# Entanglements in Glassy Polymer Crazing: Cross-Links or Tubes?

Ting Ge,<sup>\*,†</sup><sup>®</sup> Christos Tzoumanekas,<sup>‡</sup> Stefanos D. Anogiannakis,<sup>‡</sup> Robert S. Hoy,<sup>\*,§</sup> and Mark O. Robbins<sup>\*,||®</sup>

<sup>†</sup>Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, United States

<sup>‡</sup>Department of Materials Science and Engineering, School of Chemical Engineering, National Technical University of Athens, Athens 15780, Greece

<sup>§</sup>Department of Physics, University of South Florida, Tampa, Florida 33620, United States

Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218, United States

**ABSTRACT:** Models of the mechanical response of glassy polymers commonly assume that entanglements inherited from the melt act like chemical cross-links. The predictions from these network models and the physical picture they are based on are tested by following the evolution of topological constraints in simulations of model polymer glasses. The same behavior is observed for polymers with entanglement lengths  $N_e$  that vary by a factor of 3. A prediction for the craze extension ratio  $\Lambda$  based on the network model describes trends with  $N_{et}$  but polymers do not have the taut configurations it assumes. There is also no evidence of the predicted geometrically necessary entanglement loss. While the number of entanglements remains constant, the identity of the chains forming constraints changes. The same relation between the amount of entanglement exchange and



nonaffine displacement of monomers is found for crazing and thermal diffusion in end-constrained melts. In both cases, about 1/3 of the constraints change when monomers move by the tube radius. The results show that chains in deformed glassy polymers are constrained by their rheological tubes rather than by entanglements that act like discrete cross-links.

# 1. INTRODUCTION

Polymers exhibit a range of unique mechanical phenomena because of the competition between short-range intermolecular interactions and the long-range connectivity imposed by strong covalent bonds along their backbone. Their rheology in the fluid state can be understood using the concept of entanglements—topological constraints imposed by the inability of chains to pass through each other.<sup>1</sup> These constraints force polymers to move along a "tube" formed by their neighbors, leading to rapid decreases in diffusion constant and increases in viscosity as their length increases.

Entanglements also play a key role in models of the mechanical response of glassy polymers.<sup>2–6</sup> Quenching to the glassy state has little effect on the chain structure and should thus preserve topological entanglements. Most models start from the assumption that these entanglements act like permanent chemical cross-links.<sup>2–5</sup> This allows predictions of strain hardening and other experimental properties using models that treat the glass as a cross-linked network of Gaussian chains.<sup>3–7</sup> Recent simulations<sup>8–10</sup> suggest that this view of entanglements is too simple. While direct experimental observation of individual entanglements remains elusive,<sup>11</sup> recently developed algorithms allow entanglements to be identified and tracked in simulations. These algorithms<sup>12–14</sup> have enabled extensive tests of the tube model of entangled

melt dynamics. More recently, they have been applied to uniaxial strain of glassy and semicrystalline polymers and their nanocomposites.  $^{15-18}$ 

In this paper we examine the evolution of entanglements during one of the mechanical phenomena unique to polymer glasses—craze formation. As shown in Figure 1, crazes are an



**Figure 1.** Snapshot showing part of a craze simulation with the tensile axis in the horizontal direction and red indicating the active zone where plastic deformation is occurring. The slice is 10a deep into the page,  $k_{\text{bend}}/u_0 = 1.5$ , and red monomers underwent a nonaffine displacement greater than 0.2*a* over a stretch increment  $\delta\lambda = 0.01$  ending in  $\lambda = 3.4$ . Image produced using OVITO.<sup>23</sup>

Received:September 30, 2016Revised:December 5, 2016Published:December 23, 2016

intricate network of highly aligned fibrils and voids. Crazes form under the tensile stresses ahead of crack tips and can grow to micrometer widths. Deformation of this large volume enhances the fracture energy of glassy polymers by 3 orders of magnitude.  $^{3-5,19,20}$ 

Craze formation is characterized by several key features: (i) Craze growth proceeds in a narrow active zone near the interface between the craze and undeformed material. (ii) A constant plateau stress  $\sigma_p$  is needed to draw new material into the craze. (iii) Drawing expands the volume by a constant factor  $\Lambda$  called the extension ratio.

The extension ratio for a given polymer is relatively insensitive to rate, temperature, and other factors, especially for temperatures well below the glass transition temperature,  $T_{\rm g}$ . One of the main successes of the chemical cross-link model is that it captures trends in  $\Lambda$  with entanglement density for a range of polymers,<sup>4,5</sup> although the absolute values of  $\Lambda$  are typically off by about 20%. As discussed in section 3.1, this model assumes that chains are pulled taut between entanglements at  $\Lambda$ . The model and the cartoon for craze growth shown in Figure 2 have also been used to argue<sup>4</sup> that significant



**Figure 2.** (left) Common cartoon of craze formation with tension along the vertical direction.<sup>4</sup> Voids advance vertically around straight fibrils of mean diameter  $\langle D \rangle$  whose centers are separated by  $\langle D_0 \rangle$ . (right) Closeup showing the predicted geometrically necessary entanglement loss.<sup>4</sup> Entanglements above the advancing void fingers (large red circles) are assumed to be lost, while others (small green circles) survive. Blue stars show broken chain ends from lost entanglements. More refined models include horizontal "cross-tie" fibrils where entanglements could remain without loss.<sup>24</sup>

entanglement loss ( $\sim$ 30–50%) is "geometrically" necessary to accommodate void propagation. As described in the Appendix, any chains involved in entanglements that lie in the path of an advancing void finger are assumed to break to allow the finger to advance. Rottler and Robbins did not observe the associated chain scission and argued that the more complicated structure revealed by simulations (e.g., Figure 1) allowed entanglements to be preserved.<sup>8</sup> Two other studies that reported similar structure reported evidence of a decrease in the total number of entanglements by 30% or more<sup>21,22</sup> but used algorithms that become inaccurate in the highly anisotropic craze (section 2.2). Approaches that are not sensitive to anisotropy have been used to study entanglements in uniaxial strain rather than crazing and found little entanglement loss.<sup>16,17</sup>

To directly test predictions about the role of entanglements, we track the evolution of individual topological constraints (TCs) during craze formation using the Contour Reduction and Topological Analysis (CReTA)<sup>14</sup> algorithm. Results for chains with three different stiffnesses and entanglement lengths  $N_e$  that vary by a factor of 3 show the same behavior, suggesting that the findings are broadly relevant. As in experiments, the

cross-link model for the extension ratio predicts trends in  $\Lambda$  with  $N_{\rm e}$  but not the precise prefactor. Moreover, the chains are not pulled taut between entanglements as assumed by this model. Indeed, the craze can be extended by almost an additional factor of 2 before chains are pulled taut and begin to break. This suggests that  $\Lambda$  is not strictly geometrical and is determined by a balance of yield stresses in the coexisting craze and undeformed glass.

We find that there is no statistically significant change in the number of TCs during crazing. This supports the idea that TCs act like cross-links but shows that entanglement loss is not geometrically necessary. If TCs behaved exactly like cross-links, they would remain at fixed positions along each chain. This picture is only partially supported by studies of the distribution of chemical spacings (covalent bonds) between adjacent TCs. There is almost no change at large separations but some reduction in the spacing between nearby TCs. This suggests a limited mobility of TCs like that in a slip-link model of melt rheology. Examination of correlations between TCs on different chains also indicates clustering into fibrils that may be the mechanism of avoiding entanglement loss.

Examining individual TCs between specific pairs of chains at specific locations reveals a more complicated picture. While there is no change in the number of TCs during crazing, there is some change in the identity of TCs. For all systems, roughly 2/3 of the TCs in the initial state are still present in the final state. The other 1/3 are not lost but are replaced by new TCs. These new TCs are not localized near chain ends as expected if chains are pulling out of their tubes. Instead, the change in identity of the chains forming TCs can be understood by viewing entanglements as collective constraints from the chains that form the rheological "tube". This idea is confirmed by comparing the set of TCs that change during craze formation and thermal diffusion in a melt with chain ends fixed to limit motion along the tube. We find that thermally and mechanically driven diffusion cause chains to sample TCs with the same set of surrounding chains that comprise the tube. In other words, chains in crazes are not stretched between fixed chemical crosslinks but instead are confined to tubes that deform as the craze forms and are essentially the same tubes commonly analyzed in theories of entangled melt rheology.

The outline of the rest of this paper is as follows. In section 2 we describe our computational methods (molecular dynamics simulations and topological analyses) and distinguish them from those employed in recent, closely related work.<sup>16,21,22</sup> Section 3 presents the results of our simulations, and Section 4 provides a summary and conclusions. The Appendix presents a concise description of predictions of geometrically necessary entanglement loss (GNEL).<sup>4</sup>

#### 2. METHODS

**2.1. Molecular Dynamics Simulations.** We use the generic bead–spring model<sup>25</sup> that has been shown to capture many mechanical properties of polymer melts and glasses, including the process of craze formation.<sup>8</sup> Each polymer is a linear chain of N spherical monomers of mass m. Monomers that are not connected by a covalent bond interact via a truncated and shifted Lennard-Jones (LJ) pair potential

$$U_{\rm LJ}(r) = 4u_0[(a/r)^{12} - (a/r)^6 - (a/r_{\rm c})^{12} + (a/r_{\rm c})^6]$$
(1)

with the same cutoff radius,  $r_c = 1.5a$ , used in previous studies of crazing.<sup>8,20,26–28</sup> We express all quantities in terms of the molecular diameter *a*, binding energy  $u_0$ , and characteristic time  $\tau = a(m/u_0)^{1/2}$ .

Covalent backbone bonds between neighboring beads along each chain are modeled using the attractive finitely extensible nonlinear elastic (FENE) potential

$$U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln[1 - (r/R_0)^2]$$
(2)

with the canonical parameters<sup>25</sup>  $R_0 = 1.5a$  and  $k = 30u_0a^{-2}$  and a purely repulsive LJ potential ( $r_c = 2^{1/6}a$ ). This choice of parameters prevents chain crossing and is therefore suitable for simulations of entangled systems. It does not allow bond scission, but past studies with potentials that allow scission find no bond breaking under any of the conditions studied here.<sup>8,20,26–28</sup> In addition, we verified that the bond stresses always remained too low to produce scission.

The entanglement density is changed by varying the chain stiffness. We use the standard<sup>29</sup> bond-bending potential

$$U_{\rm B}(\theta) = k_{\rm bend}(1 - \cos\theta) \tag{3}$$

where  $\theta$  is the angle betweeen consecutive bond vectors along a chain and equals zero for straight trimers. The three values of  $k_{\text{bend}}$  studied span the range from the flexible limit,  $k_{\text{bend}}/u_0 = 0$ , to  $k_{\text{bend}}/u_0 = 1.5$ , about halfway to the onset<sup>30</sup> of liquid crystal order.

Table 1 gives the corresponding characteristic ratios,  $C_{\infty}$ , describing the chain statistics and the numbers of beads per rheological

Table 1. Statistical Properties of Chains and Crazes for Different Chain Stiffnesses $^a$ 

$k_{\rm bend}$	$C_{\infty}$	Λ	$N_{ m e}$	$\lambda_{\max}$	$\langle n \rangle$	$\lambda_{\max}^{ ext{topo}}$	$d_{xy}/a$
0	1.68	8.2 (5)	85 (5)	7.1 (2)	32	4.4	4.4
0.75	1.97	6.4 (6)	47 (3)	4.9 (2)	21	3.3	3.9
1.5	2.68	4.4 (4)	30 (2)	3.3 (1)	13	2.2	3.4

<sup>*a*</sup>Values of the characteristic ratio  $C_{\infty}$  for the melt at  $k_{\rm B}T/u_0 = 1$  are consistent with ref 29. The rheological entanglement length  $N_{\rm e}$  is obtained from PPA (Eq. 7 of Ref. 41) and the mean spacing between TCs  $\langle n \rangle$  is from CReTA analyses. The extension ratio  $\Lambda \equiv \rho_{\rm g}/\rho_{\rm c}$  is measured from the ratio of densities in the glass and coexisting craze. Predicted values of  $\lambda_{\rm max}$  are from eq 7, and  $\lambda_{\rm max}^{\rm top}$  is from eq 7 with  $\langle n \rangle$  replacing  $N_{\rm e}$ . The rms distance in the *x*-*y* plane between adjacent TCs along a chain,  $d_{xyn}$  is calculated in the undeformed glass. Numbers in parentheses are uncertainties in the last digit when it is greater than unity.

entanglement length,  $N_{\rm e}$ , from previous studies.<sup>12</sup> We present results for chains with N = 500 beads, which is much larger than  $N_{\rm e}$ . Past studies<sup>8,20,28</sup> show that this is long enough to reach the limiting behavior for very long chains, and we performed simulations with N =1750 that gave statistically equivalent results.<sup>31</sup>

All MD simulations are carried out using the LAMMPS<sup>32</sup> molecular dynamics code. Three-dimensional periodic boundary conditions are used, with periods  $L_i$  along the Cartesian directions i = x, y, and z. The system contained M = 500 chains, corresponding to initial periods  $L_{i0} \sim 62.7a$ . This is longer than the end-to-end distance of chains and has been shown to be large enough to minimize finite-size effects.<sup>8,33</sup>

Initial glassy states were prepared using standard protocols.<sup>33</sup> Melt states were constructed and thoroughly equilibrated at temperature  $T = 1.0u_0/k_{\rm B}$  using a standard double-bridging algorithm.<sup>29</sup> They were then rapidly quenched at a rate  $\dot{T} = -2 \times 10^{-3}u_0/(k_{\rm B}\tau)$  to T well below  $T_{\rm g} \sim 0.35 u_0/k_{\rm B}.^{34}$  During quenches, constant volume is maintained while  $k_{\rm B}T/u_0 > 0.55$ , and then constant (zero) pressure is maintained using a Nosé–Hoover barostat until the final target temperature is reached. We will show results for  $k_{\rm B}T/u_0 = 0.1$ , but equivalent results were found at  $k_{\rm B}T/u_0 = 0.01$  and 0.2.

After quenching, crazing is induced using strain-controlled MD. As in previous studies,<sup>8,20,26–28</sup> simulation cells are uniaxially stretched along the z-axis at a constant velocity  $\dot{L}_z = 0.06a/\tau$ , while their transverse dimensions ( $L_x$  and  $L_y$ ) are held fixed. Constant velocity is preferable to constant strain rate because deformation is localized in an active zone of fixed width.<sup>26</sup> The average deformation is quantified by the macroscopic stretch factor  $\lambda = L_z/L_{z0}$ . A Langevin thermostat with damping rate  $\Gamma = 1\tau^{-1}$  is applied to the peculiar velocities in *x* and *y* directions. Positions of all beads are dumped periodically during deformation for later analysis.

We also perform end-constrained melt (ECM) dynamics simulations<sup>35,36</sup> that allow us to relate lateral displacements of chains during crazing at  $k_{\rm B}T/u_0 = 0.1$  to tube exploration at  $k_{\rm B}T/u_0 = 1.0$ . The undeformed  $k_{\rm B}T/u_0 = 0.1$  glass is rapidly heated at constant pressure to  $k_{\rm B}T/u_0 = 0.55$ . All chain ends are then fixed in space, and heating to  $k_{\rm B}T/u_0 = 1.0$  is continued at constant volume. The end-constrained melts are allowed to diffuse at  $k_{\rm B}T/u_0 = 1.0$  for a time sufficient for tube exploration.<sup>36</sup> We used a time interval  $\Delta t = 5 \times 10^4 \tau \simeq 10 \tau_{\rm er}$ , where  $\tau_{\rm e}$  is the standard tube-theory "entanglement time".<sup>37–39</sup>

**2.2. Entanglement Analyses.** Although direct experimental observation of individual entanglements remains elusive, recently developed simulation algorithms provide spatial mappings of local "topological" constraints between chains. This allows us to test the various molecular pictures for entanglement evolution during craze formation and growth. These algorithms, including PPA, Z, and CReTA,<sup>12–14</sup> are based on Edwards' primitive path concept.<sup>1</sup> They have provided extensive microscopic tests confirming the microscopic validity of the tube model of entangled melt dynamics.<sup>12,40</sup> More recent work<sup>15–18,28</sup> has provided useful insights into the role of entanglements in controlling the nonlinear mechanics of glassy and semicrystalline polymers and their nanocomposites.

The various published topological analysis algorithms employ significantly different means to obtain primitive paths (PPs) and characterize entanglements. All give similar results for homogeneous systems,<sup>41</sup> but the inhomogeneous systems of interest here are more challenging. Algorithms that shorten chains via integration of Newton's laws or energy minimization,<sup>42</sup> such as standard primitive path analysis (PPA)<sup>12</sup> and the modified thin-chain PPA,<sup>43</sup> introduce nonuniform forces along the chain backbone. When applied to systems where undeformed and crazed regions coexist, monomers can move relative to each other by much more than  $N_e$  and entanglements tend to cluster together. This makes it difficult to track individual entanglements. In contrast, geometrical algorithms, such as Contour Reduction Topological Analysis (CReTA)<sup>14,36</sup> and Z,<sup>13,16</sup> suppress slippage and clustering by imposing strictly decreasing chain contour lengths via local manipulations. For these reasons, geometrical algorithms are preferable for the analyses conducted here.

We use the CReTA algorithm, which fixes chain ends in space and then reduces the contour lengths of all chains simultaneously. Effects due to primitive chain thickness<sup>14</sup> are minimized by iteratively inserting extra beads of smaller diameter during the minimization of the total contour length. The resulting configurations are networks of primitive paths with effectively zero thickness. Topological constraints (TCs) are identified with contacts between primitive paths. At these contacts, two primitive paths mutually block reduction in each other's contour length. TCs satisfy a local topological criterion based on two linked rings (see Figure 1 in ref 36). Since they are localized in space, they represent cross-link-like "entanglements" rather than delocalized tube constraints. Following their evolution with stretch or time allows us to determine if they remain in fixed locations on chains like true chemical cross-links, slide along chains like slip links in standard<sup>1,40</sup> melt-rheology models, or disappear as predicted by GNEL models.<sup>4</sup>

Mapping TCs to individual bead (monomer) positions gives the distribution of TCs along the chain, in both chemical distance and Euclidean space.<sup>14,36,44</sup> For each CReTA-reduced configuration, we count the total number of TCs,  $N_{\text{TC}}$  and find the distribution of TC spacings P(n), where n is the number of monomers between consecutive TCs along a chain. The average chemical spacing  $\langle n \rangle$  is

$$\langle n \rangle = \left( \int_0^\infty P(n) \, \mathrm{d}n \right)^{-1} \int_0^\infty n P(n) \, \mathrm{d}n \tag{4}$$

We similarly identify the Euclidean distance *d* between consecutive TCs along chains and report both the average values  $\langle d \rangle$  and distributions P(d). Specifically, we monitor the evolution of P(n) and

P(d) during deformation and compare the distributions in undeformed glasses to those from fully developed crazes.

We will often refer to TCs as entanglements, but it is important to distinguish  $\langle n \rangle$  from the rheological entanglement length  $N_{\rm e}$  (Table 1). The value of  $N_{\rm e}$  is found to correlate with the Kuhn length of the primitive path, i.e., the length over which the orientation of the primitive path becomes decorrelated.<sup>12</sup> This change of orientation requires several TCs so  $N_{\rm e}/\langle n \rangle$  is typically 2–3.<sup>14,40,45</sup>

A key feature of this paper is that we monitor the evolution of TCs in "time", i.e., with increasing stretch  $\lambda$  during crazing runs or diffusion time t in melt-dynamics runs. Suppose a TC exists between beads at position *i* along chain  $\alpha$  and position *j* along chain  $\beta$ , in the initial undeformed glass ( $\lambda = 1$ ). Then, at stretch  $\lambda$ , we search for TCs in the ranges  $[i - \langle n \rangle, i + \langle n \rangle]$  along chain  $\alpha$  and  $[j - \langle n \rangle, j + \langle n \rangle]$  along chain  $\beta$ . If a TC is found in these ranges, we determine that the corresponding initial TC is preserved. Otherwise, we say this entanglement has "died". We define  $Q(\lambda)$  as the fraction of surviving TCs. Note that *Q* does not take into account intervening  $\lambda$ , and some TCs may die and be reborn. New TCs are identified as constraints either (i) between a different pair of chains or (ii) between the same pair of chains at positions far away from the initial positions (i, j). We also apply CReTA to identify TCs at different t in the ECM runs and calculate the TC survival rate Q(t) analogously to  $Q(\lambda)$ . Note that there is some ambiguity in the range we use to define survival of a TC. The results presented below indicate that TCs do not slide much more than  $\langle n \rangle$  along chains during craze deformation and ECM runs. This motivated our definition of survival as sliding by less than  $\langle n \rangle$ , and we verified that other definitions do not change any of the trends we describe.

Two recent studies have used other methods to count entanglements during crazing or void formation. Neither followed individual constraints, and both used methods that are affected by the anisotropy of the craze. Richardson and Abrams reported a large degree of disentanglement during crazing of model nanotube-filled polymer glasses.<sup>21</sup> Their entanglement analysis used standard PPA and identified entanglements as regions of primitive paths with radius of curvature below a specified value. This approach is likely to overestimate entanglement loss because the curvature of primitive paths changes dramatically with increasing stretch.

Mahajan et al.<sup>22</sup> used a slight modification<sup>46</sup> of the original primitive path method<sup>12</sup> to follow entanglement evolution during void formation in model glassy polyethylene. They examined changes in the rheological entanglement length<sup>12,41</sup>

$$N_{\rm e}^{\rm rheo} \equiv (N-1) \langle R_{\rm ee}^2 \rangle / \langle L_{\rm pp} \rangle^2 \tag{5}$$

where  $\langle R_{ee}^2 \rangle$  and  $\langle L_{pp} \rangle$  are respectively the mean-squared chain endto-end distance and mean primitive-path contour length. Mahajan et al. found that  $N_e^{\text{theo}}$  increased by more than 50% as their system expanded to  $\lambda = 2$  where a single void had formed in part of their sample. They concluded that deformation "induces loss of rheological entanglements". However, Mahajan et al. also found that the number of kinks along the primitive paths remained unchanged up to  $\lambda = 2$ . This is consistent with our results in section 3 for much larger  $\lambda$  and fully developed crazes. Mahajan et al. argued that the discrepancy between their two measures of entanglement loss was related to long portions of chains in certain "favorable" locations being free of entanglements. However, another possibility is that the discrepancy arises because eq 5 is inappropriate for deformed systems.

Consider the case where the entire system is stretched affinely along z so that no entanglements can be lost. If chains are isotropic Gaussian coils in the initial state, segments along the primitive path sample all orientations with equal probability. One can show that the mean-squared length of these segments rises more rapidly with  $\lambda$  than the square of the mean length. In eq 5  $\langle R_{\rm ee}^2 \rangle$  is a sum of mean-squared lengths of segments of the primitive path, while  $\langle L_{\rm pp} \rangle$  is a sum of the average lengths. One finds that  $N_{\rm e}^{\rm theo}(\lambda)$  rises with  $\lambda$  as

$$\frac{N_{\rm e}^{\rm rheo}(\lambda)}{N_{\rm e}^{\rm rheo}(1)} = \frac{4}{3}(\lambda^2 + 2) \left(\frac{\sinh^{-1}(\sqrt{\lambda^2 - 1})}{\sqrt{\lambda^2 - 1}} + \lambda\right)^{-2}$$
(6)

This equation implies an increase of up to a factor of 4/3 in  $N_e$  even though an affine deformation can not change any topological property.

We have evaluated eq 5 for our isotropic and fully crazed states using CReTA to find the primitive path. For the flexible system,  $N_e^{\text{theo}}$ increases from 73 to 105 as  $\lambda$  increases from 1 to 8.5. For  $k_{\text{bend}}/u_0 =$ 1.5,  $N_e^{\text{theo}}$  increases from 32 to 46 in the fully developed craze. These increases by 44% are only slightly larger than the prediction of eq 6 and thus consistent with no entanglement loss. Mahajan et al. found larger changes at smaller  $\lambda$ . This appears to be because, as noted above, PPA produces much larger monomer displacements than CReTA. When we repeat our analysis of isotropic and fully crazed states but use PPA, we find that  $N_e^{\text{theo}}$  rises by more than a factor of 2 during crazing. We conclude that eq 5 may be quite sensitive to the method of finding the primitive path in anisotropic states and that it should not be used to measure entanglement loss during an anisotropic deformation.

# 3. RESULTS

In this section, we present the results of our MD simulations and CReTA analyses. First, we present stress—strain curves and compare  $\Lambda$  to estimates from models that assume entanglements act like chemical cross-links. Next we show that the number  $N_{\rm TC}$  of TCs is preserved to within ~1% during the entire deformation from initial dense glass to fully developed craze. Then we analyze the statistical distributions of TC spacings in both Euclidean and chemical-distance space and compare the distributions in undeformed glasses to those for fully developed crazes. Comparison of the chemical and Euclidean spacings shows that chains in the craze remain unstretched on scales of order  $\langle n \rangle$ .

We next turn to analyzing individual TCs between a given pair of chains at a given location and show that about 2/3survive from the initial state to the fully developed craze. Comparing the evolution of the identity of TCs during straindriven diffusion in crazing and thermal diffusion in endconstrained melts shows that the remaining 1/3 are replaced by TCs from other nearby chains. The results can be understood from a picture where entanglements in deformed glassy polymers do not act as chemical cross-links or slip-links between specific chain pairs but as topological constraints from a number of chains that form a rheological "tube" inherited from the melt.<sup>36</sup>

**3.1. Mechanical Response.** As in previous studies,<sup>8,20,26,27</sup> bead–spring MD simulations reproduce the key features of craze formation and drawing. Figure 3 shows the tensile stress as a function of stretch  $\lambda$  for the three different chain stiffnesses. All three curves show an initial rapid rise as the polymer deforms elastically, followed by a rapid drop when voids form ( $\lambda \sim 1.1$ ). Then polymers are gradually drawn from the glass into craze fibrils at a constant plateau stress  $\sigma_p$  until the craze occupies nearly the entire simulation cell. Subsequent expansion deforms the craze structure and requires a steadily increasing stress (strain hardening). The craze can expand by almost a factor of 2 before the stress along backbones is large enough to break chains.<sup>8,28</sup> We stop the simulations before this point.

Figure 1 shows a partial cross section of a simulation of  $k_{\text{bend}}/u_0 = 1.5$  chains at stretch  $\lambda = 3.4$ . The system is clearly separated into an undeformed region at the left and a craze containing fibrils and voids on the right. Experiments<sup>4,5</sup> and simulations<sup>8</sup> show that deformation is confined to an active zone near the interface between glass and craze. To illustrate



**Figure 3.** Tensile stress  $\sigma$  as a function of stretch  $\lambda$  during crazing of chains with different stiffness:  $k_{\rm bend}/u_0 = 0$  (black squares), 0.75 (red circles), and 1.5 (green triangles). Vertical dashed lines indicate values of  $\Lambda$  from the glass to craze density ratio. All results are for N = 500 systems at  $k_{\rm B}T = 0.1u_0$ .

this, monomers are colored by the magnitudes of their local nonaffine deformation as defined in ref 47. Monomers in red experienced a locally nonaffine root-mean-square (rms) displacement greater than 0.2*a* from  $\lambda = 3.39$  to 3.4. They are concentrated in a narrow region at the boundary between undeformed glass and craze where chains are pulled out from the glass and stretched from random walks to form fibrils. The craze structure in blue to the right remains largely unchanged until the entire glassy region is converted to a craze. It then expands as the stress rises.

The growth pattern revealed in Figure 1 is very different than the corresponding cartoon (Figure 2) used to motivate geometrically necessary entanglement loss (Appendix). GNEL theory was based on the assumption that fibrillation occurs via propagation of straight viscous fingers separating straight fibrils.<sup>4</sup> Instead, Figure 1 and previous studies<sup>8,26</sup> show fibrils form a complex branching structure that can conform to the underlying distribution of entanglements as it evolves. As we will show, no statistically significant net entanglement loss occurs during this process.

The extension ratio during deformation from glass to craze at the plateau stress is  $\Lambda = \rho_g/\rho_c$ , the ratio of the initial glass density to final craze density. Simulation values of  $\Lambda$  are given in Table 1. The results are consistent with recent work,<sup>28</sup> but slightly larger than earlier values where the chain statistics had not fully equilibrated before crazing.<sup>8,27</sup> Note that strain hardening sets in at  $\lambda$  slightly lower than  $\Lambda$  in Figure 3. This is a finite-size effect related to the periodic boundary conditions and the fact that two active zones moving from opposite directions merge as  $\lambda \to \Lambda$ .

Perhaps the greatest success of the cross-link model is its ability to predict trends in  $\Lambda$  with entanglement density.<sup>4,5</sup> If one assumes<sup>4</sup> that entanglements are uniformly spaced along chains and the chemical distance between successive entanglements along a chain is  $N_e$ , then the contour length and mean Euclidean distance between successive entanglements are respectively  $I_e = N_e I_0$  and  $d_e = \sqrt{N_e C_\infty} I_0$ , where  $I_0$  is the backbone bond length of the given polymer. Assuming that crazing can at most stretch chains taut between entanglements suggests a maximum extension ratio:

$$\lambda_{\rm max} = l_{\rm e}/d_{\rm e} = \sqrt{N_{\rm e}/C_{\infty}} \tag{7}$$

Experimental values<sup>4,5</sup> of  $\Lambda$  are within about 30% of values of  $\lambda_{\rm max}$  calculated using the rheological entanglement molecular weight  $M_{\rm e}$  from a melt near  $T_{\rm g}$ :  $M_{\rm e} = 4\rho k_{\rm B}T/5G_{\rm N}^0$ , where  $G_{\rm N}^0$  is the plateau modulus. Experiments<sup>5</sup> also show that adding either true chemical cross-links or entanglements produces a similar reduction in  $\Lambda$ .

Table 1 shows that values of  $\lambda_{\max}$  are also within 30% of our measured values of  $\Lambda$ . A similar correlation between  $\lambda_{\max}$  and  $\Lambda$  was seen in previous studies with less equilibrated chains.<sup>8</sup> One might think that the spacing between TCs should represent the distance between cross-links, but using  $\langle n \rangle$  in place of  $N_e$  in eq 7 gives extension ratios  $\lambda_{\max}^{topo}$  that are much too small (Table 1). Of course, eq 7 assumes random walk statistics with no correlations between successive segments between cross-links, which is not valid for the segments between TCs. As noted in section 2.2, past work shows the orientation of the primitive path only becomes decorrelated on scales larger than  $N_e > \langle n \rangle$ .<sup>12,14,45</sup>

Despite the success of eq 7 in predicting trends in  $\Lambda$ , past work<sup>8,</sup> <sup>7</sup> and the results presented below show that chains in the craze are not pulled taut on lengths of order  $N_{\rm e}$  or even  $\langle n \rangle$ . Indeed, the original derivation<sup>4</sup> of  $\lambda_{max}$  had an additional factor of  $\sqrt{3}$  to account for the fact that the projection of chain segments of length  $d_e$  along a given direction is only  $d_e/\sqrt{3}$ . Only segments that happen to be oriented along the extension direction should be pulled taut at  $\lambda_{max}$ . The  $\sqrt{3}$  was dropped in later work because it did not agree with experiment, but we conclude that it is needed to correctly predict the stretch needed to pull chains taut. One piece of evidence is that crazes can expand by about a factor of  $\sqrt{3}$  before the tension along the backbone rises significantly. The system with  $k_{\text{bend}}/u_0 = 1.5$ in Figure 3 has expanded to  $\lambda = 7 = 1.6\Lambda$ , and tensions in the chain are still too low to produce chain scission. Similar expansions are seen for other  $k_{\text{bend}}$  here and in refs 8 and 28 where breakable chains were used.

To further test this idea, we performed simulations of crazing employing similar protocols but with purely repulsive ( $r_c = 2^{1/\delta}a$ ) Lennard-Jones interactions. Chain ends were forced to deform affinely to limit disentanglement. Because there was no adhesion, the system deformed at nearly zero stress until chains were pulled taut. This occurred at  $\lambda \simeq 14$  for flexible chains, which is roughly  $\sqrt{3\Lambda}$  and similar to the onset of craze breakdown through chain scission in ref 28. We also expanded the same system by a factor of g in all three directions, so the volume expands by  $g^3$  compared to the undeformed glass. In this case, chains pulled taut at  $g \simeq 8$ , which is very close to  $\Lambda$ . In both cases there was no statistically significant change in the total number of TCs measured with CReTA.

A possible explanation for the success of eq 7 is suggested by considering the nature of craze formation. As chains are pulled into fibrils they align so that there are more strong covalent bonds along the direction of extension. The yield stress for further extension should rise with  $\lambda$  just as it does for  $\lambda > \Lambda$  in Figure 3. When the alignment has made the yield stress of the craze larger than that of the undeformed glass, the craze stops stretching. Thus,  $\Lambda$  is determined by the requirement that a craze stretched by  $\Lambda$  has a tensile yield stress  $\sigma_p$  equal to the stress required to deform the adjacent isotropic glass. Studies of

strain hardening in uniaxial tension show that the stress begins to rise rapidly before chains are fully stretched between entanglements.<sup>9,48</sup> It seems likely that removing the factor of  $\sqrt{3}$  approximately accounts for the fact that chains need not be taut before the yield stress of crazes reaches  $\sigma_p$ . The significant (up to 50%) variation in  $\Lambda/\lambda_{max}$  for different polymers<sup>4,5</sup> would then reflect variations in the factors that determine yield and strain hardening, including interchain friction, chain rigidity, side groups, etc.

**3.2.** Changes in TC Statistics during Crazing. Simple counting of the total number of TCs,  $N_{TC}$ , during deformation shows that this quantity is preserved during craze drawing. Figure 4 shows the percentage variation in  $N_{TC}$  with increasing



**Figure 4.** Percentage change in the total number of TCs  $N_{\text{TC}}$  with stretch  $\lambda$  for  $k_{\text{bend}}/u_0 = 0$  (black squares), 0.75 (red circles), and 1.5 (green triangles).

stretch for all three chain stiffnesses. Remarkably,  $N_{\rm TC}$  varies by no more than ~2% as  $\lambda$  increases to  $\Lambda$ . The small changes are comparable to the statistical error in  $N_{\rm TC}$ , which is about 1%. This result is inconsistent with the entanglement loss predicted by GNEL theory. To further test the nature of entanglements, we examine changes in the chemical and Euclidean distances between neighboring TCs.

If entanglements act like chemical cross-links, the probability distribution P(n) of chemical distances n between neighboring TCs should remain unchanged during deformation. Figure 5 compares P(n) in undeformed glasses and fully developed crazes at  $\lambda$  slightly larger than  $\Lambda$ . Note that when n is normalized by  $\langle n \rangle$ , the probability distributions for all chain stiffnesses collapse onto two separate but very similar curves corresponding to crazed and undeformed states. The collapse of results for systems with  $\langle n \rangle$  changing by more than a factor of 2.5 suggests that our results may be applicable to many linear polymers.

The curves for undeformed glasses are consistent with past studies of melts,<sup>14</sup> providing support for the common assumption<sup>4</sup> that entanglements in polymer glasses are largely inherited from their parent melts. There is an exponential decay at large  $n/\langle n \rangle$ , and a suppression<sup>14</sup> of P(n) at small n, that is more clearly evident in the inset.

Since  $N_{\rm TC}$  is constant (Figure 4), crazes and undeformed glasses have the same value of  $\langle n \rangle$ . Figure 5 shows that they also have the same exponential decay length in  $P(n/\langle n \rangle)$  at large *n*. The main difference in the distributions (see inset) is a shift in weight from  $n/\langle n \rangle \sim 1$  to smaller values. This implies that crazing tends to pull adjacent TCs together on scales of order  $\langle n \rangle$ . This causes a corresponding increase in the distance to the other adjacent TC and thus a small reduction in the prefactor of the exponential tail of *P* at large  $n/\langle n \rangle$ . Past studies of the nonaffine displacements produced by crazing<sup>27</sup> found



**Figure 5.** Probability distribution  $P(n/\langle n \rangle)$  of normalized chemical spacing  $n/\langle n \rangle$  for undeformed (open symbols) and fully crazed (closed symbols) systems with  $k_{\text{bend}}/u_0 = 0$  (black squares), 0.75 (red circles), and 1.5 (green triangles) at  $\lambda = 8.5$ , 6.5, and 4.5, respectively. The inset shows an expanded view of the distributions at small n with lines added to guide the eye.

that relative motion of monomers was also of order  $\langle n \rangle$ . One may speculate that craze drawing tends to pull adjacent TCs together to cluster in the intersections between fibrils and prevent GNEL. The observation of relative motion of TCs along chains suggests that they act more like slip-links than fixed cross-links during crazing. Bigger deviations from the chemical cross-link model are described in section 3.4.

The distributions of chemical and spatial distances between TCs are related to each other via polymer chain statistics. In melts and glasses, chains follow isotropic random walks at large n and the Euclidean distance d between TCs should scale as  $n^{1/2}$ . Crazing leads to stretched, anisotropic configurations. In the picture underlying eq 7, d would be proportional to n up to scales of order  $N_e$  in the craze.

Figure 6 shows results for P(d) for undeformed glasses and fully developed crazes with  $\lambda > \Lambda$ . Normalizing by the mean spacing  $\langle d \rangle$  (Table 2) collapses the results for all chain stiffnesses. For undeformed glasses, the probability is low at small *d*, just as the probability of small chemical spacings is reduced in Figure 5. There is a fairly broad peak at  $d \simeq 3\langle d \rangle/4$ , followed by an exponential decay for  $d > \langle d \rangle$ :

$$P(d) \propto \exp(-d/d^*)$$
 (8)

where  $d^*$  is the characteristic decay length. For all chain stiffnesses,  $d^* \simeq 0.7 \langle d \rangle$  (Table 2). This characteristic length should scale with the entanglement mesh size  $\varphi$ , which is smaller than the tube diameter  $d_{\text{tube}}^{12}$ .

Crazing increases  $\langle d \rangle$  by about a factor of 3 and changes the shape of P(d). In the fully developed craze, P(d) is peaked near d = 0, reflecting the increased probability of small chemical separations in Figure 5. For larger d, P(d) still decays exponentially, but now with  $d^* \simeq 1.2 \langle d \rangle$ .

The increase in P(n) and P(d) at small separations during crazing indicates that neighboring TCs along a chain are pulled together. Figure 7 shows that there is a more general spatial clustering of TCs. The solid black lines show the pair distribution functions g(r) for all TCs as a function of r.

Article



**Figure 6.** Distributions of normalized Euclidean spacing  $d/\langle d \rangle$ between consecutive TCs along chains in undeformed glasses (dashed lines, open symbols) and in fully developed crazes (solid lines and symbols) with  $k_{\text{bend}}/u_0 = 0$  (black squares), 0.75 (red circles), and 1.5 (green triangles). Here d is evaluated between TCs after CReTA.

Table 2. Best-Fit Parameters for Distributions Shown in Figure  $6^a$ 

	$k_{\rm bend}$	λ	$\langle d \rangle / a$	$d^*/a$
	0	1	4.7	3.0
	0	8.5	17.7	19.7
	0.75	1	4.3	2.9
	0.75	6.5	13.0	17.3
	1.5	1	3.7	2.5
	1.5	4.5	8.1	9.5
a	C 14			

<sup>*a*</sup>Values of  $d^*$  are obtained by fitting to eq 8. Uncertainties are a few percent.

Crazing clearly increases the number of TCs at separations less than  $\langle d \rangle$  (vertical dashed lines).

As illustrated in the upper right of Figure 7a, a given pair of TCs can share 0, 1, or 2 common chains.<sup>14</sup> Figures 5 and 6 only consider consecutive TCs along a chain, i.e., Type 1 or Type 2 TCs without any intervening TCs of any type along the common chain. Figure 7 shows the contribution to g(r) from each type of TC separately. Results for the undeformed glass are consistent with previous studies of melts (see Figure 10 and related discussion in ref 14). There is a significant number of Type 1 TCs out to  $r \sim \langle d \rangle$  in the undeformed state. Crazing reduces this number. There are very few Type 2 TCs (<1%) and almost all are at very small separations both before and after crazing. These TCs are most likely to form in cases where a third chain threads between the two chains and prevents the two TCs from moving together into a single TC or disappearing.

The biggest change produced by crazing is in the number of Type 0 TCs. While they share no common chains, crazing produces a strong peak in their contribution to g(r) at about  $0.25\langle d \rangle \sim 4a$ . We verified that this peak can not result from any affine deformation of the system, but it is consistent with TCs clustering into fibrils during crazing. Indeed, the peak position is comparable to the mean diameter of fibrils  $(D \sim 3.6a)$  as determined from the method described in ref 8. Clustering of TCs can also explain the complex branching geometry shown



Figure 7. Total pair distribution functions g(r) for TCs (black solid lines) in the (a) undeformed glass ( $\langle d \rangle = 4.7a$ ) and (b) fully developed craze ( $\langle d \rangle = 17.7a$ ) of fully fexible chains. The contribution to g(r) of TC pairs that share 0 (red dashed lines), 1 (blue dotted lines), or 2 (green dash-dotted lines) common chains are also also shown. The inset to (a) illustrates these three types of TC pairs with small black circles indicating TCs. Vertical dashed lines indicate  $\langle d \rangle$ , and the scales are chosen so that both curves extend to  $r/\langle d \rangle \approx 2$ .

in Figure 1. Moreover, lateral motion of TCs into fibrils provides a mechanism for avoiding the GNEL suggested by the simpler cartoon of craze growth in Figure 2.

3.3. Stretching of Segments between TCs. A measure of how stretched chains are can be constructed from the ratio S between the Euclidean distance d' separating monomers involved in consecutive TCs along a chain and the contour length associated with their chemical separation *n*:

$$S \equiv d'/nl_0 \tag{9}$$

We evaluate d' from the initial positions of monomers before CReTA to minimize any change in geometry. Fully taut segments are straight and have S = 1, while segments with S < 1still possess some "slack" and can be further stretched/ straightened.

The variation of the mean tautness (S(n)) with segment length is shown in Figure 8a. Covalent bonds with n = 1 are



**Figure 8.** (a) Mean value of tautness  $\langle S(n) \rangle$  (eq 9) as a function of chemical length *n* for undeformed glasses (dashed lines, open symbols) and fully developed crazes (solid lines, filled symbols) with  $k_{\text{bend}}/u_0 = 0$  (black), 0.75 (red), and 1.5 (green). (b) Distribution *P*(*S*) of tautness *S* for segments longer than  $\langle n \rangle/2$  in the same systems.

nearly rigid and always have  $S \approx 1$ . As *n* increases, chains have more possible configurations and the increased entropy makes them increasingly stretchable. In the undeformed states, chains obey Gaussian statistics for large *n*, implying  $\langle S(n) \rangle \propto C_{\infty}/n^{1/2}$ . Figure 8a is qualitatively consistent with this behavior over the available scaling range. In fully developed crazes, only segments with  $n \ll \langle n \rangle$  have an average length that is close to fully taut. For  $n > \langle n \rangle$  there is a gradual drop in  $\langle S(n) \rangle$  from about 0.7 to 0.5. This is consistent with segments being able to stretch by about a factor of  $\sqrt{3}$  since  $1/\sqrt{3} \approx 0.58$ .

Figure 8b shows the distribution P(S) for segments with chemical length larger than  $\langle n \rangle / 2$ . Shorter segments are not included since they are nearly straight even in the undeformed glass. The distributions for undeformed glasses have a broad peak at low S and almost no segments that are fully stretched. The peak moves to larger S as the stiffness increases. The distributions P(S) for fully developed crazes in Figure 8b are fairly constant at intermediate S with peaks near S = 1 and few segments to be pulled taut, presumably those that happen to be initially oriented along the tensile direction. However, integrating under the curve shows that roughly half of the

segments have  $S < 1\sqrt{3}$  and thus could still be stretched by  $\sqrt{3}$ . This is consistent with our observation that crazes can be stretched to  $\lambda \sim \sqrt{3}\Lambda$ .

**3.4. Following Individual TCs.** The results presented above examined global statistical features of TCs and their separations. While changes in P(n) indicated that TCs could move by distances of order  $\langle n \rangle$ , there was no evidence of entanglement loss. In this section we follow individual constraints defined as TCs between a given pair of mate chains at locations that slide less than  $\langle n \rangle$  along both chains. As described in section 2.2, we find the fraction  $Q(\lambda)$  of TCs between specific pairs of mate chains in the undeformed state that are still present in the same region of the same chains after a stretch of  $\lambda$ .

Figure 9 shows  $Q(\lambda)$  vs  $\lambda$  for chains of different stiffness. There is an initial jump of about 5% in  $Q(\lambda)$  that does not



**Figure 9.** Fraction of surviving TCs  $Q(\lambda)$  (solid lines) as a function of stretch for  $k_{\text{bend}}/u_0 = 0$  (black  $\blacksquare$ ), 0.75 (red  $\bullet$ ), and 1.5 (green  $\blacktriangle$ ). Vertical dashed lines indicate the corresponding values of  $\Lambda$ . The inset shows the fraction of exchanged TCs,  $R(\lambda) \equiv 1 - Q(\lambda)$ , as a function of the scaled stretch  $\lambda/\Lambda$ .

represent a true effect of deformation. Instead, it reflects an intrinsic ambiguity in the identity of TCs produced by CReTA.<sup>36</sup> For example, changes in the order in which chain sections are shortened can change which chains touch.

At larger deformations,  $Q(\lambda)$  decreases linearly but about 2/3 of the initial TCs are retained in the fully developed crazes for all chain stiffnesses. Since the number of TCs is constant, about 1/3 of TCs change identity during crazing. The linear variation in Q for  $\lambda < \Lambda$  follows from the fact that deformation and associated exchanges in TCs are localized in the active zone. As  $\lambda$  increases to  $\Lambda$ , the fraction of the system that has been transformed into a craze rises linearly to unity. If about 1/3 of TCs change identity in the active zone, there will be a linear drop of Q to 2/3 as  $\lambda$  rises to  $\Lambda$ .

The inset of Figure 9 shows the fraction of exchanged TCs,  $R(\lambda) \equiv 1 - Q(\lambda)$ , as a function of the normalized stretch,  $\lambda/\Lambda$ . Results for all chain stiffnesses collapse onto a common straight line that extends to  $\lambda/\Lambda > 1$  and R = 0.5. Once again, this suggests that chains with very different statistics undergo universal behavior during craze formation and that our results may be relevant for typical glassy polymers.

One possible mode of TC exchange would be motion of chains along their tubes. In this case, both lost and new TCs would tend to be near the end of one of the mate chains. Direct analysis of the location of lost and new TCs shows that there is no statistically significant increase in the probability that they lie near chain ends.<sup>49</sup> This mechanism of TC exchange would also be strongly suppressed by increasing the chain length. This would decrease the density of chain ends and the rate of exchange by a corresponding factor. Separate simulations with chains of length N = 1750 gave similar values of  $Q(\Lambda)$  even though the number of chain ends that can participate in exchange is 3.5 times lower. This confirms that most of the decrease in  $Q(\lambda)$  does not reflect disentanglement through mechanisms like the chain retraction or constraint release observed in nonlinear melt rheology.<sup>50,51</sup> Instead, we now show that entanglements reflect collective constraints by a number of chains that form the rheological tube. Small diffusive displacements of monomers within the tube change which chains from the tube provide the local uncrossability constraints (TCs).

3.5. TC Changes in Crazing and Melt Dynamics. Deformation into a craze and melt diffusion both produce nonaffine relative displacements of monomers that are limited by entanglements. In the tube model of melt dynamics, monomers diffuse perpendicular to the chain backbone until they feel constraints from neighboring chains that form the tube at the entanglement time  $\tau_{e}$ . The distance normal to the tube that a chain diffuses over  $\tau_e$  corresponds to the tube radius. Ultimately, entanglements force chains to reptate slowly along their tube until they escape it at the much longer disentanglement time  $\tau_{d}$ . In a recent study of perfect networks with fixed tubes,<sup>36</sup> the tube constraint was examined microscopically by using CRETA. It was found that during thermal diffusion the identities of chains forming TCs exchange, while the instantaneous TC density remains relatively constant. This is consistent with the view that entanglements represent constraints from a collection of chains that form a tube rather than chemical cross-links or chain-specific slip links.

Many studies of glassy systems show that mechanical deformation can produce nonaffine displacements that are similar to those produced by thermal diffusion.<sup>52,53</sup> Here we compare the loss of TCs due to nonaffine displacements from crazing or diffusion in end-constrained melts. Because crazing is anisotropic, we focus on the total rms displacement  $\delta_{xy}(\lambda)$  of monomers in the plane transverse to the imposed extension. There is no affine displacement in this plane. Thermal exploration of the tube in a melt is also related to transverse diffusion of monomers in the plane locally perpendicular to the tube. At small times diffusion is isotropic, and to avoid identifying the tube direction for each monomer we define  $\delta_t(t) = \sqrt{2\langle (\delta \mathbf{r}(t))^2 \rangle/3}$ , where  $\delta \mathbf{r}(t)$  is the 3D displacement vector during ECM diffusion for a time t and the factor of 2/3 gives the mean projection onto a plane.

Figure 10a shows that the fraction *R* of exchanged TCs varies in the same way with  $\delta_{xy}$  and  $\delta_t$ . As in Figure 9, there is an initial change of about 5% due to systematic variations in the identities of TCs.<sup>36</sup> The fraction of exchanged TCs then rises linearly with the planar displacement in both crazing and thermal motion. There is no change in the total number of TCs in either system and since the ends are constrained during thermal diffusion there should be almost no entanglement loss. Thus, these observations are consistent with entanglements in deformed glassy polymers acting as preserved, collective



**Figure 10.** (a) Fraction of exchanged TCs, *R*, as a function of the planar displacement during crazing  $\delta_{xy}$  (symbols) or thermal diffusion of end-constrained melts  $\delta_t$  (lines) for chains with  $k_{\text{bend}}/u_0 = 0$  (black, squares), 0.75 (red, circles), and 1.5 (green, triangles). Points are at  $\lambda = 0, 1.5, 2, 2.5, ...,$  and the last points are near  $\Lambda$  ( $\lambda = 4.5, 6.5,$  and 8.5). (b) Same data with displacement rescaled by  $d_{xy}$  the planar separation between TCs in the glass.

constraints formed by multiple chains making up a tube rather than cross-links between specific chains.

Figure 10a shows a linear change in *R* for crazes at  $\lambda < \Lambda$ . As in Figure 9, this follows from the fact that deformation is localized in the active region and the fraction of material that has been deformed rises linearly with  $\lambda$ . Direct analysis of  $\delta_{xy}$  as a function of height in partially crazed systems shows almost stretch-independent values of ~0.2*a* in undeformed regions and  $\delta_{xy}(\Lambda)$  in crazed regions. There is a smooth transition between these values in the active zones. The probability of changed TCs shows the same variation with height. The local variation of both quantities in the active zone allows us to examine how  $\delta_{xy}$  and *R* scale at values of  $\lambda$  between 1 and  $\Lambda$ . Plots of the local *R* vs local  $\delta_{xy}$  show the same linear rise in *R* as is observed in thermal diffusion.

Increasing the chain stiffness reduces the size of the tube because  $N_{\rm e}$  decreases and the TC density rises (Table 1). Thus, R rises more rapidly with displacement for larger  $k_{\rm bend}$ . A natural measure of the size of the tube is  $d_{xyy}$  the rms length of the projection onto the *xy*-plane of the vector between neighboring TCs along a chain. Values from the undeformed

glass are quoted in Table 1. Figure 10b shows that normalizing displacements by  $d_{xy}$  collapses both thermal and craze data at different  $k_{bend}$ . This is clear evidence that the amount of TC exchange is directly related to the fraction of the tube that chains have explored through thermal or mechanical diffusion.

If thermal and mechanical diffusion cause chains to explore the same tube, then exchanged TCs should involve the same set of mate chains that collectively form the tube. We tested this idea explicitly for flexible chains ( $k_{\text{bend}} = 0$ ). In any given configuration, each 500 monomer chain forms TCs with about 13 different chains. During deformation to  $\Lambda$  or diffusion to  $\delta_t$  $= d_{ry}$  the identities of these chains change. In both cases the cumulative number of different chains that a given chain formed a TC with was about 18. This is consistent with about a third (5/13) of the initial 13 TCs changing identity and involving a TC with a different chain. For each chain we stored all specific mate pairs that were found during deformation to  $\Lambda$ and compared them to the corresponding set sampled during diffusion over time t. The overlap between the two sets of mate pairs rises rapidly with *t* and exceeds 99% before  $\delta_t = d_{xy}$ . This is clear evidence that a tube formed by the same set of chains constrains motion during craze deformation and thermal diffusion.

#### 4. CONCLUSIONS

In this paper, we used MD simulations to study crazing of glassy polymers. As in previous MD studies, <sup>8,20-22,26-28</sup> the simulations reproduce many key features of experiments on craze growth, including a fixed extension ratio  $\Lambda$ , a constant plateau stress, and localization of deformation into a thin active zone (Figure 1). Extending past studies by following the evolution of individual topological constraints allowed us to test a common microscopic picture underlying phenomenological models for deformation of glassy polymers. Many start from the idea that entanglements inherited from the melt act like permanent chemical cross-links.<sup>2-6</sup> Then, assuming that the resulting network is pulled taut in the fully developed craze gives a prediction for  $\Lambda$  (eq 7) that describes trends in experimental data with entanglement length and chain stiffness. While eq 7 also describes trends in our calculated  $\Lambda$ , the microscopic evolution of entanglements is not consistent with a simple cross-linked network.

The entanglement network was characterized by following the topological constraints between primitive paths obtained via CReTA.<sup>14</sup> The network model for  $\Lambda$  assumes that chains are pulled taut over a length equal to the rheological entanglement length  $N_{\rm e}$ . This corresponds to the Kuhn length of the primitive path and is longer than the mean spacing  $\langle n \rangle$  between TCs. Past simulations<sup>8</sup> found that the mean length over which chains were pulled taut was much less than Ne. Here we directly analyzed chain segments between individual TCs in the fully developed craze. While a small fraction were pulled taut, most could still be extended by about a factor of 2. This is consistent with the fact<sup>8,20,28</sup> that chain scission does not occur until  $\lambda$  is roughly twice  $\Lambda$ . As noted previously,<sup>8</sup> eq 7 originally included an additional factor of  $\sqrt{3}$ . Separate tests were performed to check that the original expression correctly predicted the stretch where chains were pulled taut between entanglements. We conclude that  $\Lambda$  is determined by a balance of stresses in coexisting undeformed and crazed regions that occurs well before chains are taut.

Another influential prediction of network models is that there is geometrically necessary entanglement  $loss.^{4,24,54-58}$ 

Based on the simple model for craze growth in Figure 2, any initial entangled segments that span regions that deform into separate fibrils are assumed to be lost. For the long-chain limit considered here ( $N > 5-10N_e$ ), this entanglement loss is assumed to require chain scission.<sup>4</sup> Previous simulations found no scission until  $\lambda \gg \Lambda$ ,<sup>8,20,28</sup> but some presented evidence of a decrease in entanglement number.<sup>21,22</sup> As discussed in section 2.2, these papers used metrics that are not accurate for the anisotropic structure of a craze. In particular, a purely affine deformation of polymers reduces the number of entanglements from both measures even though no topological change occurs.

By directly counting TCs on primitive paths, we showed that the number of TCs was essentially unchanged during craze formation. The mean chemical spacing  $\langle n \rangle$  between TCs along a given chain was also constant. The distribution of chemical spacings changed only slightly, showing a tendency for nearby TCs to move closer together. Other measures of the Euclidean distances between TCs (Figure 7) also showed a tendency for them to cluster during craze formation. Geometrical models of entanglement loss do not allow for any correlation between the fibril surface and entanglement locations or for the fibril branching observed in crazes (Figure 1). We argue that clustering of entanglements allows the polymer to create a fibril structure without entanglement loss.

While there was no drop in the number of TCs during crazing, we found changes in the identities of TCs as defined by contacts<sup>36</sup> between primitive paths of specific pairs of chains at specific locations. These changes were not localized near chain ends as would be expected for entanglement loss by chain pullout or retraction. Instead, they occurred uniformly along the chain. Model polymers with very different entanglement lengths showed very similar behavior, with about 1/3 of TCs changing by  $\lambda = \Lambda$ . We argued that during deformation of glassy polymers constraints from entanglements do not act like chemical cross-links between specific pairs of chains. Instead, chains feel collective constraints from the chains making up the tube used in theories of melt rheology.<sup>1</sup> To test this equivalence, we compared the changes in TC identity during mechanical crazing and thermal diffusion in melts (with ends fixed to minimize disentanglement). The number of exchanged TCs grows in the same way with the rms nonaffine displacement of monomers whether motion is driven by thermal diffusion or mechanical deformation. Results for melts and crazes with different  $N_e$  all collapsed onto a single curve when the rms displacement was normalized by a measure of the tube radius. At  $\lambda = \Lambda$ , mechanical deformation produces displacements that are comparable to the transverse distance between TCs,  $d_{xy}$ .

As a further test of the tube concept, we compared the set of chains constraining thermal diffusion in end-constrained melts<sup>35,36,59</sup> and craze formation. During diffusion by about 10 times the entanglement time or crazing to  $\Lambda$ , about 1/3 of TCs changed identity. There was a 99% overlap of the new pairs of chains forming TCs during thermal diffusion and mechanical deformation, confirming that the same tube constrains both types of motion. Chain ends could move during crazing, but there was no evidence of TC exchange at chain ends. This and the equivalence between TC exchange during thermal and mechanical diffusion suggest that the tube remains intact during crazing. Note that chain pullout may be important close to the glass transition where  $\Lambda$  often rises.<sup>4</sup> This effect has been included in tube-models of disentanglement during crazing.

Our simulations have used a very simple bead—spring model but show strikingly universal behavior over a range of chain stiffnesses that change the entanglement density by a factor of 3. This suggests that the results may apply to a range of experimental systems. We hope that our work will inspire simulations with more realistic potentials and also the development of improved microscopic models. One interesting avenue would be tube models that incorporate glassy or frictional models of deformation and tube exploration. It will also be interesting to explore how the results are affected by adding true chemical cross-links to an entangled system.

# APPENDIX. GEOMETRICALLY NECESSARY ENTANGLEMENT LOSS

The final failure of crazes must occur at a fracture plane where chains pull out of the opposing surface or break. The frictional forces required for chain pull out grow rapidly with chain length, and experiments<sup>4,61</sup> and theory<sup>20,28</sup> show that chain scission dominates when chains are longer than  $5-10N_e$ .

There has been greater debate about the amount of chain scission during craze drawing to an extension ratio of  $\Lambda$ . Simulations have found negligible scission at these stretches, <sup>8,20,27,38</sup> but there is some evidence for chain scission in experiments<sup>4,54,55</sup> that led Kramer to formulate a theory of "geometrically necessary entanglement loss" (GNEL). The model is motivated by the cartoon of craze formation in Figure 2. It assumes fibrils are straight cylinders with average separation  $D_0$  and diameter  $D = D_0/\Lambda^{1/2}$ . The simplest version of GNEL theory predicts that all entanglements between chains that initially span regions that are deformed into different fibrils are lost. The fraction  $\mathcal{R}_0$  of entanglements that are lost is then<sup>4</sup>

$$\mathcal{R}_{0} = \frac{d}{D_{0}} - \frac{1}{3} \left( \frac{d}{D_{0}} \right)^{2}$$
(10)

where d is the Euclidean distance between entanglements in the undeformed state.

Predicted values of  $\mathcal{R}_0$  for typical glassy polymers are about 1/2, e.g., measurements of polystyrene<sup>54</sup> show (d = 9.6 nm,  $D_0 = 12$  nm) and thus predict  $\mathcal{R}_{GNEL} \simeq 0.6$ . This estimate is in fact an upper bound since it does not allow for entanglements to move laterally to avoid the voids. Later generalizations accounted for the presence of horizontal cross tie fibrils that connect the main fibrils. The fraction of entanglements that could survive by localizing in cross-tie fibrils was assumed to be proportional to the mass fraction  $p_c$  of cross-tie fibrils. The corrected fraction of lost entanglements is

$$\mathcal{R}^* = (1 - p_c)\mathcal{R}_0 \tag{11}$$

Typical values of  $p_c$  for synthetic-polymer glasses are in the 10%-20% range.

Historically, GNEL has been widely accepted and was used in followup theoretical and experimental work, including (e.g.) predicting the effect of entanglement loss via chain scission on the plateau stress  $\sigma_p^{58}$  and the critical craze width,<sup>56</sup> as well as explaining the strain rate and chain length dependence of the craze initiation stress.<sup>62</sup> However, since experiments cannot directly identify individual entanglements and thus cannot directly measure  $\mathcal{R}$ , GNEL theory has never been conclusively confirmed. In section 3.4, we showed that formation of stable crazes does not produce any significant entanglement loss. This result is consistent with previous alternate proposals that do not require such high levels of disentanglement. For example, extensive molecular dynamics simulations by Rottler and Robbins<sup>8</sup> suggest that entanglements can survive the fibrillation process via lateral motions of size comparable to d and  $D_0$ . Indeed, pictures like Figure 1 and electron microscope images show that fibrils are far from being straight cylinders and suggest they can angle to accommodate the location of entanglements.

# AUTHOR INFORMATION

#### **Corresponding Authors**

- \*E-mail: get@live.unc.edu (T.G.). \*E-mail: rshoy@usf.edu (R.S.H.). \*E-mail: mr@jhu.edu (M.O.R.).
- E man. m(w)na.edu (m.

# ORCID <sup>©</sup>

Ting Ge: 0000-0003-2456-732X

Mark O. Robbins: 0000-0001-7160-3608

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant DMR-1006805, 1411144 and DMR-1555242. The work of SDA and CT forms part of the Research Programme of the Dutch Polymer Institute (DPI), Eindhoven, The Netherlands, Project No. 744. We thank Gary S. Grest for providing equilibrated melt configurations, Doros N. Theodorou and E. J. Kramer for useful discussions, and Thomas C. O'Connor and Marco Galvani Cunha for help in rendering graphics.

#### REFERENCES

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.

(2) Ward, I. M. Mechanical Properties of Solid Polymers; Wiley: New York, 1983.

(3) Haward, R. N.; Young, R. J. The Physics of Glassy Polymers; Chapman & Hall: London, 1997.

(4) Kramer, E. J. Microscopic and molecular fundamentals of crazing. *Adv. Polym. Sci.* **1983**, *52*, 1–56.

(5) Kramer, E. J.; Berger, L. L. Fundamental Processes of Craze Growth and Fracture. *Adv. Polym. Sci.* **1990**, *91*, 1–68.

(6) Arruda, E. M.; Boyce, M. C. Evolution of plastic anisotropy in amorphous polymers during finite straining. *Int. J. Plast.* **1993**, *9*, 697. (7) Argon, A. S. *The Physics of Deformation and Fracture of Polymers*; Cambridge Solid State Science: 2013.

(8) Rottler, J.; Robbins, M. O. Growth, microstructure, and failure of crazes in glassy polymers. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* 2003, 68, 011801.

(9) Hoy, R. S.; Robbins, M. O. Strain hardening in polymer glasses: Limitations of network models. *Phys. Rev. Lett.* **2007**, *99*, 117801.

(10) Hoy, R. S. Why is understanding glassy polymer mechanics so difficult? J. Polym. Sci., Part B: Polym. Phys. 2011, 49, 979–984.

(11) One exception is work on specially prepared mixtures of linear and ring polymers.  $^{63}$ 

(12) Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. Rheology and microscopic topology of entangled polymeric liquids. *Science* **2004**, *303*, 823–826.

(13) Kröger, M. Shortest multiple disconnected path for the analysis of entanglem ents in two- and three-dimensional polymeric systems. *Comput. Phys. Commun.* **2005**, *168*, 209–232.

(14) Tzoumanekas, C.; Theodorou, D. N. Topological Analysis of Linear Polymer Melts: A Statistical Approach. *Macromolecules* **2006**, 39, 4592–4604.

(15) Riggleman, R. A.; Toepperwein, G.; Papakonstantopoulos, G. J.; Barrat, J. L.; de Pablo, J. J. Entanglement Network in nanoparticle reinforced polymers. *J. Chem. Phys.* **2009**, *130*, 244903.

(16) Toepperwein, G. N.; Karyiannis, N. C.; Riggleman, R. A.; Kröger, M.; de Pablo, J. J. Influence of Nanorod Inclusions on Structure and Primitive Path Network of Polymer Nanocomposites at Equilibrium and Under Deformation. *Macromolecules* **2011**, *44*, 1034– 1045.

(17) Leonforte, F. Evolution of entanglements during the response to a uniaxial deformation of lamellar triblock copolymers and polymer glasses. *Phys. Rev. E* 2010, *82*, 041802.

(18) Kuo, J. M.; Locker, R.; Rutledge, G. C. Plastic deformation of semicrystalline polyethylene under extension, compression and shear using molecular dynamics simulations. *Macromolecules* **2014**, *47*, 2515–2528.

(19) Brown, H. R. A Molecular Interpretation of the Toughness of Glassy Polymers. *Macromolecules* **1991**, *24*, 2752–2756.

(20) Rottler, J.; Barsky, S.; Robbins, M. O. Cracks and Crazes: On calculating the macroscopic fracture energy of glassy polymers from molecular simulations. *Phys. Rev. Lett.* **2002**, *89*, 148304.

(21) Richardson, D. G.; Abrams, C. F. The effects of nanotube fillers on craze formation in simulated glassy polymers under tensile load. *Mol. Simul.* **2007**, 33, 421.

(22) Mahajan, D. K.; Singh, B.; Basu, S. Void nucleation and disentanglement in glassy amorphous polymers. *Phys. Rev. E* 2010, *82*, 011803.

(23) Stukowski, A. Visualization and analysis of atomistic simulation data with OVITO - the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18*, 015012.

(24) Miller, P.; Buckley, D. J.; Kramer, E. J. Microstructure and origin of cross-tie fibrils in crazes. *J. Mater. Sci.* **1991**, *26*, 4445–4454.

(25) Kremer, K.; Grest, G. S. Dynamics of Entangled Linear Polymer Melts: A Molecular-Dynamics Simulation. *J. Chem. Phys.* **1990**, *92*, 5057–5086.

(26) Baljon, A. R. C.; Robbins, M. O. Simulations of Crazing in Polymer Glasses: Effect of Chain Length and Surface Tension. *Macromolecules* **2001**, *34*, 4200–4209.

(27) Rottler, J.; Robbins, M. O. Jamming under tension in polymer crazes. *Phys. Rev. Lett.* **2002**, *89*, 195501.

(28) Ge, T.; Grest, G. S.; Robbins, M. O. Tensile Fracture of Welded Polymer Interfaces: Miscibility, Entanglements, and Crazing. *Macromolecules* **2014**, *47*, 6982–6989.

(29) Auhl, R.; Everaers, R.; Grest, G. S.; Kremer, K.; Plimpton, S. J. Equilibration of long chain polymer melts in computer simulations. *J. Chem. Phys.* **2003**, *119*, 12718–12728.

(30) Faller, R.; Kolb, A.; Müller-Plathe, F. Local chain ordering in amorphous polymer melts: influence of chain stiffness. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2071.

(31) Ge, T. Entanglements in Large Deformation and Mechanical Failure of Glassy Polymers. Ph.D. Thesis, Johns Hopkins University, Baltimore, 2013.

(32) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. **1995**, 117, 1–19.

(33) Hoy, R. S.; Robbins, M. O. Effect of equilibration on primitive path analyses of entangled polymers. *Phys. Rev. E* 2005, *72*, 061802.

(34) Rottler, J.; Robbins, M. O. Shear yielding of amorphous polymer glasses: effect of temperature and strain rate. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2003**, *68*, 011507.

(35) Zhou, Q.; Larson, R. G. Direct Calculation of the Tube Potential Confining Entangled Polymers. *Macromolecules* **2006**, *39*, 6737–6743.

(36) Anogiannakis, S. D.; Tzoumanekas, C.; Theodorou, D. N. Microscopic description of entanglements in polyethylene networks: strong, weak, pairwise, and collective attributes. *Macromolecules* **2012**, 45, 9475–9492.

(37) Pütz, M.; Kremer, K.; Grest, G. S. What is the entanglement length in a polymer melt? *Europhys. Lett.* **2000**, *49*, 735.

(38) Ge, T.; Robbins, M. O.; Perahia, D.; Grest, G. S. Healing of polymer interfaces: Interfacial dynamics, entanglements, and strength. *Phys. Rev. E* **2014**, *90*, 012602.

(39) Hsu, H.-P.; Kremer, K. Static and dynamic properties of large polymer melts in equilibrium. *J. Chem. Phys.* **2016**, *144*, 154907.

(40) Tzoumanekas, C.; Theodorou, D. N. From atomistic simulations to slip-link models of entangled polymer melts: Hierarchical strategies for the prediction of rheological properties. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 61–72.

(41) Hoy, R. S.; Foteinopoulou, K.; Kröger, M. Topological analysis of polymeric melts: Chain-length effects and fast-converging estimators for entanglement length. *Phys. Rev. E* 2009, *80*, 031803.

(42) Shanbhag, S.; Larson, R. G. Chain retraction potential in a fixed entanglement network. *Phys. Rev. Lett.* **2005**, *94*, 076001.

(43) Hoy, R. S.; Grest, G. S. Entanglements of an End-Grafted Polymer Brush in a Polymeric Matrix. *Macromolecules* **2007**, *40*, 8389.

(44) Tzoumanekas, C.; Lahmar, F.; Rousseau, B.; Theodorou, D. N. Onset of Entanglements Revisited. Topological Analysis. *Macromolecules* **2009**, *42*, 7474–7484.

(45) Everaers, R. Topological versus rheological entanglement length in primitive-path analysis protocols, tube models and slip-link models. *Phys. Rev. E* **2012**, *86*, 022801.

(46) Sukumaran, S. K.; Grest, G. S.; Kremer, K.; Everaers, R. Identifying the primitive path mesh in entangled polymer liquids. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 917.

(47) Falk, M. L.; Langer, J. S. Dynamics of viscoplastic deformation in amorphous solids. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1998**, *57*, 7192.

(48) Hoy, R. S.; Robbins, M. O. Strain Hardening of Polymer Glasses: Entanglements, Energetics and Plasticity. *Phys. Rev. E* 2008, 77, 031801.

(49) The main statistical effect is related to the definition of survival as sliding by less than  $\langle n \rangle$  along the chain (section 2.2). In the center of the chain a region of width  $2\langle n \rangle$  contributes to a surviving TC, while this shrinks to  $\langle n \rangle$  at a chain end. The affected fraction of chains near a chain end changes from  $2\langle n \rangle/N = \sim 0.13$  to 0.05 with stiffness and  $Q(\Lambda)$  remains unchanged.

(50) McLeish, T. C. B.; Plummer, C. J. G.; Donald, A. M. Crazing by disentanglement: non-diffusive reptation. *Polymer* **1989**, *30*, 1651–1655.

(51) McLeish, T. C. B. Tube theory of entangled polymer dynamics. *Adv. Phys.* **2002**, *51*, 1379.

(52) Ono, K.; O'Hern, C. S.; Durian, D. J.; Langer, S. A.; Liu, A. J.; Nagel, S. R. Effective temperatures of a driven system near jamming. *Phys. Rev. Lett.* **2002**, *89*, 095703.

(53) Maloney, C. E. Evolution of displacements and strains in sheared amorphous solids. *J. Phys.: Condens. Matter* **2008**, *20*, 244128.

(54) Henkee, C. S.; Kramer, E. J. Crazing and Shear Deformation in Crosslinked Polystyrene. J. Polym. Sci., Polym. Phys. Ed. **1984**, 22, 721-737.

(55) Berger, L. L.; Kramer, E. J. Chain disentanglement during high-temperature crazing of polystyrene. *Macromolecules* **1987**, *20*, 1980–1985.

(56) Berger, L. L. On the mechanism of craze fibril breakdown in glassy polymers. *Macromolecules* **1990**, *23*, 2926–2934.

(57) Hui, C. Y.; Kramer, E. J. Molecular weight dependence of the fracture toughness of glassy polymers arising from crack propagation through a craze. *Polym. Eng. Sci.* **1995**, *35*, 419–425.

(58) Krupenkin, T. N.; Fredrickson, G. H. Crazing in Two and Three Dimensions. 2. Three-Dimensional Crazing. *Macromolecules* **1999**, *32*, 5036–5045.

(59) Bisbee, W.; Qin, J.; Milner, S. T. Finding the Tube with Isoconfigurational Averaging. *Macromolecules* **2011**, *44*, 8972–8980.

(60) Han, H. Z. Y.; McLeish, T. C. B.; Duckett, R. A.; Ward, N. J.; Johnson, A. F.; Donald, A. M.; Butler, M. Experimental and theoretical studies of the molecular motions in polymer crazing. 1. Tube Model. *Macromolecules* **1998**, *31*, 1348–1357.

(61) Wool, R. P. Polymer Interfaces: Structure and Strength; Hanser: Munich, 1995.

470

(62) de Focatiis, D. S. A.; Buckley, C. P.; Hutchings, L. R. Roles of chain length, chain architecture, and time in the initiation of visible crazes in polystyrene. *Macromolecules* **2008**, *41*, 4484–4491.

(63) Goossen, S.; Krutyeva, M.; Sharp, M.; Feoktystov, A.; Allgaier, J.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. Sensing Polymer Chain Dynamics through Ring Topology: A Neutron Spin Echo Study. *Phys. Rev. Lett.* 2015, 115, 148302.