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# Swelling molecular entanglement networks in polymer glasses

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Entanglements in a polymer network are like knots between the polymer chains, and they are at the root of many phenomena observed in polymer systems. When a polymer glass is strained, cracklike deformations called crazes may be formed and the study of these regions can reveal much about the nature of entanglements. We have studied crazes in systems that are blends of long polymer chains diluted with chains of various small molecular weights. The range of diluting chain lengths is such that a fraction of them have conformations leading to entanglements. It has been found that a system with more short chains added acts like one in which the entanglement density is smaller than that in an undiluted system. We propose a model that quantitatively predicts the density of effective entanglements of a polydisperse system of polymer chains which is consistent with our experimental data.

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## I. INTRODUCTION

Much of what makes polymer systems distinct from other forms of condensed matter can be traced to the fact that they are composed of long, chainlike molecules whose backbones cannot pass through one another [1]. In a melt of long polymers, thermal fluctuations cause chain conformations to be such that a given chain entangles with other chains in the space that it explores. As a result of these interactions, the mobility of the molecule is severely reduced as compared to smaller molecules. Entanglements restrict the chain's motion perpendicular to its contour length and are affected by several parameters including the volume occupied by the chain and the *pervaded volume*—the volume explored by the chain [1–4].

In equilibrium, polymer chains in the melt state are considered *ideal*, that is, they take on conformations corresponding to random walks [1]. While the volume taken up by a chain scales simply as the molecular weight, $V_c \propto M$, the actual volume explored by the chain through its random path is typically much larger. The pervaded volume of a polymer chain, $V_p$, can be defined by a sphere whose radius is given by the radius of gyration, $R$ (the root-mean-square distance of all monomers from the center of mass of the chain). For random walks $R \propto M^{1/2}$ [1]. Since the pervaded volume increases with the molecular weight as $V_p \propto R^3 \propto M^{3/2}$, the ratio $V_c/V_p$ is *decreasing* with $M$: on average a longer chain interacts with more other chains. As we will see, because the pervaded volume of a chain is, on average, occupied by more other chains as $M$ increases, it is more likely for higher molecular weight chains to be entangled. Simply put, the more chains a given polymer chain interacts with the more likely it is to be entangled.

Of fundamental importance in polymer systems are the questions of whether chains are entangled and the nature of the spacing between entanglements. Rheological and glassy state properties of polymers depend crucially on the answers to these questions [5–7] and underpin polymer theory [1,8–10]. The former of these questions receives significant attention in the polymer literature [1,5,11–14]. There is growing consensus in theoretical, computational, and experimental studies that in a monodisperse system of sufficiently long chains the average molecular weight of a segment between entanglements, $M_e$, is constant [9,11–13]. In blends of two or more weight fractions of the same polymer species, however, the case is not so clear. Even when the molecular weights of blend components are quite long compared to $M_e$, it is possible to describe $M_e$ as having been dilated. Recent theoretical and experimental treatments have demonstrated this dilation [10,14] for blends of a long component with either a short or another long component (here "long" or "short" is always in comparison to $M_e$).

The question of whether a chain is entangled has received considerably less attention. Kavassalis and Noolandi have addressed this question and propose a model which predicts an abrupt transition from zero to finite probability of entanglement as $M$ passes through some critical molecular weight [15]. Here we present a model that also has a low-$M$ region for which the probability of entangling with other molecules is zero, while the transition to finite values is continuous. Our model is compared to measurements of the density of effective entanglements in blends of long- and short-chain polymers shown schematically in Fig. 1(a). The model can be applied to systems with any number of molecular weight components, so we have prepared ternary systems to test the model beyond binary systems. Previous works have focused on blends of long chains with the second component either much shorter than [14,16,17] or significantly longer than $M_e$ [10,14]. In contrast with these studies our work focuses on the transition *through* $M_e$ where one cannot assume that the short chains do not entangle. The questions we seek to answer are, (1) what is the effect of swelling the entanglements that connect a polymer network; and, (2) how does the length of a polymer chain relate to the *probability* that it will be entangled with other chains?

When a polymer glass is strained, microscopic cracklike deformations called crazes may be formed [18–20]. Crazes are composed of a load bearing, interconnected fibrillar structure bridging a gap between undeformed material, and they exist because polymers are entangled [18,19]. Previous

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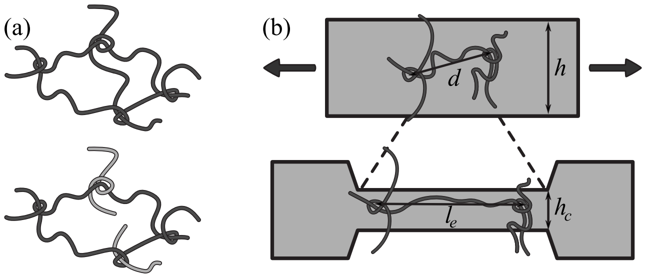

FIG. 1. (a) The entanglements that exist on the vertically oriented chain are rendered ineffective when replaced by short segments. (b) Schematic of the crazed and uncrazed system before and after straining, overlaid with a representation (not to scale) of one polymer molecule, aligned along the strain direction, before and after straining.

studies have focused on understanding the microscopic processes that govern the nucleation, growth, and failure of crazes as the strain increases [18–25]. Drawing on these seminal studies, recent work used atomic force microscopy (AFM) of crazes to probe the configurations of polymers in confinement [26]. It is the aim of this work to continue the use of crazing experiments to understand properties of molecular entanglement in equilibrium. We stress from the outset that the work presented here is done on glassy systems which is in contrast to many dynamic studies of entanglements (e.g., rheology, neutron spin echo). However, since the structure of a glass is inherited from that of the melt, entanglement properties can be elucidated through the use of crazing [18–25]. In this work, we find that there is a range of molecular weights for which the entanglement density can be interpreted as having been reduced from that of long chains. The reduction in the entanglement density is even apparent for chains with molecular weights well above $M_e$.

In the thin films we study here, crazes are characterized by the ratio of the deformation-induced neck height to the height of the undeformed film, $h_c/h$. A schematic of a craze region is shown in Fig. 1(b), while an AFM topography image of a craze is seen in Fig. 2. The connection between the essentially macroscopic quantity $h_c/h$ and the microscopic $M_e$ was made some time ago in experiments by Donald and Kramer [18,21,22]; simulations by Rottler and Robbins have further verified the connection [20]. The average distance between entanglements prior to crazing is $d \propto M_e^{1/2}$ since polymers in the melt are random walks. After crazing, the random network of entanglements is expanded in the strain direction. It was shown by Kramer and co-workers that after straining $l_e \propto M_e$ [18,21,22]. Rottler and Robbins determined the proportionality constant in this relationship using simulations [20]. The lengths $d$ and $l_e$ are shown schematically in Fig. 1(b) for the specific case of an entanglement strand aligned along the strain direction (in a random network all orientations are equally probable). Since the deformation of the chains is reflected in the macroscopic deformation of the thin film, it is easy to show that $h_c/h \propto d/l_e \propto 1/M_e^{1/2}$.

A system of very long polymer chains whose molecular weights $M_\ell \gg M_e$ will have a density of entanglements, $\nu \propto 1/M_e$, which is large compared to a system of chains whose molecular weights are small. Just as a string must be long enough to tie a knot, if the molecular weight of the short chains is too small, then there can be no entanglements. However, because of the random configurations of polymer chains in the melt, an intermediate case also exists, where some short chains are entangled and others are not. Here we consider a *blended* system of very long chains to which one adds some mass fraction, $\phi$, of short chains, see Fig. 1(a). The blending approach allows us to elucidate the importance of the entanglement behavior of the shorter chains where this would be much more difficult in monodisperse systems (for example, in the work by Kramer and co-workers [27] it was found that stable crazes could not be observed in monodisperse 37 and 50 kg/mol systems). In a blended system we can say that the entanglements of the large $M$ system have been *swelled* or *diluted* by the small $M$ chains [14,16,17]. We define a density of effective entanglements, $\nu_{eff} \propto 1/M_{eff}$, dependent on the blend concentration, $\phi$, that will be intermediate to that of the long- and short-chain systems, $0 < \nu_{eff}(\phi) < \nu$. Since $h_c/h \propto 1/M_{eff}^{1/2}$, we have

$$\left(\frac{h_c}{h}\right)^2 \propto \nu_{eff}. \tag{1}$$

## II. EXPERIMENT

Samples were prepared by blending long and short chains of polystyrene (PS) with various mass fractions of the short component, $\phi$, in toluene (all PS obtained from Polymer Source Inc.). The number averaged molecular weight of the long chains was $M_\ell$=734 kg/mol, and that of the short chains was $M_s$=4.8 or 18.4 kg/mol. Ternary systems were prepared in which the mass fraction of long chains with $M_\ell$=734 kg/mol is always 0.50. A mass fraction $\phi$, of $M_s^{(1)}$=18.4 kg/mol chains was added while $M_s^{(2)}$=64.0 kg/mol chains made up the rest of the system. The polydispersity index for all PS was ≤1.07. Films approximately 110 nm thick were spincast from solution onto freshly cleaved mica substrates and annealed for 12 h at 120 °C to remove residual stress and solvent. Films were floated onto

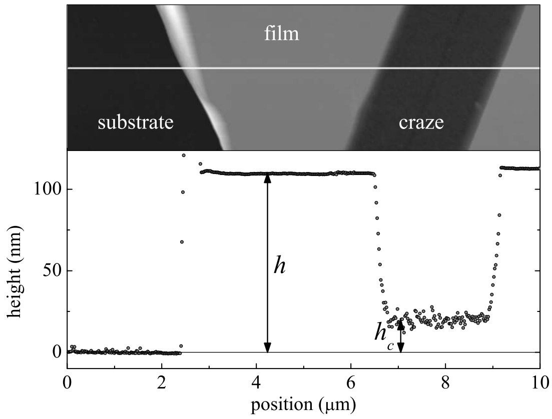

FIG. 2. An atomic force microscope image of a crazed sample showing the substrate, regions of the sample that have been deformed by crazing, and undeformed regions. The plot is a line profile corresponding to the white line.

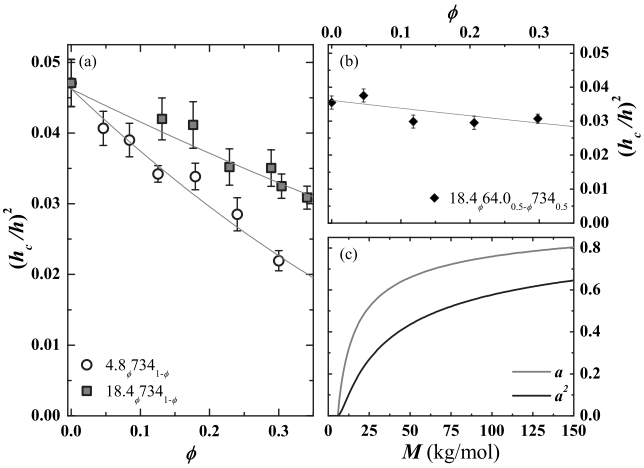

FIG. 3. (a) A plot of $(h_c/h)^2$ as a function of $\phi$ for the two binary systems with $M_\ell=734$ kg/mol and $M_s=4.8$ kg/mol (○) or $M_s=18.4$ kg/mol (□). (b) A plot of $(h_c/h)^2$ as a function of $\phi$ for the ternary system with $M_l=734$ kg/mol, $M_s^{(1)}=18.4$ kg/mol, and $M_s^{(2)}=64.0$ kg/mol. The solid lines in (a) and (b) are best fits of the model obtained with $\mu=5.8$ kg/mol. (c) The functions $a(M)$ and $a(M)^2$ as given by Eq. (3) with $\mu=5.8$ kg/mol for $0<M<150$ kg/mol.

the surface of a clean water bath (Milli Q) and picked up across a 1.5 mm gap between two aluminum blocks with sharp edges and allowed to dry. One of the blocks was fastened to a single-axis translation stage (Newport MFA-CC, SMC100CC), and slowly pulled apart at room temperature until crazes were formed. A constant strain rate of $\dot{\gamma}=2\times10^{-4}$ s$^{-1}$ was used and samples were strained to about $\gamma=0.1$.

Berger and Kramer [28] have performed crazing experiments at temperatures approaching the glass transition. In these experiments, they observe that an enhanced mobility as the temperature is increased and $T_g$ is approached affects the crazing measurements. These same studies found that deep in the glassy state (approximately 40 K below $T_g$) the results were independent of temperature. Since the measurements reported here were carried out approximately 80 K below $T_g$, they are a robust probe of the entangled network in the melt state.

The strained PS samples were transferred to a Si substrate by placing them onto the Si surface and letting surface forces pull the film into contact with the substrate [26]. A scratch was made along the sample exposing the substrate, and the heights $h_c$ and $h$ were measured using AFM in tapping mode (Veeco-Digital Instruments Multimode), an example is shown in Fig. 2. In the image one can see the substrate, the craze, and the unstrained film simultaneously. As suggested by Eq. (1), we plot $(h_c/h)^2$ as a function of $\phi$ in Fig. 3 [31].

## III. RESULTS AND DISCUSSION

Examining the data of Fig. 3(a), we see that as the mass fraction of short chains increases, a decrease in $\nu_{eff}$ results. Furthermore, the smaller molecular weight diluent shows stronger attenuation of $\nu_{eff}$. These results can be interpreted as follows: a crazed polymer system whose constituents are a blend, with $M_\ell \gg M_e$ and other chains with $M_s$ in the vicinity of $M_e$, acts like a system whose entanglement density is less than the long chain $\nu$ of the polymer.

To understand how adding short chains to the network affects $\nu_{eff}$ we first suggest how to find the probability that an individual chain with molecular weight $M$ is effectively entangled, and then generalize to the case of a blend. The model is an extension of the chain packing ideas presented by Fetters *et al.* [2,3]: for a given chain to participate in the entanglement network, it must share its pervaded volume with a sufficient number of other chains. The average fraction of interactions a specific chain has with other chains is the same as the average amount of space in the pervaded volume that is available to other chains:

$$a(M)=\left\langle 1-\frac{V_c}{V_p}\right\rangle. \tag{2}$$

Since $V_c \propto M$ and $V_p \propto R^3 \propto M^{3/2}$ on average, we find

$$a(M)=1-\sqrt{\frac{\mu}{M}}, \tag{3}$$

where $\mu$ is a constant that is proportional to $M_e$.

A more rigorous derivation of Eq. (3) can be obtained by averaging over all possible conformations of an ideal chain. Since $V_c=M/\rho_n$, where $\rho_n$ is the polymer's molar mass density, all that remains to evaluate Eq. (2) is to obtain $\langle 1/V_p\rangle \propto \langle 1/R^3\rangle$ as a function of $M$. For an ensemble of random walks with a given number of steps (or molecular weight, $M$), Rudnick and Gaspari [30] have calculated an approximate probability distribution of their radii of gyration. They obtain

$$P(R,M) \propto \left(\frac{R^2}{\beta M}\right)^{1/2} \exp\left(-\frac{3}{2}\frac{R^2}{\beta M}\right), \tag{4}$$

where the proportionality constant is chosen such that $\langle R^2\rangle = \beta M$. Using this probability distribution, we can calculate $\langle 1/R^3\rangle$ and thus find that $\langle V_c/V_p\rangle \propto (\rho_n^2\beta^3 M)^{-1/2}$. Having calculated the second term in Eq. (2), we obtain Eq. (3), with $\mu \propto 1/\rho_n^2\beta^3$ a polymer specific constant that is *proportional* to $M_e$. The proportionality between $\mu$ and $M_e$ is demonstrated in Refs. [2,3] where Fetters and co-workers argue that the onset of entanglement occurs when the molecular weight of a chain in the melt is large enough such that $V_c/V_p$ is sufficiently small. These authors use the relations $V_c=M/\rho_n$ and $V_p \propto (\beta M)^{3/2}$ to obtain the result stated above: $M_e \propto 1/\rho_n^2\beta^3 \propto \mu$.

As in the work by Si *et al.* [26], we assume that the total number of entanglements is given by the sum of the interchain and self-entanglements in a system; $a$ is the fraction of interchain entanglements. Clearly a negative value of $a$ is unphysical and $a=0$ for $M \leq \mu$. The interpretation of the cutoff, $M=\mu$, is physically intuitive: a chain must have some minimum length, $\mu$, before it can entangle. Since there is a distribution of entanglement lengths, with $M_e$ being the average, $\mu$ must be less than and on the order of $M_e$.

To determine the degree to which a network of polymer chains with molecular weights $M$ is entangled, we consider that an entanglement is the result of an interaction between two chains. In order for an entanglement to contribute to the network integrity, both chains must be entangled. Above we have calculated $a(M)$ which is the probability of having an interchain entanglement. As is implicit in the chain packing models [2,3] and discussed in the work of Si *et al.* [26], we also assume that the effective entanglements, those that contribute to the network integrity, are with *other* chains. Since the probability of having an interchain entanglement is $a(M)$, the probability that the interaction between two chains contributes to the network is $a^2$. Hence, the density of effective entanglements in a network is given by $\nu_{eff}=\nu a^2$, where $\nu$ is the entanglement density of a system composed of infinitely long chains $(a=1)$.

The previous analysis is easily extended to polydisperse systems. The bimodal blend is made up of long and short chains with molecular weights $M_\ell$ and $M_s$. There are three distinct entanglements between the chains: those between like chains ($M_\ell$-$M_\ell$ and $M_s$-$M_s$) as well as those between unlike chains ($M_\ell$-$M_s$). The probability that any one entanglement in a system involves a short or long chain is given by the mass fraction of that type of chain in the system, $\phi$ or $1-\phi$, respectively. The probability that a short chain in a binary system is effectively entangled is then the product $a_s\phi$, where $a_s=a(M_s)$ is given by Eq. (3). Furthermore, the probability that an entanglement between two short chains is effective is $a_s^2\phi^2$. If we take into account the other two types of interactions, we can write down an expression for the effective entanglement density of the system as the sum of contributions from distinct types of entanglements: $\nu_{eff}=\nu[a_s^2\phi^2+2a_sa_\ell\phi(1-\phi)+a_\ell^2(1-\phi)^2]$ [32]. This analysis is not limited to binary systems, since one only needs to account for all possible types of interactions between chains in a polymer blend to model the expected entanglement behavior. Taking all interactions into account one obtains

$$\nu_{eff}=\nu\left[\sum_{i=1}^{k}a_i\phi_i\right]^2, \qquad (5)$$

where $a_i$ is given by Eq. (3), $\phi_i$ is the volume fraction of the $M_i$ molecular weight component, and $k$ is the number of components in the blend.

The data in Fig. 3(a) were fit using Eqs. (1), (3), and (5), with the only free parameters being $\mu$ and a prefactor (taking the place of $\nu$ in Eq. (5)). The best fit was obtained with $\mu=5.8\pm0.8$ kg/mol. Given this value of $\mu$, we show a plot of $a(M)$ and $a(M)^2$ for PS in Fig. 3(c). Using the parameters obtained for the two binary systems, one can easily extend to the *ternary blends* shown in Fig. 3(b). The fit of the model with only two free parameters for three distinct blend systems (two binary systems and a ternary system) is excellent. Furthermore the value obtained for $\mu$ is less than and on the order of $M_e$ for PS as expected ($M_e\sim13.5$ kg/mol [3]). Indeed we find that $\mu\sim M_e/2$.

The boundary set by $\mu=5.8$ kg/mol indicates that $a_s=0$ for chains with $M_s\leq\mu$. Indeed, for $M_s=4.8$ kg/mol, the smallest value of $M_s$ used in this study, $a_s=0$ is a good description of the data for the binary blend. Blends of PS chains where the short chains are much less than $M_e$ have been studied in similar experiments by Kramer and coworkers [16]. The molecular weight of the diluting chains used in their study was approximately 2 kg/mol which corresponds to $a_s=0$. Our simple model, with $a_s$ set to 0 in Eq. (5), results in $\nu_{eff}\propto(1-\phi)^2$ which gives a satisfying description of the data obtained in [16].

In the blending experiments presented we have been able to probe not only the case where the small chain diluent can be assumed to be entirely nonentangling (i.e., $a=0$), but also the intermediate case where $0<a<1$. Because the binary blends with the short-chain diluent $M_s=18.4$ kg/mol show a change in the effective entanglement density that is not equivalent to that of $M_s=4.8$ kg/mol, we must conclude that $a\neq0$ [see Fig. 3(a)]. The data with $M_s=18.4$ kg/mol indicate that there is some range of molecular weights for which $0<a<1$. Hence, there is a range of molecular weights for which $0<\nu_{eff}<\nu$; this is in contrast to the often assumed idea that polymers are unentangled below $M_e$ and entangled above $M_e$. Since the 18.4 kg/mol chains have $M$ which is similar to $M_e$, it may be remarked that this result is not surprising. However, the ternary data shown in Fig. 3(b) provides us with strong evidence that even for a blend with molecular weights considerably above $M_e$ the network is diluted. In particular for the case of the ternary blend with $\phi=0$, the high molecular weight is diluted with only 64.0 kg/mol chains and $\nu_{eff}$ is reduced from that of a pure high molecular weight system. To reiterate, even though $M_s=64$ kg/mol chains are well above $M_e$, we must conclude that some of these chains are diluting the entanglements of the very high molecular weight network. The degree to which a specific molecular weight will contribute to the entanglement network is given by $a(M)$ in Fig. 3(c).

## IV. CONCLUSIONS

Polystyrene blends have been prepared and their thin films have been crazed and measured using AFM. We observe that systems with lower overall molecular weight show crazing behavior consistent with a system that has a lower entanglement density. As in the chain packing models [2,3] and the work of Si *et al.* [26], a model that assumes the effective entanglements are those with *other* chains in the system is proposed. We assume that the fraction of space in a chain's pervaded volume occupied by other chains in the system is equal to the probability of interchain entanglements. The density of effective entanglements that are predicted by this model are quantitatively consistent with our measurements for two binary blend systems and a ternary blend with only two fitting parameters. Furthermore, the model is easily extended to the broad molecular weight distributions found in many industrial polymers. The parameter $\mu$ is physically significant and represents the length a chain must have before it is even possible to entangle. This cutoff

1982chain length is found to be approximately one half of the entanglement molecular weight. Our model predicts a continuous change in the entanglement density as a function of molecular weight. The polymer melt is not unentangled below $M_e$ and entangled above $M_e$, as is often assumed. Rather, we find that low molecular weight chains ($M \leq \mu$) have zero probability to be found in the entangled state, but for $M > \mu$ the probability rises continuously from zero and asymptotes to unity for infinitely long chains.

## ACKNOWLEDGMENT

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[31] Lin and Yang [29] and Si *et al.* [26] have shown that AFM can be used to obtain information consistent with the well established transmission electron microscopy (TEM) technique of Kramer and Brown [24,25]. We have further verified this assumption here by directly comparing TEM and AFM measurements.

[32] If the short component is too short to entangle, then $a_s=0$. In this case the expression is equivalent to the one found elsewhere [14,16,17].