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Clustering, glass transition and gelation in a reactive fluid

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Abstract

We study the dependence of the dynamics on the size of particle clusters that grow by stepwise aggregation in a two-component reactive mixture. The data reveal the cluster property involved in the glasslike arrest and its quantitative link with the structural relaxation time. Specifically, we measured the number-average cluster size x_n —i.e., the average number of bonded monomers per molecule—and, independently, the characteristic time τ for decay of the photon correlation function, throughout the reaction. We find that x_n diverges as the system freezes at the glass transition, x_n and τ being exponentially related. The comparison with the gel transition that occurs at the divergence of the weight-average cluster size provides evidence that the two transitions are associated to distinct properties of the same underlying clustering process.

1. Introduction

Glass formation entails slowing down the particles in a liquid to such an extent that the structure of the liquid is no longer able to change over the duration of a macroscopic experiment. Gel formation entails increasing the shear viscosity in a liquid to such an extent that the ability of the system to flow is lost. Disparate fluids can evolve into structurally arrested states, either of glass or gel type, with different variables serving as a control parameter. Glass and gel phases are found in molecular liquids, colloidal suspensions, proteins, micelles, and other aggregates, where such phases can be induced by changing temperature, pressure, particle concentration or some chemically relevant parameter such as pH or ionic strength. Moreover, they can result from a polymerization reaction that converts initially liquid monomers into

macromolecules. Understanding the nature of these arrested states and their distinguishing features poses an outstanding problem to the physics of condensed matter [1–4]. In this respect, reactive systems exhibit a great potential: they can be used to test experimentally certain ideas that involve quantities difficult to measure in other real systems [5], and can reveal important aspects of universality in the dynamics of different systems [6]. Here, we concentrate on the idea that particle clusters may be at the core of glass formation—as suggested by cooperativity studies [7–14] in conjunction with the Adam–Gibbs model [15]—as well as of gel formation, and investigate how the dynamics and clustering are, in fact, fundamentally related.

We focus on step polymers [16] because of their characteristics. First, clustering of a rather specific type is involved in their formation. In contrast to chain polymers [16], the topology of step-growing clusters closely resembles that of clusters of dynamically correlated particles observed in simulation of supercooled liquids (see, e.g., figure 1 in [7, 14]). Second, a rich phase diagram is possible including gel and glass phases. When monomers with sufficiently high functionality (i.e., reactive groups per molecule) bond to each other, they generate three-dimensional branched molecules that can develop into a network structure spanning a macroscopic portion of the sample (gel), before further developing into a rigid glass. Third, size distributions of molecular clusters are theoretically predicted [17], from which average sizes can be calculated, upon ideal conditions that can approximately be met in real systems. In particular, while the weight-average cluster size x_w depends on a number of factors, the number-average cluster size x_n (i.e., the average number of monomers per molecule) turns out to be only dependent on the functionality of the reagents and the number of bonds created.

By exploiting these advantageous characteristics of the step-growth mechanism, we have previously been able to establish a connection of the glassy dynamics in reactive systems with configurational entropy models [6], and to study the connection between particle clustering and cooperative dynamics [5]. In this paper, we study in more depth the relation between clustering and arrested states, with an emphasis on the gel–glass relationship. Specifically, we study the dependence of the dynamics on the size of particle clusters that grow by stepwise polymerization in a two-component reactive mixture, and show that this may be informative of the relation existing between the gel and glass transitions.

2. Materials and experiments

The system we study is a mixture of an epoxide—diglycidyl ether of bisphenol-A (DGEBA)—with an aliphatic amine—diethylenetriamine (DETA)—which react by stepwise polyaddition. In reacting, DGEBA is a bifunctional monomer and DETA is pentafunctional. The two chosen substances are reacted isothermally in different molar ratios $N_e:N_a$, including a moderate excess of epoxide (DGEBA-DETA 10:3), the stoichiometric mixture (DGEBA-DETA 5:2), and an increasing excess of the amine (DGEBA-DETA 5:2.8, DGEBA-DETA 4:3, DGEBA-DETA 10:9). For each mixture, the reaction temperature is set low enough for the rate of reaction to be lower than the relaxation rate, so that no appreciable reaction occurs over a relaxation measurement.

The structural dynamics of our reactive system is monitored by depolarized photon correlation spectroscopy, probing optical anisotropy fluctuations, which arrest at the glass transition. The technique is blind to the formation of a gel phase [20], which also may occur in DGEBA-DETA mixtures [17]. Autocorrelation functions of the scattered field are obtained at different reaction times, using equipment and procedures as described previously [20]. A fair compromise between a negligible advancement of the reaction (full duration ~ 7 h) during an acquisition and a reasonable signal-to-noise ratio is achieved with an acquisition time of 2 min

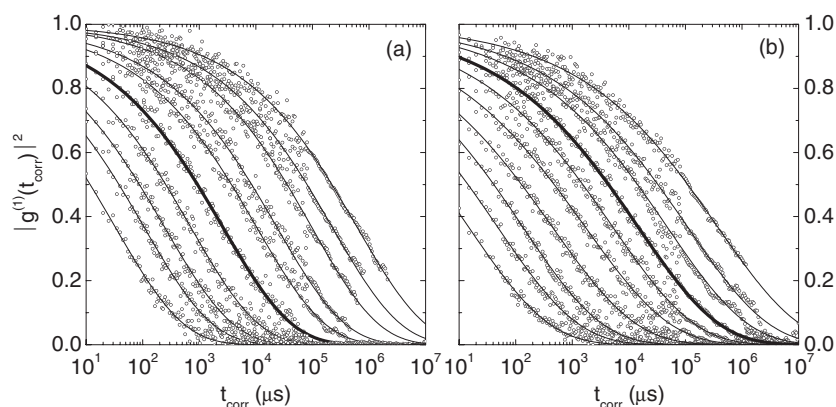


Figure 1. Normalized autocorrelation functions $g^{(1)}(t_{\text{corr}})$ of the system (a) DGEBA-DETA 4:3 at 30 °C, and (b) DGEBA-DETA 5:2.8 at 26 °C. Solid lines represent the best fit with a stretched exponential. The bold line indicates the gelation point as calculated from [16].

for each spectrum. Examples of the bonding-driven evolution of the normalized autocorrelation functions $g^{(1)}(t_{\text{corr}})$ are given in figure 1 for two compositions investigated. The time decay of $g^{(1)}(t_{\text{corr}})$, reflecting structural relaxation, is well described by a stretched exponential (solid lines) shifting toward longer correlation times on increasing the amount of covalent bonds. From the fit procedure a structural relaxation time τ is obtained for any time of reaction t , spanning a dynamic range of about five decades. Some of our measurements extend across the gelation point, as shown with bold lines in figure 1, but no observable change of the dynamics occurs in the autocorrelation function. In particular, the stretching exponent (between 0.21 and 0.37 depending on the mixture) is constant during reaction.

The extent of reaction at any time t is measured by the epoxy conversion α , i.e., the fraction of epoxy groups that have reacted until then. To determine α we exploit the heat release associated with bond formation. At any reaction time t , α is measured via differential scanning calorimetry by the ratio $\Delta H(t)/\Delta H_{\text{tot}}$, where $\Delta H(t)$ is the heat released up to the time t , and ΔH_{tot} is the heat release associated to the total consumption of epoxy functional groups (figure 2(a)). From repeated measurements we estimate the accuracy of our conversion data to be 1.5%.

From the calorimetric and photon-correlation measurements, the extent of reaction and the structural relaxation data versus time are known for the different reacting systems. Figure 2(b), where the data of τ are plotted as functions of α , shows that in the range investigated (at least five time decades within the region relevant to assess the near-glass transition behaviour, i.e., for $\tau > 10^{-5}$ s) the progressive slowdown of the dynamics strongly resembles the classical vitrification process of supercooling, with a rapidly increasing and apparently diverging relaxation time at sufficiently high conversions.

3. Results and discussion

The choice of our reactive system heavily relies on known features of the reaction mechanism [18] that make it easy to determine the values of x_n and x_w . First, the basic reaction taking place is the addition of the amino hydrogen to the epoxy group, while other types of reaction can be neglected, or suppressed, avoiding large excess of epoxide. Second, the occurrence of reactions intramolecularly, with the formation of rings, is negligible in species of

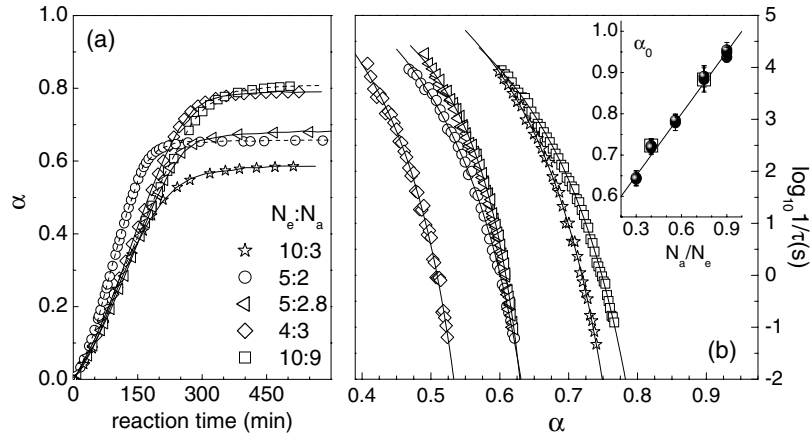


Figure 2. (a) Conversion of epoxy groups, α , as a function of the reaction time for five DGEBA-DETA $N_e:N_a$ compositions as indicated. Each composition is reacted isothermally (temperature not indicated). (b) Dependence of the structural relaxation time, τ , on the epoxy conversion, α , for the same reactions as in panel (a). Solid lines represent the best fit with $\tau = \tau_0 \exp[B/(1 - \alpha/\alpha_0)]$. In the inset: dependence of the divergence point α_0 on the molar ratio N_a/N_e between the amino and epoxy components. Open squares are used to distinguish a different reaction temperature. The solid line is $1/\bar{f} = [1 + (N_a/N_e)]/2$, where \bar{f} is the average epoxy functionality.

finite size because of the rigidity of the DGEBA molecule. Finally, an almost equal reactivity of all functional groups can be assumed, as the substitution effect in the amino group of aliphatic amines is generally non-negative and the reactivity of both epoxy groups in DGEBA is the same. Following Flory [17] and Stockmayer [19], under these conditions one has

$$x_n(\alpha) = 1/(1 - \bar{f}\alpha) \quad (1)$$

where α is the epoxy conversion, and $\bar{f} = 2N_e/(N_e + N_a)$ denotes the average epoxy functionality of the system, i.e., the average number of epoxy groups per monomer initially present in the mixture. A more complex expression, instead, gives x_w as a function of the extent of reaction [19]. For our system, it specializes into

$$x_w(\alpha) = \frac{1}{\bar{M}_0} \frac{(N_a/N_e)[1 + (2N_e/5N_a)\alpha^2]M_a^2 + [1 + (8N_e/5N_a)\alpha^2]M_e^2 + 4\alpha M_a M_e}{(M_a N_a/N_e + M_e)[1 - (8N_e/5N_a)\alpha^2]} \quad (2)$$

where $M_a = 103.17$ and $M_e = 348$ are the molecular masses of the amino and epoxy reagents, respectively, and $\bar{M}_0 = (M_a + M_e)/2$ denotes the average monomer mass. Thus, knowing the amount of reagents for a given mixture and measuring α enables us to calculate, from equations (1) and (2), the average sizes x_n and x_w of molecular clusters making up the system at any time of reaction. It should be noted that according to equations (1) and (2) both x_n and x_w display critical behaviour, with a divergence at $\alpha = 1/\bar{f} = [1 + (N_a/N_e)]/2$ and $\alpha = \sqrt{5N_a/8N_e}$, respectively. The molar ratio of the amino and epoxy reagents in the initial mixture, N_a/N_e , is therefore the one and only control parameter of the critical behaviour of x_n and x_w . We have used this tunability to generate systems whose number-average cluster size diverges for very distinct values of α between 0.65 and 0.95, as the weight-average cluster size does for values between 0.43 and 0.75.

On increasing α , an increase of both the size of the step-growing clusters and of τ occurs. Figure 3 addresses the problem of how the dynamic slowdown and the attendant clustering process relate to each other, by showing $\log \tau$ versus x_n and $\log \tau$ versus x_w for different reactions. In the format of figure 3(a) the strongly nonlinear behaviour of $\log \tau$ versus α (see

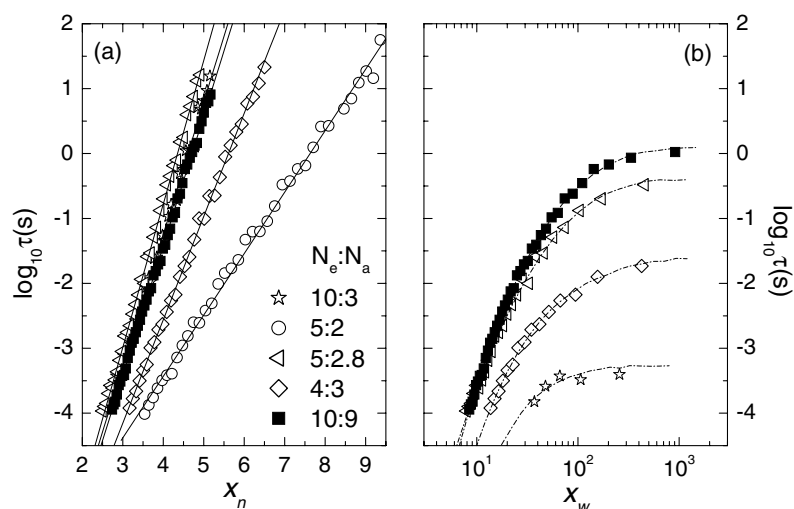


Figure 3. (a) Semilogarithmic plot of the structural relaxation time, τ , versus the number-average cluster size x_n for the same reactions as in figure 2. (b) Bilogarithmic plot of τ versus the weight-average cluster size x_w (only the data corresponding to a finite value of x_w can be shown). The dash-dot lines are guides for the eyes.

figure 2(b)) is surprisingly linearized, revealing that the x_n dependence of τ can be represented with astonishing accuracy by an exponential law, that is, $\tau \propto \exp(Bx_n)$. This means that the relaxation time diverges, determining a structurally arrested glass state, when x_n becomes infinite. To rule out the possibility that the representation in figure 3(a) has a poor sensitivity to the value of \bar{f} used to calculate the abscissa x_n , we analyse directly our data of τ as a function of α . Because an exponential variation of τ with x_n implies $\tau \propto \exp[B/(1 - \bar{f}\alpha)]$, for each reaction we fit the data with $\tau = \tau_0 \exp[B/(1 - \alpha/\alpha_0)]$, and compare the divergence point α_0 with $1/\bar{f}$ (inset of figure 2(b)). We observe that the variation of α_0 strictly follows the expected variation of $1/\bar{f}$. Moreover, it is independent, as expected, of the reaction temperature. These results, demonstrating that the dynamical arrest in our system is controlled by its average functionality, corroborate the key finding that glassy freezing is achieved when x_n diverges.

Our finding brings out a major difference between the glass and gelation transitions in terms of the property of the cluster-size distribution which is relevant to the transition: a glass state results when the average number of particles in a cluster (x_n) tends to infinity; by contrast, there are sufficient experimental results [17, 21] to assert that the gelation transition, manifested by an infinitely high value of the shear viscosity η , occurs when the weight-average cluster size x_w diverges due to the formation of the first particle network of macroscopic size. Since x_n increases during reaction, but more slowly than does x_w , when the flow properties indicate gel-like solidification, structural rearrangements are still possible with a relatively short τ (see figure 1). This decoupling between the behaviours of η and τ in stepwise polymers is emphasized in figure 3(b), which confronts the data of τ with the relation that correlates the shear viscosity to x_w , i.e., a power law $\eta \propto x_w^\alpha$ [21]. If τ were to couple with η , $\log \tau$ should be linear versus $\log x_w$. Instead, figure 3(b) shows that the data deviate from linearity and asymptotically tend to a finite, even small value of relaxation time. On this basis, one should note the failure for step polymers of the Debye–Stokes relation, used to understand the relationship between the rotational correlation time and the shear viscosity in molecular liquids.

Our measurements reveal the specific cluster property involved in the glasslike arrest and its quantitative link with the structural relaxation time. As was previously evidenced [5], the specific exponential link of τ with x_n can be conveniently interpreted in the frame of the Adam–Gibbs model for simple liquids. In this frame, built on the idea of cooperatively rearranging regions (CRRs) of progressively increasing size, an exponential variation of τ with x_n , in a process at constant temperature, supports a direct relationship between x_n and the size z of the CRRs. In fact, the basic relationship $\tau \propto \exp(z\Delta\mu/k_B T)$, where $\Delta\mu$ is a free-energy barrier per particle, almost constant, translates at constant T into $\tau \propto \exp(Bx_n)$ if x_n provides a measure of the CRRs' size. This is interesting in the light of analogous findings from numerical simulations of supercooled liquids [7, 14]. While the CRRs are not precisely defined, a recent simulation study of supercooled water [14] has considered the possibility that the average size of molecular clusters formed by particles with spatially correlated motion relates to the size of the CRRs. As one can argue that the average number of particles that exhibit correlated displacements in step polymer systems grows proportionally to x_n , our results strongly support this new idea experimentally.

4. Conclusions

Clustering comes up in the context of general understanding of both gelation and glass transitions. Step polymerizations provide useful insight into which cluster property is directly involved in each phenomenon. In a reactive epoxy–amine mixture, where branched clusters of bonded monomers grow randomly and their number-average and weight-average sizes, x_n and x_w , can be measured, we have found that x_n diverges as the system freezes at the glass transition ($\tau \rightarrow \infty$) as probed by depolarized photon correlation measurements. More specifically, we provide experimental evidence that the structural relaxation time relates to x_n in the form of an exponential law. The comparison with the gel transition ($\eta \rightarrow \infty$), which occurs at the divergence of the weight-average cluster size, shows that the two transitions are associated to distinct properties of the same underlying clustering process.

Interestingly, x_n relates to the structural relaxation time in a manner formally similar to that predicted for the size of the cooperatively rearranging regions within the Adam–Gibbs model for glass forming liquids. Insofar as x_n provides a measure of the average size of molecular clusters formed by particles with spatially correlated motion, our finding has an analogy in numerical simulation results for supercooled liquids. Despite the differences between supercooling and polymerization, it appears that glass formation relies on a common property of the underlying clustering process. This opens the way to a more extensive use of step polymer systems for obtaining quantitative information on aspects relevant to the structural arrest of condensed matter.

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