

Clustering and Cooperative Dynamics in a Reactive System

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We study the dependence of the dynamics on the size of particle clusters that grow by stepwise aggregation in a reactive epoxy-amine mixture. The data reveal the cluster property involved in the glasslike arrest and its quantitative link with the structural relaxation time. We find that the number-average cluster size x_n governs the formation of a glassy phase as distinct from a gel phase, and that x_n correlates to the size of the “cooperatively rearranging regions” postulated by the Adam-Gibbs model for glass forming liquids. These results suggest that the step polymerization process generates clusters that behave much like dynamical heterogeneities observed in supercooled liquids.

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Disparate fluids can evolve into an amorphous, solid, glass state, with different variables serving as a control parameter. A glasslike solidification process occurs in most liquids when cooled or compressed, in colloidal suspensions when the packing fraction increases [1], in reactive systems when monomers associate to form polymer structures [2]. Some of these systems, like colloidal suspensions with attractive interparticle interaction [3] and three-dimensional step polymers [4], also share an ability to form a gel phase. While it is not initially clear to what extent a common approach can be exploited to interpret the behavior of different systems, we consider that reactive glass formers are a potential for studying the fundamental mechanisms involved in the structural arrest of matter, and can be used to test experimentally certain ideas that involve quantities difficult to measure in other glass formers. Specifically, we concentrate on the idea that clusters of correlated particles are at the basis of glass formation and investigate how the dynamics and clustering are, in fact, intimately related.

The idea of cooperative molecular motion is commonly invoked to rationalize increasingly sluggish response of a system near its glass transition. Cooperativity has been observed experimentally [5–8] and via computer simulations [9–12] to take the form of transient molecular clusters, reflecting spatially heterogeneous dynamics. A recent simulation study [12] of supercooled water considered the possibility that the average size of these clusters relates to the size of the cooperatively rearranging regions (CRRs) postulated by the Adam and Gibbs (AG) theory [13]. In a dielectric noise experiment [6] the clusters lifetime was found comparable to the timescale for structural relaxation. An indication that dynamics and clustering might be re-

lated also emerges from a Flory-Huggins model of equilibrium polymerization [14]. However, experimental studies providing evidence for a quantitative connection between clusters of correlated particles and formation of a glassy phase are lacking, generally prevented by the absence of direct access to relevant cluster properties in real systems.

Here we exploit particle clustering that occurs by covalent interactions in a two-component step polymerizing mixture, where polymerization proceeds via the formation of chemical bonds at random between pairs of mutually reactive monomers [4]. Step polymerization is a self-organization process able to generate *permanent* molecular clusters similar in shape (i.e., stringlike or branched) to the transient ones observed in simulations of simple liquids [10,12]. While their geometry and mass distribution depends on a number of factors [4], their average size x_n (i.e., the average number of monomers per molecule) turns out to be only dependent on the functionality (i.e., reactive groups per molecule) of the reagents and the number of bonds created. We measured x_n and, independently, the characteristic time τ for decay of the photon correlation function, throughout reaction. Both x_n and τ display critical behavior. We find that increasing the average size of clusters of bonded particles causes the dynamics to slow down progressively in such a way that, differently from gelation, an arrested glass state forms ($\tau \rightarrow \infty$) when x_n diverges. The location of this arrested state can be tuned using the molar ratio of the reagents as the only control parameter. We interpret our results in the context of the AG theory, and find a close parallel between the size of the CRRs and the average cluster size.

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 step-wise polyaddition. The choice of our reactive system heavily relies on known features of the reaction mechanism [15] that make it easy to determine the value of x_n . 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 finite size because of the rigidity of the DGEBA molecule. Following Flory [16], under these conditions one can show that, at any time of reaction, $x_n(\alpha) = 1/(1 - \bar{f}\alpha)$, where α is the epoxy conversion, i.e., the fraction of epoxy groups that have reacted till then, and \bar{f} denotes the average epoxy functionality of the system, i.e., the average number of epoxy groups per monomer initially present in the mixture. If N_e moles of DGEBA and N_a moles of DETA are mixed to form the system DGEBA-DETA $N_e:N_a$, one has $\bar{f} = 2N_e/(N_e + N_a)$ [17]. To determine the epoxy conversion α we exploit the heat release associated with bonds formation. At any reaction time t , α is measured via differential scanning calorimetry by the ratio $\Delta H(t)/\Delta H_{\text{tot}}$ (per gram of mixture), 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 [18]. From repeated measurements we estimate the accuracy of our conversion data to be 1.5%. Thus, knowing \bar{f} for a given mixture and measuring α enables us to calculate the average size x_n of molecular clusters making up the system at any time of reaction. The two chosen substances are reacted isothermally in different ratios, including a moderate excess of epoxide (DGEBA-DETA 10:3, $\bar{f} = 1.538$), the stoichiometric mixture (DGEBA-DETA 5:2, $\bar{f} = 1.428$), and an increasing excess of the amine (DGEBA-DETA 5:2.8, $\bar{f} = 1.282$; DGEBA-DETA 4:3, $\bar{f} = 1.143$; DGEBA-DETA 10:9, $\bar{f} = 1.053$). For each mixture, the reaction temperature is set low enough for the rate of reaction to be lower than the relaxation rate, so that the state of the system at any given α could be seen as a quasi-equilibrium state, and no appreciable reaction occurs over a relaxation measurement. An important aspect needs to be underlined, which motivates our choice to investigate different compositions: x_n displays critical behavior, with a divergence at $\alpha = 1/\bar{f} = [1 + (N_a/N_e)]/2$. The molar ratio of the amino and epoxy reagents in the initial mixture can therefore be used as the one and only control parameter of the critical behavior of x_n . We use this tunability to generate systems whose average cluster size diverges for very distinct values of α between 0.65 and 0.95.

The structural dynamics of our reactive system is monitored by VH depolarized photon correlation spectroscopy, probing optical anisotropy fluctuations, which arrest at the glass transition. Instead, the technique is blind to the formation of a gel phase [19], which also may occur in

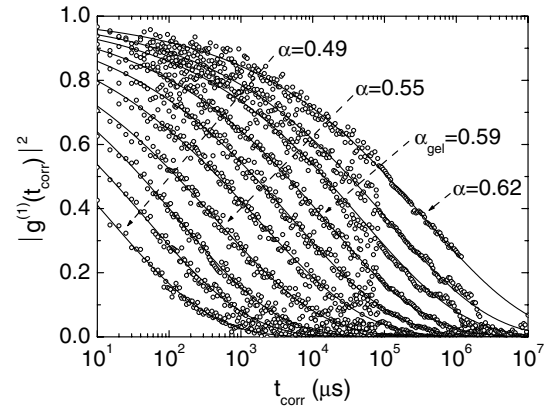


FIG. 1. Changes induced in the normalized autocorrelation function $g^{(1)}(t_{\text{corr}})$ of the system DGEBA-DETA 5:2.8 by increasing the amount of covalent bonds formed at 26 °C (some epoxy conversions α are indicated; the gel point is calculated from Ref. [4]). Fair compromise between a negligible 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 for each spectrum. The time decay of $g^{(1)}(t_{\text{corr}})$, reflecting structural relaxation, is well described by a stretched exponential (solid lines).

DGEBA-DETA mixtures [16]. Autocorrelation functions of the scattered field are obtained at different reaction times (e.g., see Fig. 1), using equipment and procedures as described previously [19]. It can be seen in Fig. 1 that they exhibit features typical of usual glass formers—stretched exponential decay, and progressive shift toward longer correlation times—although with a bonding-driven evolution. The stretching exponent (between 0.21 and 0.37 depending on the mixture) is constant during reaction. Some of our measurements extend across the gelation point but no observable change of the dynamics occurs in the autocorrelation function. A structural relaxation time τ for any α is obtained as described in Ref. [19], and shown in the inset of Fig. 2. In the range investigated (at least five time decades within the region relevant to assess the near-glass transition behavior, i.e., for $\tau > 10^{-4}$ 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.

With both the x_n and the τ data, independently determined, we now study how they relate to each other. Figure 2 addresses this issue, by showing $\log \tau$ versus x_n for different reactions. In this format the strongly nonlinear behavior of $\log \tau$ versus α (see inset) is surprisingly linearized, revealing that the x_n dependence of τ is expressed remarkably well 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 the average size of particle clusters becomes infinite. This brings out a major difference between the glass and gelation transitions in terms of the property of the cluster-size

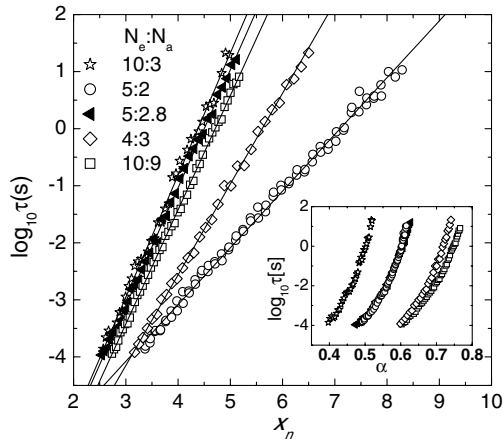


FIG. 2. Semilogarithmic plot of the structural relaxation time τ vs the average size x_n of clusters grown by polymerization, for five DGEBA-DETA $N_e:N_a$ compositions as indicated. The data follow straight lines for more than five decades in τ . In the frame of the AG model, an exponential variation 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. Inset: Dependence of τ on the epoxy conversion, α , for the same reactions as in the main frame.

distribution which is relevant to the transition: A glass state results when the number-average value of the particles in a cluster (x_n) tends to infinity; by contrast, the gelation transition is known [16] to occur when the weight-average cluster size x_w diverges due to the formation of the first particle network of macroscopic size. As a reaction proceeds x_n increases, but more slowly than does x_w . Thus, when the flow properties or the density fluctuations indicate gel-like solidification, structural rearrangements are still possible with a relatively short τ (see Fig. 1).

To rule out the possibility that the representation in Fig. 2 has a poor sensitivity to the value of \bar{f} used to calculate the abscissa x_n , we analyze directly our data of τ as a function of α . Because an exponential variation of τ with x_n implies $\tau \propto \exp[B/(1 - \bar{f}\alpha)]$, one expects the $\tau(\alpha)$ data to be described by a well-defined form—Vogel-Fulcher-Tamman like [20]—with an apparent divergence at $\alpha = 1/\bar{f}$. For each reaction, we fit the data with $\tau = \tau_0 \exp[B/(1 - \alpha/\alpha_0)]$, and determine the divergence point α_0 , together with τ_0 and B , by a least-squares minimization procedure. The derived values for α_0 are reported in Fig. 3, as a function of the molar ratio between the monomer constituents. The data (symbols) are shown with error bars, which we estimate ranging from $\pm 1.5\%$ (for DGEBA-DETA 5:2.8) to $\pm 3\%$ (for DGEBA-DETA 4:3), α representing a major source of error. In the same figure, the straight line represents $1/\bar{f}$. There is a clear increase of α_0 by increasing N_a/N_e ; that is, the higher the relative amount of the amino reagent, the higher the conversion at which the relaxation time tends to diverge. More importantly, Fig. 3 reveals that α_0 not only changes with the mixture composition but (within the

experimental error) actually follows the expected linear variation of $1/\bar{f}$ with N_a/N_e , in a wide N_a/N_e range spanning excess both of amino and epoxy functional groups. Notice that the temperature, while having an implicit role, does not appear explicitly in the expression of x_n ; therefore, the point of structural arrest should be independent of it. Indeed, the temperature of reaction is different for each mixture investigated. Moreover, the same arrested point is obtained by reacting a given mixture at different temperatures, despite the time-dependent evolution is greatly affected. This is shown in Fig. 3 by filled and open symbols. In the same figure, isoabscissa filled points refer to reactions repeated at the same temperature to check reproducibility. These results demonstrate unequivocally that the dynamical arrest in our system is controlled through its molar composition, whose variation causes the average functionality of the system to change. This effect, never reported before, corroborates the key finding that glassy freezing is reached when x_n diverges, which constitutes a distinguishing feature from the gelation transition.

The AG model provides a convenient framework for interpreting our finding. Owing to the random nature of the step-growth mechanism and the rigidity of covalent bonds, provided x_n has not grown very much (as it is the case in the α range investigated, see Fig. 2) we argue that a monomer involved in a rearrangement is likely to take its bonded monomers along, and in any case all the monomers in a molecule must retain spatially correlated motions, so that the average number of particles in the system that exhibit correlated displacements grows proportionally to x_n . The AG model explains the increase of the relaxation time in a system as it nears the glass transition in terms of

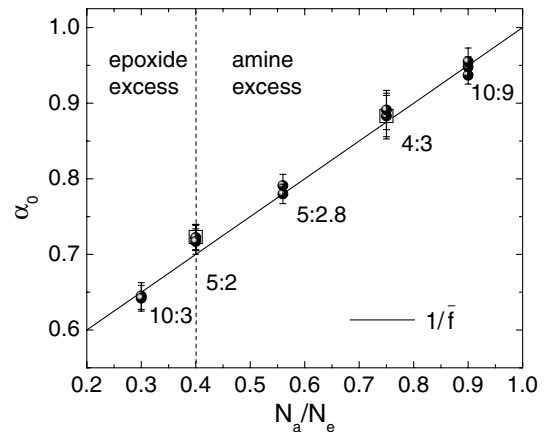


FIG. 3. Dependence of the divergence point α_0 on the molar ratio N_a/N_e between the amino and epoxy components in the system DGEBA-DETA $N_e:N_a$. The experimental points for different compositions are labeled by their $N_e:N_a$ values; a vertical line marks the stoichiometric composition. Open squares 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.

an increase in the CRRs' size z , which eventually diverges. The relationship is $\tau \propto \exp(z\Delta\mu/k_B T)$, where $\Delta\mu$ is a free-energy barrier per particle, almost constant. Therefore, in case x_n measures the number of particles in a CRR, exactly the relation $\tau \propto \exp(Bx_n)$ should prove satisfied for any reaction at constant T , as we find to be the case. Notably, the connection we find experimentally between a cluster property and a property of cooperative relaxation near the bonding-driven glass transition parallels the one observed in liquid water simulated near the mode-coupling transition [12]. In passing, we also note that in our initial mixtures a small cooperativity is expected [21] (τ extrapolates to $\sim 10^{-7}$ – 10^{-8} s at $x_n = 1$); hence, the number of particles which cooperate to move at any time of reaction should be of the order of x_n . At $\tau \sim 10^2$ s (a reference value for the experimental liquid-glass transition) we find x_n does not exceed ten particles, consistent with simulations of supercooling [10,12].

In conclusion, in a reactive epoxy-amine mixture, where branched clusters of bonded molecules grow randomly and their average size x_n can be measured, we have found that x_n diverges as the system freezes at the glass transition, as probed by photon correlation. The comparison with the gel transition, which occurs at the divergence of the weight-average cluster size, evidences that the two transitions are associated to distinct properties of the underlying clustering process. The quantity x_n provides a measure of the growing range of the spatial correlations in the monomer motions, and identifies a diverging length scale associated with the cooperative dynamics of the system. Interestingly, in the frame of the AG model x_n actually correlates to the size of the CRRs postulated by the theory. An important aspect of the findings reported here is the analogy with the physics of supercooling. The step polymerization process seems to be an efficient mechanism to generate clusters that, although they are of a nontransient nature, behave much like dynamical heterogeneities observed in supercooled liquids. It appears that glass formation relies on a common property of the clustering process. It appears that a common link exists between the cluster size and the structural relaxation time. While information about particle clusters in supercooled liquids are difficult to obtain experimentally, knowledge of the reaction mechanism in step polymers allows one to access specific cluster features, and to some extent, to control related dynamic behaviors—as we have shown by tuning the structural arrest in our system by varying the relative amounts of the reactive species. This might be exploited further for obtaining new insight into the relation between gel and glass formation, a still open issue in the physics of dynamically arrested states of matter.

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- [18] In practice, we measure the conversion of the functional groups which are initially present in minority: $\Delta H(t)/\Delta H_r$, with ΔH_r the total heat of reaction. This conversion corresponds with the conversion α of epoxy groups in the mixtures with no excess of epoxide. Otherwise, it corresponds with the conversion α_a of amino groups, $\alpha_a = (2N_e/5N_a)\alpha$. For each mixture investigated, ΔH_r is the mean value of up to ten determinations (standard deviation $\sim 1\%$) from independent dynamic scans at different heating rates, each performed on a fresh sample.
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- [20] Any deviations from the predicted form are revealed as deviations from a straight line in Fig. 2 and hence clearly identifiable. Since previous workers [e.g., M. A. Golub and N. R. Lerner, *J. Appl. Polym. Sci.* **32**, 5215 (1986); R. Casalini *et al.*, *Chem. Phys. Lett.* **258**, 470 (1996); G. Gallone *et al.*, *Polym. Int.* **50**, 545 (2001)] have successfully interpreted their data for epoxy-amine systems in terms of an empirical law formally equivalent to that of the present analysis, yet such law has been questioned by others [D. A. Wasylyshyn and G. P. Johari, *J. Polym. Sci., Part B: Polym. Phys.* **35**, 437 (1997); E. Tombari *et al.*, *J. Chem. Phys.* **113**, 6957 (2000)], verification of this issue is of importance in itself.
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