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Local Chain Dynamics and Dynamic Heterogeneity in Cross-Linked Epoxy in the Vicinity of Glass Transition

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ABSTRACT: We studied the local chain dynamics as well as the dynamic heterogeneity in highly cross-linked epoxy near glass transition by molecular dynamics simulation. In previous work (Lin and Khare in *Macromolecules* **2009**, *42*, 4319), we had reported creation of fully relaxed atomistic structures of cross-linked epoxy; the glass transition temperature of these structures was also determined from volume−temperature behavior. The local chain dynamics in these structures is characterized by using molecular dynamics simulation in this work. Local translational mobility of cross-linked epoxy as measured by mean-squared displacement of atoms exhibited two subdiffusive regimes within the simulation time of 200 ns. Local orientational mobility was determined by monitoring the autocorrelation function (ACF) of a vector associated with the epoxy monomer. Time dependence of an order parameter based on this ACF showed that there was almost no orientational relaxation when the temperature was near or below glass transition temperature and the system cannot completely relax orientationally even at temperatures that are 120 K higher than the glass transition temperature. Furthermore, a time scale for the identification of glass transition in simulations was determined using the kinetic interpretation of glass transition. Dynamic heterogeneity was studied by identifying the mobile and immobile atoms in the system. Simulation results confirmed the existence of dynamic heterogeneity in the cross-linked system with the fraction of the immobile domains in the structures showing a rapid increase as the temperature dropped below the glass transition temperature. Results are also presented for the probability of percolation of the system by the immobile domains in the vicinity of glass transition.

Introduction

As the glass-forming material is cooled in the vicinity of glass transition temperature (T_g), its behavior starts deviating from thermodynamic equilibrium and the relaxation times of molecular processes exhibit a sharp increase.[1] The connection between molecular motion and glass transition continues to be a matter of intense research. For polymeric systems, the dependence of segmental dynamics of polymer chains on T_g is of interest. In literature, glass transition as well as the predicted T_g has been characterized in terms of the local chain mobility for polymer thin film and polymer melt systems.[2−5]

The dynamics of unentangled and entangled polymer chains can be characterized using the well-established theoretical frameworks of Rouse model and the reptation model (i.e., tube model) respectively.[6−9] In a pioneering simulation study, Kremer and Grest[10] utilized the bead−spring model to investigate the chain dynamics of entangled linear polymer melts by employing molecular dynamics (MD) simulation. In agreement with the reptation model, they observed the crossover from unentangled to the entangled regime with the slope of the monomer mean-squared displacement (MSD) changing from 0.5 to 0.25. Baljon et al.[2] used a bead−spring model to investigate the glass transition behavior of nanoscale polymer thin films on an idealized face centered cubic lattice substrate. In terms of the chain dynamics, T_g was identified in that work as the temperature at which the relaxation time calculated from the bead diffusivity diverged. Morita et al.[3] proposed an alternative method of measuring T_g by analyzing the MSD values at a particular time as a function of temperature. Analogous to the volume-temperature behavior, the slope of MSD against temperature plot in the rubbery region was shown to differ from that in the glassy region and the T_g was thus obtained as the point of intersection of the linear fits to the MSD data in the glassy and rubbery regions, respectively. The T_g predicted using this procedure in that simulation study was found to be consistent with the T_g obtained from volume-temperature behavior in the simulation. Lyulin et al.[4] reported a MD simulation study of the segmental mobility of amorphous atactic polystyrene (PS) at a number of temperatures ranging from 100 to 650 K (T_g of the model system was 373 K) by using an united-atom model. The diffusive behavior of atactic PS as determined from monomer MSD agreed with Rouse model as indicated by the slope of 0.54 for temperatures higher than T_g, while a plateau in MSD values was observed below the T_g indicating that the motion of chain beads became more and more restricted at these temperatures. Moreover, local orientational mobility was also measured by the first and second order Legendre polynomials or autocorrelation functions (ACFs). The system showed significant degree of orientational relaxation above T_g. A reduction in the temperature slowed down the orientational mobility as measured by both ACFs and the orientational relaxation of atactic PS backbone almost stopped in the vicinity of T_g.

Glass transition has been demonstrated to be a dynamic phenomenon with strongly heterogeneous character in experiments[11−13] and simulations.[14−24] In particular, glass-forming materials exhibit coexistence of mobile and immobile domains in the vicinity of T_g. MD simulations performed by Glotzer and co-workers showed the existence of dynamic heterogeneity in several systems such as supercooled Lennard-Jones liquid,[14−16] supercooled polymer

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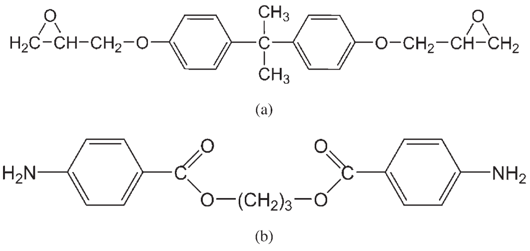


Figure 1. Chemical structures of (a) DGEBA (epoxy monomer) and (b) TMAB (cross-linker).

melt[17−19] and viscous silica.[20,21] These studies reported spatial correlations of the particles with similar mobility. Recently, several theoretical models have been proposed to describe the dynamic heterogeneity in supercooled liquids, that are based on ideas such as dynamic facilitation[25] and the random first order transition theory.[26] In another model, Long and Lequeux[27] proposed that the glass transition phenomenon is governed by the percolation of immobile domains that are generated by density fluctuations in the system. These ideas of percolation of immobile domains near T_g were consistent with the simulations of polymer thin films[22,23] and polymer nanocomposites.[23] An alternative view based on percolation of mobile domains as temperature is increased near T_g was also proposed by Lois et al.[24]

Highly cross-linked epoxy resin is a polymeric material that possesses excellent mechanical strength, resistance against chemicals, moisture, and corrosion, and good adhesive and electrical properties.[28] It has thus been widely used in a variety of applications in electronic and aerospace industries. In spite of this widespread usage of epoxy, theoretical and simulation studies of chain dynamics in this system are scarce. Early simulation work was only able to probe the mean squared displacement of atoms of cross-linked epoxy over a time scale of 1 ns.[29] In our previous work, we presented an efficient approach for building atomistically detailed models of cross-linked epoxy.[30] The predicted thermal and volumetric properties of the system showed good agreement with the experimental data. These atomistic model structures of cross-linked epoxy that were described in our previous study[30] are used here for studying the dynamics in cross-linked epoxy over a time scale of 200 ns.

The purpose of this work is 2-fold. We analyze the detailed molecular motions of cross-linked epoxy near T_g in terms of both local translational and orientational mobility. Second, we characterize the dynamic heterogeneity in cross-linked epoxy in the vicinity of T_g. These data are used to test the possible percolation of system near T_g by immobile domains as predicted by theory.[27]

Simulation Method

The system studied consisted of diglycidyl ether bisphenol A (DGEBA) as the epoxy monomer and trimethylene glycol di-*p*-aminobenzoate (TMAB) as the cross-linker. The chemical structure of these molecules is shown in Figure 1. In previous work,[30] we reported creation and characterization of atomistically detailed model structures of cross-linked epoxy that contained 100 epoxy monomers and 50 cross-linker molecules; the same model structures were used in this work for studying chain dynamics. Briefly, all molecules were described by the general AMBER force field (gaff) supplemented by literature parameter values.[30] The MD simulations were carried out using the GROMACS 4.0.3 package.[31] For MD simulations, a time step of 1 fs was used. A cutoff distance of 10 Å with the buffer of 1 Å was used for the van der Waals interactions, whereas the particle mesh Ewald (PME) algorithm[32] was used to handle the electrostatic interactions. The temperature and pressure values were kept constant by using the Nose−Hoover thermostat[33,34] and the Parrinello−Rahman[35,36] methods, respectively.

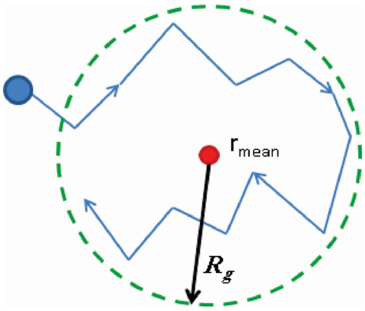


Figure 2. Illustration of the concept of the radius of gyration of atom trajectory.

In order to study the local chain dynamics in epoxy, each of the five model structures was subjected to constant *NPT* (i.e., constant number of atoms, constant pressure and constant temperature) MD simulation for the duration of 200 ns at several temperatures in the range from 420 to 600 K. These simulation data were analyzed to determine the translational and orientational mobility as well as the dynamic heterogeneity in the system. Local translational mobility of the atoms in the system was characterized by MSD; local orientational mobility of cross-linked epoxy was characterized by the second order Legendre polynomials[4]

$$P_2(t) = \frac{3}{2}\langle \hat{v}(0)\cdot\hat{v}(t)\rangle^2 - \frac{1}{2} \tag{1}$$

where $\hat{v}(0)$ and $\hat{v}(t)$ represent the unit vectors connecting the end carbon atom to the central carbon atom in DGEBA at the initial time snapshot and at time t.

The dynamic heterogeneity was studied by partitioning the simulated system into "mobile" and "immobile" spatial domains. This was achieved by identifying the mobile and immobile atoms in the system. For this purpose, the mobility of the atoms was quantified by using the approach proposed by Baljon et al.[22] In particular, the radius of gyration R_g of a given atom along its simulation trajectory over a period of time was calculated as

$$R_g = \sqrt{\frac{1}{N}\sum_i^N (r_i - r_{mean})^2} \tag{2}$$

where N is the number of snapshots along the trajectory, r_i is the position of the atom in each snapshot and r_{mean} is the mean position of the atom along the trajectory (see Figure 2). It has been argued previously that R_g thus calculated provides a comprehensive measure of the atom mobility for the given time period.[22] We note that this R_g value will be a function of time duration over which the atom motion is tracked; as expected, its value will increase with an increase in the time duration. Therefore, it is essential to select an appropriate time scale to calculate R_g for identifying the immobile and mobile atoms. In this work, we estimated the time scale by using ideas from the calorimetric measurement of T_g.[37] In this approach, T_g measurement is considered to be a kinetic event. In the rubbery region, the glass-forming system relaxes on a time scale that is much smaller than the time scale of experimental observation, whereas in glassy region, the system relaxes on a time scale that is much longer than the experimental time scale thus leading to lack of any measurable change in the properties. T_g can be defined as the temperature at which the time scale of the experimental observation is comparable with the relaxation time of the glass-forming system. As described in Hodge's review paper,[37] the average time scale for T_g observation at the given cooling rate (Q_c) can thus be estimated from the expression:

$$\tau(T_g) \approx \frac{R{T_g}^2}{\Delta H_{eff}}\frac{1}{Q_c} \tag{3}$$

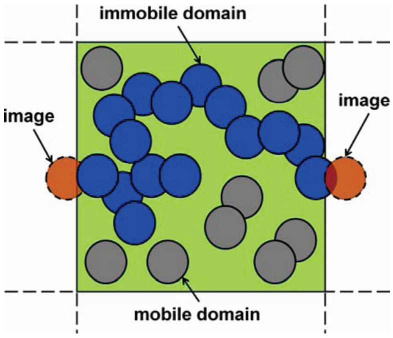


Figure 3. Illustration of percolation of immobile domains in a periodic simulation box. Each blue circle represents the domain of an immobile atom in the system. If two circles overlap with each other, they belong to the same cluster. The system is considered to be percolated by immobile domains if an immobile domain and its periodic image are part of the same cluster.

where ΔH_{eff} is the apparent activation energy at T_g and R is the gas constant. On the basis of the cooling rate (i.e., 7.5 K/ns) used in our simulations and the predicted T_g from our previous work (i.e., 481 K),[30] as well as the $\Delta H_{eff}/R$ value of epoxy from the literature (i.e., 116 000 K),[38] the time scale $\tau(T_g)$ was estimated as 0.26 ns. In this work, we have thus tracked the motion of the atoms over four different time durations of 0.24, 1, 2, and 10 ns.

Once the immobile atoms in the system were identified, these data were then used to assess any possible percolation of the system by these immobile domains at glass transition as has been proposed theoretically.[27] For this purpose, the algorithm proposed by Seaton and Glandt[39] was used to identify the presence of percolation in our periodic simulation box. Thus, as illustrated in Figure 3, if an atom and its periodic image belonged to the same cluster, then the cluster was considered to span the simulation box and hence was considered to percolate the system. The numerical procedure for utilizing this idea as reported by Škvor and Nezbeda[40] was used in this study.

Results and Discussion

A. Local Translational Mobility. Local translational mobility was characterized by MSD of the central atoms of epoxy monomers and the nitrogen atoms at cross-linking points in the temperature range from 420 to 600 K. The former represents a set of relatively mobile atoms that are located far away from the cross-linking points, while the latter, being the cross-linking points, should be the most restricted atoms in the system. As can be seen in Figure 4, qualitatively similar results are obtained for both sets of atoms. As expected, the local translational mobility of the central carbon atoms of epoxy monomers is higher than that of the nitrogen atoms at the cross-linking points. Our predictions for the MSD of nitrogen atoms at cross-linking points agree well with the previous simulation work[29] in that the values of the MSD are of the same order of magnitude at the same time scale (e.g., 100 ps) and at a similar temperature above T_g (e.g., $T_g + 120$ K) for cross-linked epoxy systems. We also note that as deduced from the translational mobility, cross-linked epoxy is relatively immobile compared to linear polystyrene melt that was studied by Lyulin et al.[4] The predicted values of MSD for both sets of atoms in our cross-linked epoxy system are at least an order of magnitude lower than the previously reported value for linear polystyrene systems at the same time scale (e.g., 10 ns) and at the same temperature above T_g (e.g., $T_g + 120$ K). We attribute this low translational mobility to the highly cross-linked nature of the epoxy network. Since all the molecules are chemically connected in the cross-linked network, the motion of atoms in cross-linked epoxy is highly constrained.

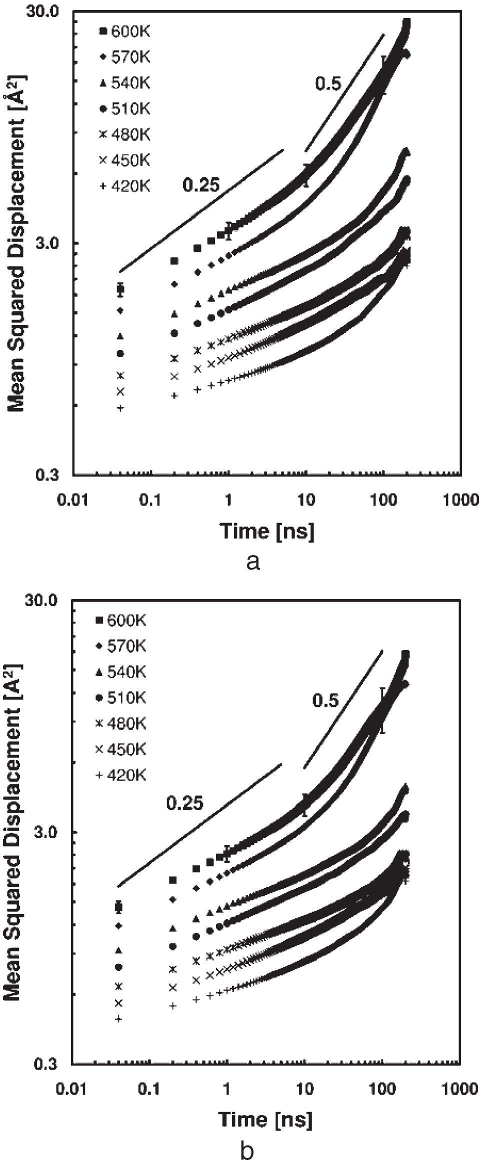


Figure 4. Mean-squared displacement as a function of time for (a) the central carbon atoms of the epoxy monomers and (b) the nitrogen atoms of the cross-linkers. Lines with slopes of 0.25 and 0.5 are shown as a guide for the eye. For clarity, error bars are shown only for a few representative points of one data set.

Previous simulation studies have demonstrated the existence of subdiffusive behavior as deduced by MSD for both unentangled and entangled linear polymer chains.[4,10,41,42] Theoretical work has also predicted subdiffusive behavior for chain segments of cross-linked polymer networks.[43,44] Specifically, Vilgis and Heinrich[43] predicted that at short times, the segmental dynamics of cross-linked networks will be Rouse like where the MSD of chain segments will scale with time as $t^{0.5}$. At long times, the MSD was predicted to reach a plateau value due to localization. The MD simulation results for polymer networks that were obtained using either bead–spring[45] or tangent hard sphere[46] chain models were consistent with these theoretical predictions in that the MSD of chain segments scaled as $t^{0.5}$ at short times while it approached a plateau value at longer times. For the highly cross-linked epoxy systems studied in this work, we have observed two subdiffusive regimes for MSD over the simulation time scale. In the first subdiffusive regime (time < 10 ns), the slope of MSD vs time graph on the log–log plot was

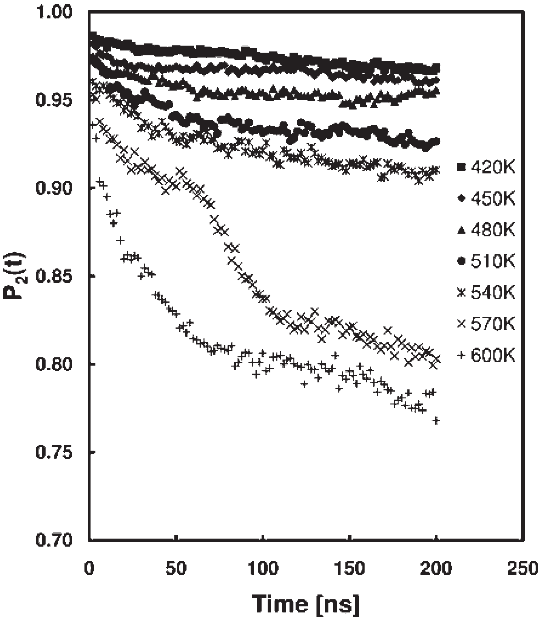


Figure 5. Time dependence of the orientational order parameter (eq 1) for the epoxy monomers. Results are shown at seven different temperature values as indicated.

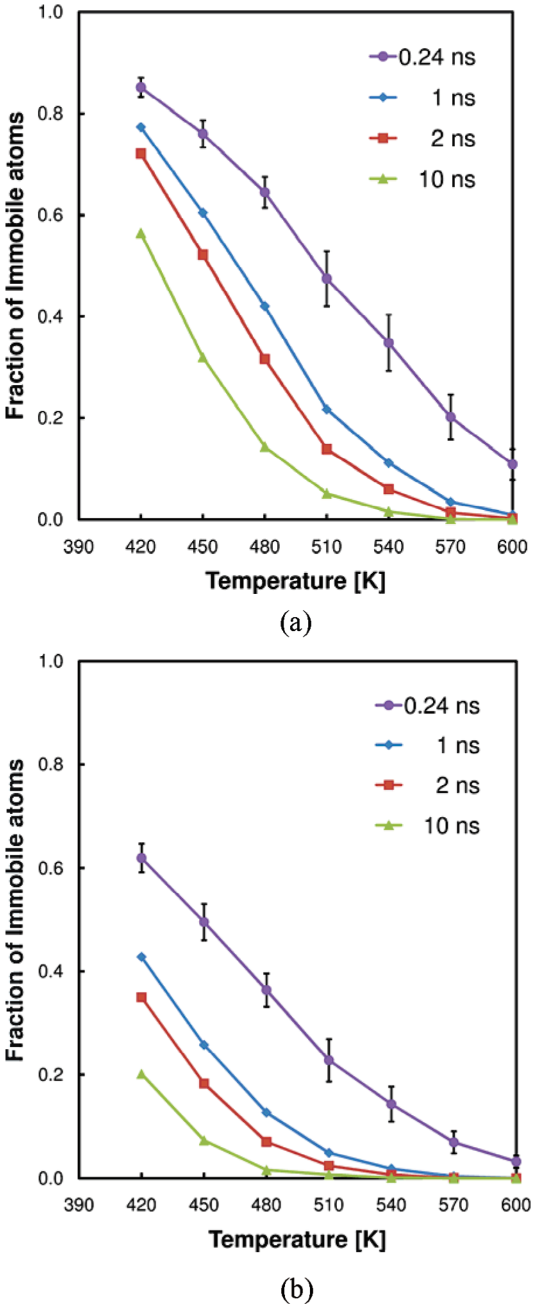
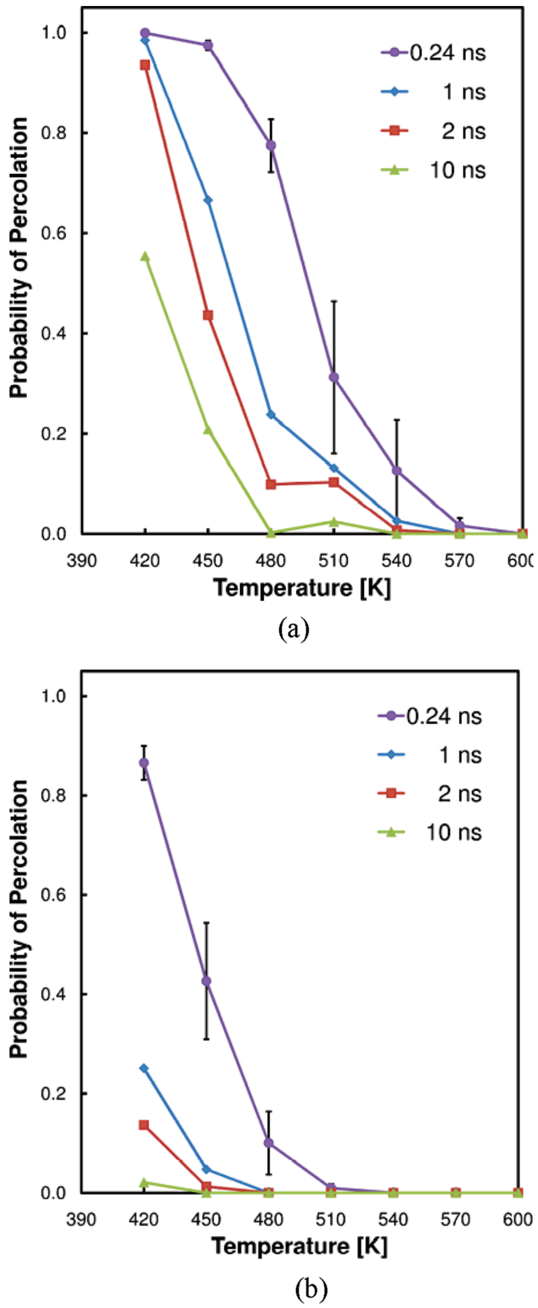


Figure 6. Temperature dependence of the fraction of immobile atoms in the cross-linked epoxy. Results are shown for (a) the central atoms of epoxy monomers and (b) the central atoms of both the epoxy monomers and the cross-linkers. For clarity, error bars are shown on only one set.

lower than 0.2 at all the temperatures, while in the second regime (time > 10 ns) this slope was higher and approached a value of 0.5, especially at temperatures above the glass transition temperature. We note that the crossover between these two regimes occurred at earlier times with an increase in the temperature. Furthermore, our results also indicated a weak temperature dependence of the slopes of MSD. In the first subdiffusive regime, the slopes increased from 0.1 to 0.2 with an increase in temperature. The origin of the additional subdiffusive regime of lower slope that was observed at short times in our simulations is not entirely clear. We attribute it to the highly cross-linked nature of our epoxy structure that leads to the occurrence of very short chain segments between the cross-linking points. Furthermore, usage of atomistically detailed models with the associated potentials for the chain internal coordinates imposes severe restrictions on the conformations of such short chain segments.

B. Local Orientational Mobility. As can be seen from Figure 5, the orientational mobility of DGEBA as deduced from the order parameter was almost completely suppressed when the temperature was near or below 480 K. At temperatures higher than 480 K, the order parameter decayed with time, suggesting some orientational relaxation of the structure. This observation agreed with the predicted T_g (i.e., 481 K) from the volume-temperature behavior in our previous work.[30] In literature, for the unentangled polymer chains, the orientational ACF for main chain bonds was reported to decay and approach a value close to zero over the time scale of 100 ns at the temperatures above T_g.[4] However, as seen from Figure 5, the cross-linked epoxy structure retained strong orientational correlation between the initial and the final configuration on a time scale of 200 ns in this work. Even at the highest temperature studied in this work (*i.e.* the predicted $T_g + 120$ K), the order parameter did not decay to a value below 0.75 after a time duration of 200 ns. Again, we attribute this observation to the highly cross-linked nature of the system which prevents large scale conformational changes and restricts orientational freedom of the chain segments.

C. Dynamic Heterogeneity near Glass Transition. From the MD trajectory of the epoxy, the trajectory R_g for atoms was calculated over time scales of 0.24, 1, 2, and 10 ns. This analysis was carried out for two sets of atoms in the system: the first one included only the central carbon atoms of DGEBA (epoxy monomer) while the second set contained the central carbon atoms of both DGEBA and TMAB (cross-linker). These data were then used to determine the dynamic heterogeneity by classifying the atoms into "mobile" and "immobile" atoms. In literature, Baljon and coworkers[22] used ideas similar to the Lindemann criterion of melting to propose a criterion that if the radius of gyration is less than one-tenth the value of the location of the first peak in the radial distribution function (RDF) for the collection of selected atoms, the atom is considered to be "immobile", else it will be designated as a "mobile" atom. In our previous work,[30] it was shown that the location of the first peak in the



(a)

(b)

Figure 7. Temperature dependence of the percolation probability of immobile domains in the cross-linked epoxy. Results are shown for (a) the central atoms of the epoxy monomers and (b) the central atoms of both the epoxy monomers and the cross-linkers. For clarity, error bars are shown on only one set.

RDF for the central carbon atoms of DGEBA does not show any temperature dependence. The peak was located at 6.3 Å and thus an atom in this set was considered to be immobile if its trajectory R_g value over the chosen time scale was less than 0.63 Å. Figure 6a shows the fraction of these immobile atoms as a function of the temperature for four different trajectory durations. The uncertainties shown are estimated as the standard error in the mean from simulations on the five different model structures studied in this work. As expected, trajectory R_g increases with an increase in the trajectory time, thus leading to a decrease in the fraction of the immobile atoms in the system. For the second set consisting of the central carbon atoms of both DGEBA and TMAB, the location of the first peak in RDF shows a small dependence on the temperature with the average value of the location of the first peak being 5.43 Å.[30] In this case, an atom was considered to be immobile if its R_g for the chosen time scale was less than 0.543 Å. The results for this set of atoms are shown in Figure 6b and are qualitatively similar to those in Figure 6a; however, the fraction of immobile atoms was lower in this case as expected due to the application of a less severe criterion for the purpose of defining the immobile atoms.

Dynamic heterogeneity in the vicinity of T_g was further investigated by focusing on the possible percolation of immobile domains in the system. For the purposes of this calculation, each immobile domain was considered to be a spherical region centered on each of the immobile atoms. The diameter of this domain was set to the location of the first minimum in the RDF for this set of atoms (this definition captures the complete first shell of atoms that surround the atom under consideration). Figure 7a shows the probability of percolation for the first set (i.e., the central atoms of DGEBA) as a function of temperature. For this calculation, each immobile atom was considered to occupy a sphere of diameter 9.25 Å as determined from the RDF.[30] The uncertainties in the data are very large at two values of temperature; we attribute this to the highly heterogeneous nature of chain dynamics near glass transition. As expected, the probability of percolation increased with a reduction in the temperature due to the presence of larger number of immobile atoms in the system at the lower temperatures. In addition, we note that the probability of percolation started rising steeply at 480 K, which is very close to the predicted T_g (i.e., 481 K) from our previous simulation study.[30] We also note that the probability of percolation approached one at 450 K (i.e., $T_g - 30$ K) only for the shortest time scale (which is also close to the time scale suggested by the kinetic interpretation of glass transition), while it approached one at 420 K for longer time scales of 1 and 2 ns.

Figure 7b shows the temperature dependence of the probability of percolation for the second set (i.e., the central atoms of DGEBA and TMAB). For this calculation, as determined from the RDF,[30] each immobile atom was considered to occupy a sphere of diameter 8.00 Å. In this case, for all time scales studied except one, the probability of percolation was very small when the temperature was higher than the predicted T_g but rose rapidly when the temperature fell below it.

Conclusions

The chain dynamics of highly cross-linked epoxy was characterized by studying its local translational and orientational mobility using molecular simulations. Local translational mobility as determined by the mean-squared displacement shows that the atomistic mobility of cross-linked epoxy within the time duration of 200 ns is rather small. Compared to the linear polystyrene melt at the same time scale and at the same temperature above T_g (e.g., $T_g + 120$ K),[4] the values of MSD for cross-linked epoxy are smaller by at least an order of magnitude. In addition, we also observed two subdiffusive regimes over the time scale studied in this work. In terms of the local orientational mobility as characterized by the orientational order parameter, our simulations show that the cross-linked system is unable to relax completely in a time duration of 200 ns even at a temperature 120 K higher than the predicted T_g. We also note that the cross-linked structure shows very small orientational relaxation at the temperatures near or below the predicted T_g. We attribute the low translational and orientational mobility in cross-linked epoxy to the tightly cross-linked nature of the network in which all of the molecules are chemically bonded and thus the motion of atoms in this system is highly restricted.

A time scale for the observation of glass transition in simulations was identified based on the kinetic interpretation of glass transition. Dynamic heterogeneity in the system was studied by analyzing the spatial distribution of the mobile and immobile atoms in the system near the glass transition temperature. Two different sets of atoms were tested for this purpose: the central atoms of the epoxy monomers only and the central atoms of both the epoxy monomers and the cross-linkers. Calculations for both sets indicated the presence of dynamic heterogeneity in the system as deduced from the presence of both mobile and immobile atoms. The fraction of immobile atoms as well as the probability of percolation of immobile domains in the system was found to increase rapidly at temperatures below the T_g. However, quantitative differences in the degree of percolation were found to exist between the two sets of atoms.

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