Dynamical Studies of Polymeric Cluster Solutions Obtained near the Gelation Threshold: Glasslike Behavior

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We report preliminary dynamical structure-factor $G(q,t)$ measurements performed on polydisperse polymer cluster solutions at concentrations such that the largest clusters are partly penetrated by smaller clusters. Upon increase of the polymer concentration, the $G(q,t)$ profile goes from a stretched-exponential function, with an exponent which decreases as concentration increases, to a power-law function. These features suggest that the dynamical properties of this system exhibit glasslike behavior.

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Relaxation processes in random materials, mineral, polymeric, and spin-glasses, have attracted a great deal of attention in recent years.[1] From a theoretical point of view the analysis has mainly focused on spin-glasses where microscopic interactions can be well defined. Spin-glasses are magnetic systems where the spins are randomly coupled and for which an analysis of the time dependence of the susceptibility shows a nonexponential behavior.[2] A similar feature is exhibited in mineral and polymeric glasses,[3,4] where a nonexponential time dependence of the density correlation function is observed. The different approaches to explain such behavior are always based on the percolation concept.[5,6] Percolation allows a statistical description of the connectivity properties between a great number of objects, whatever these properties may be on a microscopic level.[7]

With these motivations in mind, we have studied the dynamical properties of interacting polymer clusters having a mass distribution of the percolation type. The system is polyurethane clusters obtained by chemical gelation. Gelation is the growth process of randomly multiconnected polymer clusters starting from multifunctional monomer units which can link together by chemical reaction.[8] At a precise degree of advancement of the reaction, the gel point, a giant cluster having a macroscopic size appears. Below the gel point, clusters of finite size are present, whereas above the gel point, the giant polymer cluster or gel phase coexists with the population of finite clusters. Dynamical measurements have been performed on such polyurethane clusters fixed in the melt. Quenching the chemical reaction, at different degrees of advancement below and near the gel point, allows us to obtain samples having their largest clusters at different sizes.

In order to characterize the system, intensity scattering experiments[9,10] were performed in the zero-concentration limit ($C \rightarrow 0$), and the following were found: (a) The polymer system is polydisperse; the mass distribution decays monotonically[9] as $M^{-\tau_p}$ with $\tau_p = 2.20 \pm 0.04$. (b) M_w, the mean weight average which characterizes the mean degree of connectivity of clusters, diverges at the gel threshold[10] as $\epsilon^{-\gamma}$ with $\gamma = 1.71 \pm 0.06$, where ϵ is the distance to the gel point. M_w is proportional to the intensity scattered per monomer, I/C, extrapolated to zero transfer vector. (c) The size of the largest cluster, R_Z, is related to the intensity scattered per monomer[10] by $R_Z \sim (I/C)^{1/(3-\tau_p)D}$, D being the fractal dimension of the swollen cluster[9] ($D = 1.98 \pm 0.03$). (d) The interaction parameter B,

$$(I/C)|_{q\rightarrow 0} = (I/C)|_{\substack{c\rightarrow 0\\ q\rightarrow 0}}[1 - 2BC + O(C^2)],$$

was measured and found[10] to be an increasing function of R_Z.

Here we are concerned with the dynamical properties of polyurethane clusters in solutions in a concentration range $C \gtrsim 4/B$ such that the smaller clusters partly penetrate the largest clusters.[11] We report preliminary results obtained by quasielastic light-scattering experiments performed at room temperature, far above the glass transition temperature of polyurethane ($T_g \approx -40\,°\mathrm{C}$). Using a correlator, we measure the time correlation function of the intensity scattered at a wave vector q,

$$\langle I_q(t) I_q(0)\rangle / \langle I_q\rangle^2 = AG^2(q,t) + 1 .$$

A is a numerical factor which depends on the geometry of the experiment and $G(q,t)$ is the dynamical structure

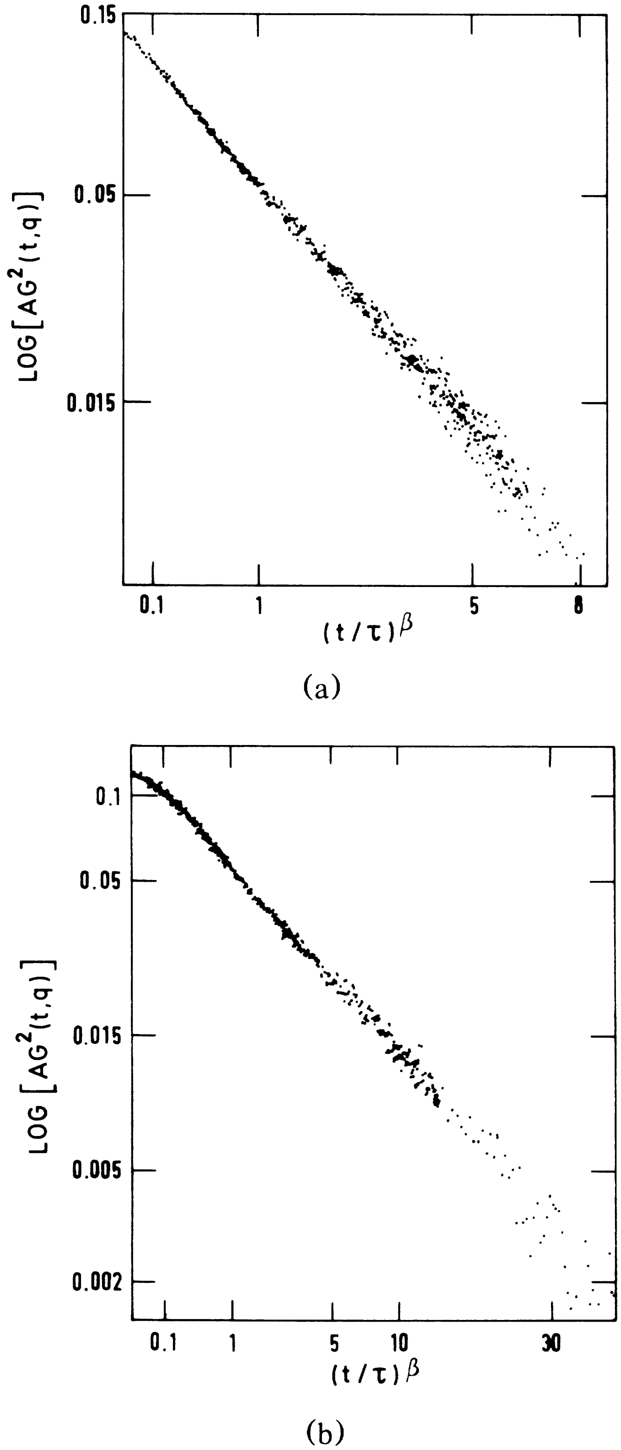

FIG. 1. Typical stretched-exponential profile of the square of the dynamical structure factor, $G^2(q,t) = \exp[-(t/\tau)^\beta]$, observed for $C < 6\times10^{-2}$ g/cm^3. Semilogarithmic scales, with marks on the abscissa which correspond to $(t/\tau)^\beta$ values (numerical values are t/τ values). (a) Sample with $R_Z = 2700$ Å, $C = 2.75\times10^{-2}$ g/cm^3, $\beta = 0.56$, and $\tau = 113$ μs; (b) sample with $R_Z = 485$ Å, $C = 4.6\times10^{-2}$ g/cm^3, $\beta = 0.4$, and $\tau = 95$ μs. Departure to stretched exponential occurs at the time (a) $t \approx 0.03\tau$ and (b) $\tau \approx 0.1\tau$.

factor. Here, the entities observed by light scattering are concentration fluctuations, and $G(q,t)$ is by definition the normalized correlation function of the concentration fluctuations:

$$G(q,t) = |\langle \delta C_q(t)\delta C_{-q}(0)\rangle| / \langle |\delta C_q|^2\rangle .$$

The profile of the square of the dynamical structure factor $G^2(t,q)$ is measured on a correlator time window such that $G^2(q,t)$ has a dynamical range of 100 (usually the time window is extremely wide and extends from 0.2 μs to 10 ms).

The profile of $G^2(q,t)$ changes drastically when the polymer concentration C is increased from 0.02 to 0.16 g/cm^3. Two different well-characterized profiles are observed: one at low concentration ($C < 6\times10^{-2}$ g/cm^3) and the other at a higher concentration ($C > 8\times10^{-2}$ g/cm^3). There exists a crossover regime for 6×10^{-2} g/cm$^3 < C < 8\times10^{-2}$ g/cm^3.

In the low-concentration regime, $C < 6\times10^{-2}$ g/cm^3, the square of the dynamical structure factor has a stretched-exponential profile, except for very short time windows ($t/\tau \ll 1$):

$$G^2(t,q) = \exp[-(t/\tau)^\beta] .$$

This is evident in Fig. 1, where we have plotted $\ln[AG^2(t,g)]$ as a function of $(t/\tau)^\beta$. A, β, and τ are determined by our fitting the experimental profile using a least-mean-squares program.

The exponent β, which is independent of the wave vector q, decreases as the concentration increases (see Fig. 2) but it is independent of the size R_Z of the largest cluster. Actually, we obtain $\beta = 0.46$ at $C = 4.5\times10^{-2}$ g/cm^3 with two samples which differ by a factor of 10 in R_Z.

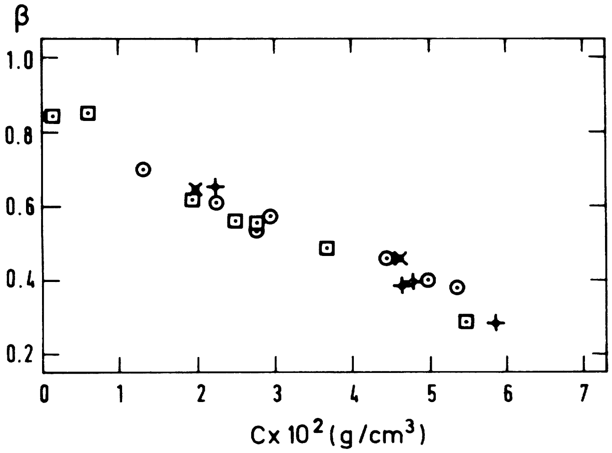

FIG. 2. Variation as a function of the polymer concentration of the exponents β which are independent of the size of the largest clusters. Crosses, plusses, squares, and circles represent samples having R_Z (Å) = 250, 480, 1200, and 2700, respectively.

This profile of $G^2(q,t)$ indicates that concentration fluctuations relax toward equilibrium with a continuous spectrum of relaxation times. Two mean values can be defined: the harmonic mean value τ_0,

$$\tau_0^{-1}=\lim_{t\to 0}\left\{-\frac{1}{2}\frac{d}{dt}[\ln G^2(q,t)]\right\}$$

and the arithmetic mean value $\langle\tau\rangle$,

$$\langle\tau\rangle=\int_0^\infty G(q,t)dt\,.$$

In the case of a stretched-exponential function, $\langle\tau\rangle$ is calculable from the measured values of β and τ:

$$\langle\tau\rangle=2^{1/\beta}(\tau/\beta)\Gamma(1/\beta)\,,$$

where Γ represents the gamma function. Experimentally, it is found that these two mean values are not proportional: They do not have the same q dependence. For a variation by a factor of 5 in q^2, $\tau_0 q^2$ is constant within 15%, whereas $\langle\tau\rangle q^2$ decreases by a factor 1.5. In order to determine the value at zero transfer vector, we used $\langle\tau\rangle q^2=\langle\tau\rangle q^2|_{q\to 0}(1-l^2q^2)$. One has to note that l^2 increases with R_Z^2 but is not directly proportional to R_Z^2. At a given concentration, using two samples which differ by a factor of 30 in R_Z^2, we find that l^2 changes only by a factor of 2.

In the high-concentration regime, $C>0.08$ g/cm^3, the dynamical structure factor scales as tq^2 (see Fig. 3). At short times ($t<\tau_0/4$), $G^2(q,t)$ could be approximated by an exponential function: $G^2(q,t)=\exp(-2t/\tau_0)$, where τ_0 is inversely proportional to q^2. At long times $t>\tau_0/4$, $G^2(q,t)$ is a power law (see Fig. 3):

$$G^2(q,t)\propto(t/\tau_0)^{-2\alpha}.$$

The exponent α is q independent but depends slightly on R_Z and on the concentration. For a given sample ($R_Z=1200$ Å), α increases from 0.2 to 0.3 as the concentration increases from 0.08 to 0.16 g/cm^3. For a given concentration ($C=0.11$ g/cm^3), α takes the values of 0.38, 0.26, 0.25, and 0.23 for $R_Z=250$, 480, 1200, and 2700 Å, respectively.

This profile indicates that concentration fluctuations relax to zero with a spectrum of relaxation times of which the longest time is infinite. However, as the samples are viscous, the longest time is infinite in the time scale of quasielastic light-scattering experiments but finite in the time scale of rheological experiments.

From these results, we deduce two diffusion coefficients which are not proportional (see Fig. 4). Over the whole concentration domain, $D_0=1/\tau_0q^2$ increases as

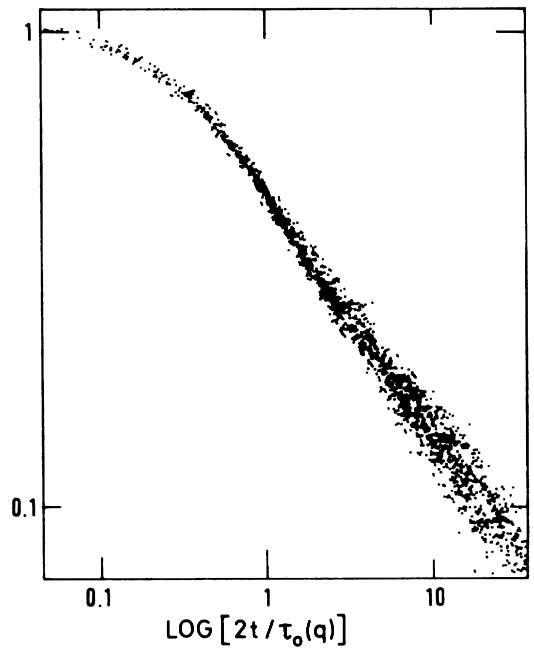

FIG. 3. Log-log plot of the power-law profile of the square of the dynamical structure factor $G^2(t,q)\sim(2t/\tau_0)^{-2\alpha}$ with τ_0 determined from the short-time behavior of $G^2(t,q)$ (q^2 dependent) observed at three different q vectors [$q\times10^{-5}$ (cm^{-1})$=1.78$, 3.21, 3.60]. The best fit of the linear part of the curve yields $\alpha=0.25$. The data reported were obtained with a sample having an R_Z value of 1200 Å and a concentration of 0.11 g/cm^3. Such typical behavior is obtained if the concentration is larger than 8×10^{-2} g/cm^3.

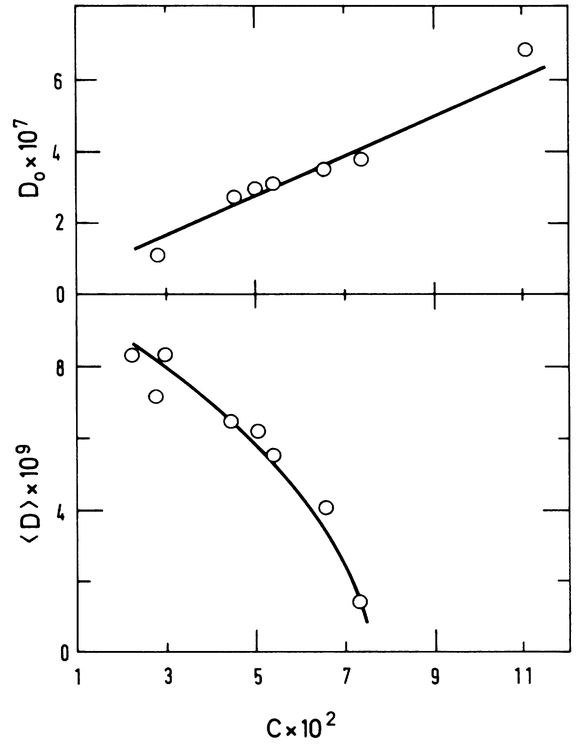

FIG. 4. Variation of the diffusion coefficients D_0 and $\langle D(q\to 0)\rangle$ deduced from the harmonic and arithmetic mean time values, respectively. The data reported are measured on a sample having an R_Z value of 2700 Å and the unit used for the diffusion coefficient is cm^2/sec.

the concentration increases and depends slightly on R_Z. In the concentration regime $C < 7.5 \times 10^{-2}$ g/cm^3, the mean diffusion coefficient $\langle D \rangle = 1/\langle \tau \rangle q^2 |_{q \to 0}$ is a decreasing function of R_Z and decreases as the concentration increases.

The striking fact of these results is their similarity to the time decay of magnetization observed in spin-glasses[2] or the quasielastic light scattering observed on polymeric glasses,[4] near the glass transition temperature T_g. For temperature higher than T_g, in both cases a stretched-exponential behavior is found with an exponent β which decreases as T_g is approached and reaches the value $\frac{1}{3}$ at T_g. For temperature lower than T_g, a power-law profile is observed.

In our case, the inverse of the concentration seems to play the same role as temperature in the case of glasses. In the crossover concentration regime between 6×10^{-2} g/cm^3 and 7.5×10^{-2} g/cm^3, the square of the dynamical structure factor presents roughly three behaviors: (1) at shortest time, an exponential profile; (2) at longest time, a cutoff function having approximately a stretched-exponential behavior; (3) at intermediate time, a power-law function.

These findings are similar to those obtained in spin-glasses when the glass transition is approached from above.[12] However, in the high-concentration regime ($C > 8 \times 10^{-2}$ g/cm^3), the exponent α of the power law increases as the concentration increases, whereas α, in spin-glasses, decreases as the inverse of the temperature increases.

Pursuing further the analogy to spin-glasses, we find that the experimental values of $\langle D \rangle$ vary as a power law of $C - C_f$, where C_f is the concentration at which $\langle D \rangle$ goes to zero or equivalently where the longest relaxation times goes to infinity. At this concentration and for $C > C_f$, concentration fluctuations affect all the clusters which are interacting dynamically. As a preliminary result, we find that $\langle D \rangle \sim (C - C_f)^x$, with $0.5 < x < 1$ and $C_f \approx 7.5 \times 10^{-2}$ g/cm^3, independent of R_Z. We plan to continue this work in order to determine precisely the behavior of D_0 and $\langle D \rangle$ with R_Z and the concentration.

We note that we are dealing with two percolation thresholds: a threshold linked to spatial connectivity which can be approached by the change of the degree of advancement of the chemical reaction, and a dynamic threshold which can be approached, for a given advancement of the chemical reaction, by the change of the concentration. Above a given concentration, perturbations cause a cascade of energy dissipation on all length scales.[13]

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