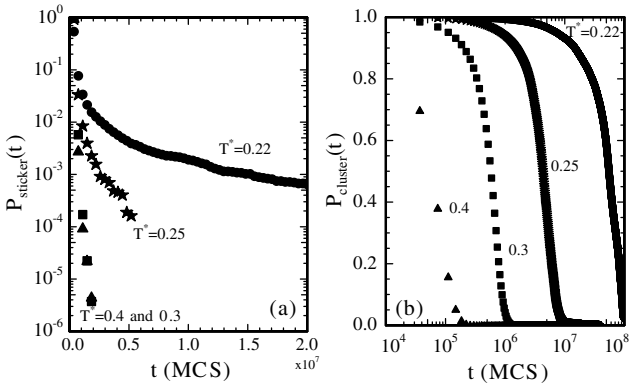


FIG. 4. (a) Plot of probability that a sticker does not move up to a time t, but then moves at that time, $P_{\text{sticker}}(t)$ as a function of time t in units of Monte Carlo cycles. Data are shown for 4 temperatures at $\phi = 0.2$. (b) Percolating cluster survival probability, $P_{\text{cluster}}(t)$, for the same systems as in (a).

appropriate. We find $C = 1$ for $\phi = 0.15$ and $C = 2$ for $\phi = 0.2$, which strongly argue in favor of using the VF form to describe the D data. Thus, the diffusive behavior of these systems is consistent with the behavior of fragile glass formers [23]. Following experimental practice [17,27], we define the gelation line as a locus of points where the viscosity of the solution diverges, i.e., $T_0(\phi)$. Figure 1 shows that T_0 varies weakly over the ϕ range considered in our work. While some of the extrapolated T_0 values lie inside the binodal, we note that all of our extrapolations were conducted with data in the single phase alone. Thus, T_0 is a hypothetical temperature relevant to describing the slowing down of polymer solution dynamics in the single phase region. Further, we emphasize that the gel formation in these situations is driven primarily by the clustering of stickers which slow down their dynamics, and hence those of the chains. The geometrical percolation of chains connected by these frozen sticker clusters then yields solidlike behavior akin to gel formation.

The term "gelatinous" derives from the Latin "gelare" which means to freeze [35]. Consistent with this notion, we find that the vitrification of typical liquids is remarkably similar to the thermoreversible gelation of associating polymers [36]. In both cases, we find a rapid drop in diffusivity, transient particle localization, and increasingly long structural relaxation times upon cooling. A striking aspect of our results is that such glasslike phenomena occur for associating polymers and colloid solutions [17] even at low solution concentrations, due to the dominance of sticker pairing interactions.

Financial support was provided by the National Science Foundation (CTS-9975625) and the American Chemical Society (S. K.). We thank Ralph Colby, George Stell, Ken Schweizer, Michael Rubinstein, Kurt Binder, and Gregorsz Szamel for insightful comments. In particular, we thank Bill Russel for suggesting the connection between the gelation of associating polymers and the corresponding phenomena in colloidal gel formers. Further, Austen Angell suggested the importance of the fragility parameter in this context.

*Author to whom correspondence should be addressed. E-mail address: kumar@plmsc.psu.edu

[1] D. N. Schulz and J. E. Glass, *Polymers as Rheology Modifiers,* ACS Symposium Series 462 (American Chemical Society, Washington, DC, 1991).
[2] J. E. Glass, *Hydrophilic Polymers: Performance with Environmental Acceptability,* Advances in Chemistry Series 248 (American Chemical Society, Washington, DC, 1996).
[3] J. M. V. Blanshard and P. I. Lillford, *Food Structure and Behavior* (Academic Press, New York, 1987).
[4] P. S. Russo, *Reversible Polymeric Gels and Related Systems,* ACS Symposium Series 350 (American Chemical Society, Washington, DC, 1987).
[5] F. C. MacKintosh, J. Kas, and P. A. Janmey, Phys. Rev. Lett. **75**, 4425 (1995).
[6] B. Hinner, M. Tempel, E. Sackmann, K. Kroy, and E. Frey, Phys. Rev. Lett. **81**, 2614 (1998).
[7] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).
[8] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943).
[9] A. Coniglio, H. E. Stanley, and W. Klein, Phys. Rev. Lett. **42**, 518 (1979).
[10] D. Stauffer and A. Aharony, *Introduction to Percolation Theory,* (Taylor & Francis, London, 1992).
[11] F. Tanaka and A. Matsuyama, Phys. Rev. Lett. **62**, 2759 (1989).
[12] F. Tanaka and W. H. Stockmayer, Macromolecules **27**, 3943 (1991).
[13] F. Tanaka, Macromolecules **31**, 384 (1998).
[14] A. N. Semenov and M. Rubinstein, Macromolecules **31**, 1373 (1998).
[15] I. Y. Erukhimovich, Sov. Phys. JETP **81**, 553 (1995).
[16] R. M. Ziff and G. Stell, J. Chem. Phys. **73**, 3492 (1980).
[17] M. Grant and W. B. Russel, Phys. Rev. E **47**, 2606 (1993).
[18] J. Bergenholz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).
[19] W. A. Petka *et al.,* Science **281**, 389 (1998).
[20] F. Ikkai and M. Shibayama, Phys. Rev. Lett. **82**, 4946 (1999).
[21] K. Kobayashi, C. i. Huang, T. P. Lodge, Macromolecules **32**, 7070 (1999).
[22] M. Rubinstein and A. N. Semenov, Macromolecules **31**, 1386 (1998).
[23] C. A. Angell and K. J. Rao, J. Chem. Phys. **57**, 470 (1972).
[24] S. K. Kumar and A. Z. Panagiotopoulos, Phys. Rev. Lett. **82**, 5060 (1999).
[25] A. Z. Panagiotopoulos, V. Wong, and M. A. Floriano, Macromolecules **31**, 912 (1998).
[26] P. G. DeGennes, *Scaling Concepts in Polymer Physics,* (Cornell University Press, Ithaca, 1979).
[27] C. J. Rueb and C. F. Zukoski, J. Rheol. **41**, 197 (1997).
[28] C. Crabb and J. Kovacs, Macromolecules **18**, 1430 (1985).
[29] K. F. Mansfield and D. Theodorou, Macromolecules **22**, 3143 (1989).
[30] F. Mallamace *et al.,* Phys. Rev. Lett. **84**, 5431 (2000).
[31] T. Odagaki, Phys. Rev. Lett. **75**, 3701 (1995).
[32] At the lowest temperature it is unclear if the dynamics have reached their Brownian limit. In this sense the diffusion coefficient value reported at this temperature represents an upper limit.
[33] C. Donati, S. C. Glotzer, P. H. Poole, W. Kob, and S. J. Plimpton, Phys. Rev. E **60**, 3107 (1999).
[34] A. Meller, T. Gisler, D. A. Weitz, and J. Stavans, Langmuir **15**, 1918 (1999).
[35] T. P. Stossel, Sci. Am. **271**, No. 3, 54 (1994).
[36] J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **111**, 7116 (1999).