Macromolecules **2003,** *36,* 5839−5844

Entanglement Density at the Interface between Two Immiscible Polymers

Robert Oslanec and Hugh R. Brown*

BHP Steel Institute University of Wollongong Wollongong, NSW 2522 Australia

Received July 2, 2002; Revised Manuscript Received May 29, 2003

ABSTRACT: The variation of entanglement density with interface width at an interface between two polymers is calculated using the relationships between chain packing and entanglement. The chain packing is obtained by the use of self-consistent mean-field techniques to calculate the average chain conformations within the interface region. The interface width is controlled by an assumed value of Flory−Huggins interaction parameter χ between the two polymers. As the value of χ is increased from 0 (completely miscible) to 0.1 (immiscible with a sharp interface), the calculated entanglement density is found to decrease by about a factor of 2. These modified entanglement densities are used within an existing model of interface coupling to estimate the effect of entanglement changes on the variation of interface toughness with interface width.

Introduction

Entanglements of polymer chains are topological constraints to motion that have a profound effect on the mobility of the molecules. Qualitatively, they can be envisioned as crossings of polymer chains that remain intact when the material is subject to strain and so are mechanically active. They therefore strongly influence dynamic properties of polymer melts such as viscosity and diffusion. The main glassy state properties that are influenced by entanglements are the high strain properties, such as natural draw ratio, craze extension ratio, and toughness. The density of entanglements, often described by the molecular weight of a chain between entanglements M_e, can be obtained from the plateau modulus of a high molecular weight melt. The mean distance between entanglements serves as the tube diameter within the dominant reptation model of polymer dynamics.

Although the precise nature of entanglements is not well understood, there is good evidence that the density of entanglements is strongly related to the chain topology. A number of authors have suggested that entanglements, and hence M_e, are controlled by the packing of the polymer chains.[1−5] They proposed that the volume of space pervaded by a single chain of molecular weight M_e is a fixed constant of order 10 times the hard core volume occupied by that chain. The actual value of the fixed constant depends on the precise definition of the pervaded volume. Their arguments, which are supported by strong experimental evidence, are based on the idea that it is the chain packing that that defines the constraints, placed by surrounding chains, on the motion of a single chain. If a chain is in a more compact form, then a relatively longer length of chain is required before it interacts significantly with other chains (high M_e), whereas if the chain is extended, then a much shorter length interacts with other chains (low M_e).

Entanglement in the polymer bulk is thus reasonably well understood in broad terms, but the situation at an interface or surface is much less clear. Russell and one of the current authors[6] have suggested that, as chain packing is modified close to an interface, entanglement is likely to be modified also. They argued, following Silberberg,[7,8] that chains are “reflected” at an interface and so tend to pack more densely than in the bulk, decreasing the entanglement density and increasing M_e from the bulk values.

The aim of the current work is to use the ideas on the relation between chain contours and entanglement to calculate the entanglement density close to an interface between immiscible polymers. The structure of the interface is controlled by the repulsion between the polymers, described by the Flory−Huggins interaction parameter χ. The mean chain contours, and hence the chain packing, will be obtained as a function of χ using self-consistent mean-field theory (SCMF). Hence, the interface entanglement density will be obtained as a function of χ.

The main motivation for this work derives from the relationship between chain entanglement and fracture. Chain entanglement controls fracture in two basically separate ways. It controls both the saturation toughness of a polymer at high molecular weight and the molecular weight at which the toughness saturates. Failure of glassy polymers normally occurs through a crazing mechanism, and craze microstructure is strongly influenced by the entanglement density within high molecular weight material and hence by the M_e of the material. Thus, entanglement controls the high molecular weight toughness. The toughness of glassy polymers increases with molecular weight until it saturates at a molecular weight of about $8M_e$. The use of diblock coupling agents has demonstrated that this increase and saturation in toughness are related to the molecular failure mechanism. Short chain strands that cross the fracture plane can pull out, whereas longer chains tend to fail by scission. The chain length at which this transition occurs is related to M_e.

The use of diblock copolymers at interfaces has also demonstrated that the areal density of chains that cross the interface, and thus have to undergo pullout or scission when the interface fails, controls the toughness of an interface between polymers. Hence, it has been suggested that, for high molecular weight polymers without specific coupling agents, the areal density of coupling chain strands controls the toughness of the

10.1021/ma021044q CCC: $25.00 © 2003 American Chemical Society
Published on Web 06/25/2003

interface. The relevant strands are those that have adjacent entanglements on either side of the interface. Thus, the toughness of an interface between glassy polymers should be controlled by the ratio of the interface width to the mean distance between entanglements (a_I/L_e). A simple model based on these ideas has been proposed and found to be quite inconsistent with the experimental data,[9] but the model did assume that the entanglement density was not influenced by the interface. The aim of this current work is to estimate the effects of the interface width between two immiscible polymers on the entanglement density and hence on the expected interface toughness.

The paper is organized as follows. First, we summarize the entanglement model to obtain the relation used to calculate entanglement density. Next we use the SCMF model to calculate the mean chain packing density close to a polymer/polymer interface as a function of χ and hence estimate the χ dependence of the entanglement density close to an interface. Finally, we use this entanglement density to estimate the expected variation of toughness with interface width.

Entanglement Model

We need to obtain the relationship between the mean conformation of a chain and its entanglement molecular weight. Following Fetters et al.,[4] we are concerned with the local density of packing of a chain. We assume that the chain locally follows random coil statistics so that we can find a relation between the fraction of a chain within a test volume centered on the chain center of mass and the density of entanglements.

The pervaded volume of the polymer chain, V_{sp}, is defined as the volume of a smallest sphere that completely contains the chain. We will assume that this volume is proportional to the radius of gyration, R_g, of the chain:

$$V_{sp} = AR_g^{\ 3} \tag{1}$$

where A is a proportionality constant. But R_g varies with the number of repeat units in a chain N as

$$R_g = A''N^{1/2}a \tag{2}$$

where the repeat unit volume is a^3 and A'' is a constant describing the density of chain packing. So

$$V_{sp} = A'N^{3/2}a^3 \quad \text{where } A' = AA''^3 \tag{3}$$

The total volume actually occupied by the chain V_o is Na^3, so the ratio of occupied to pervaded volume relevant within the model is given by

$$V_{sp}/V_o = A'N^{1/2} \tag{4}$$

The packing density model for entanglements assumes that, when V_{sp}/V_o is equal to a constant B that is about 10, then N equals the number of repeat units between entanglements, N_e, and so

$$N_e = \frac{B^2}{A^2A''^6} \tag{5}$$

Now, if we take a certain test volume, V_{test}, as a sphere of radius R_t centered on the center of mass of a chain, such that $V_{test} \leq V_{sp}$, we see that the number of repeat units N_{test} of the chain in the test volume is

$$N_{test} = \left(\frac{R_t}{A''a}\right)^2 \tag{6}$$

The fraction of the test volume occupied by the polymer chain, f, is

$$f(R_t) = \frac{N_{test}a^3}{V_{test}} = \frac{3a}{4\pi R_t A''^2} \tag{7}$$

Combining eqs 5 and 7, we obtain

$$N_e \sim f^{\ 3}(R_t) \tag{8}$$

The density of entanglements, ρ_e, varies as N_e^{-1} and so

$$\rho_e \sim f^{-3}(R_t) \tag{9}$$

and the mean distance between entanglements L_e is given by

$$L_e \sim A''N_e^{\ 1/2} \sim f(R_t) \tag{10}$$

In this work we use the SCMF technique to calculate the variation of f through the interface using a V_{test} similar to the normal volume defined by the distance between entanglements on a chain. We then use this variation of f to estimate the variation in entanglement density through the interface. The choice of the size of the test sphere is somewhat arbitrary. The chain conformation is expected to be constant in the bulk and change as the interface is approached. The particular test volume was chosen as there is difficulty in defining a measure of entanglement density that changes over distances much shorter than the distance between entanglements.

The argument above assumes that the chain contours are Gaussian. Near an interface the chains are compressed on one direction so the relation eq 9 may no longer hold. Within the packing model ρ_e is bound to vary inversely with f, the question is only, what is the form of the variation? The variation of f near the interface is a measure of this distortion, and as it is not more than 30% we shall assume that eq 9 remains approximately correct. It is worth noting that, within the SCF model, the interface does not alter the chain dimensions in the plane of the interface. The distortion is just normal to the interface plane.

Although the packing length model for entanglement has been well tested for situations where the chain contours are isotropic, there is no experimental evidence that, as assumed here, it also applies for anisotropic contours.

SCMF and MDE Calculations

We use a fairly standard self-consistent mean-field approach to calculate the properties of an interface between two immiscible polymers[10−14] A and B. The self-consistent calculation is used to obtain the variation of the mean field through the interface as a function of the interaction parameter between the polymers, χ_{AB}. This mean field is then used in conjunction with Edward's modified diffusion equation,[15−17] MDE, to calculate the segment probability distribution functions for chains with a defined position for one end of the chain. These probability distribution functions are then used to calculate the position of the center of mass of the chains and the value of f using a spherical volume centered at the chain center of mass. Finally, as the center of mass is moved by changing the position of the chain end, the variation of f through the interface is obtained.

The SCMF calculations followed the approach described in detail by Shull and Kramer.[11−14] In brief, this technique involves assuming a segment density profile (or volume fraction profile) of the polymer chains, calculating a mean field $w(\mathbf{r})$ from it and then solving the diffusion equation to recalculate the segment density profile. This process is repeated until it converges with a self-consistent mean-field and segment density profile. As the interface between the two polymers is planar, the problem is essentially one-dimensional. The only relevant spatial coordinate is z, the coordinate normal to the plane of interface. The input parameters for the SCMF calculations are the segment numbers of both A and B polymers, chosen as 1200, and the Flory−Huggins segment−segment interaction parameter, χ_{AB}. The value of χ_{AB}, which enters in the relation between the segment density profile and the mean field, was varied between 0.005 to represent a broad interface and 0.1 to give a sharp interface. The resulting volume fraction profiles were compared with the well-known hyperbolic tangent predictions,[18,19] and a good agreement between the two was found. In addition, experimental evidence[20] suggests that the density profiles calculated using the SCMF approach describe the interface between two immiscible polymers sufficiently well. For comparison with experiment the lattice size was chosen to equal the statistic segment length for polystyrene, 0.67 nm.[21]

The mean field $w(\mathbf{r})$ obtained from SCMF calculations was then used in the modified diffusion equation, MDE:[15−17]

$$\frac{\partial Q(\mathbf{r},n;\mathbf{r}_0)}{\partial n} = \frac{a^2}{6}\nabla^2 Q(\mathbf{r},n;\mathbf{r}_0) - w(\mathbf{r})\, Q(\mathbf{r},n;\mathbf{r}_0) \qquad (11)$$

where $Q(\mathbf{r},n;\mathbf{r}_0)$ is the segment probability distribution function which represents the probability that a polymer chain with one end at position $\mathbf{r}_0$ has the nth segment of the chain at position $\mathbf{r}$. The nonnormalized concentration $c(\mathbf{r})$ of such chains of total number of segments N is given by

$$c(\mathbf{r}) = \sum_{n=1}^{N} \int_{r_0}\int_{r_1} Q(\mathbf{r},n;\mathbf{r}_0)\, Q(\mathbf{r}_1,N-n;\mathbf{r})\, \mathrm{d}\mathbf{r}_0\, \mathrm{d}\mathbf{r}_1 \qquad (12)$$

Equation 12 illustrates that the density of polymer chains at position $\mathbf{r}$ is proportional to the probability that a chain has one end is at position $\mathbf{r}_0$ and the other end is at position $\mathbf{r}_1$. Because the chain ends can be anywhere in space, the probabilities are integrated over all possible values of $\mathbf{r}_0$ and $\mathbf{r}_1$. In addition, any segment of a chain can contribute to the overall density at a given point; hence, the final density is a sum of contributions from each segment in the chain. In eq 12 the $Q(\mathbf{r},n;\mathbf{r}_0)$ component represents a path from one end, whereas the $Q(\mathbf{r}_1,N-n;\mathbf{r})$ component represents a path from the other end of the chain. Note that $\mathbf{r}_1$, $\mathbf{r}_0$, and $\mathbf{r}$ are 3-dimensional position vectors. Since the mean field, w, calculated from SCMF model varies only in the z direction, we assume that w is constant in the $x-y$ plane.

The SCMF calculation was performed by choosing a value for χ and using the standard SCMF technique to calculate $w(z)$ which could be easily transformed into $w(\mathbf{r})$. Equation 11 was then numerically solved in 3 dimensions on a cubic lattice to obtain a set of 3-D concentration profiles, $c(\mathbf{r})$, for chains that start at various distances from the interface. The chain starting positions were chosen along the z-axis by setting $x_0 = y_0 = 0$; thus $\mathbf{r}_0 = z_0$. To obtain $c(\mathbf{r})$ using eq 12, both $Q(\mathbf{r},n;\mathbf{r}_0)$ and $Q(\mathbf{r}_1,N-n;\mathbf{r})$ need to be calculated. For each chain starting position the $Q(\mathbf{r},n;\mathbf{r}_0{=}z_0)$ matrix was first calculated using the following initial condition:

$$\begin{aligned} Q(\mathbf{r},n{=}1;\mathbf{r}_0) &= 1 \quad \text{for } \mathbf{r}_0 = z_0 \\ Q(\mathbf{r},n{=}1;\mathbf{r}_0) &= 0 \quad \text{for } \mathbf{r}_0 \neq z_0 \end{aligned} \qquad (13)$$

To calculate the $Q(\mathbf{r}_1,N-n;\mathbf{r})$ matrix, we assumed that the other chain end can be at any position in the system with a probability governed by the SCMF calculated volume fraction of the polymer chain, $\phi_A(z)$. Similar to the case for w, we assumed that chain volume fraction in the $x-y$ plane is constant. Therefore, the initial condition to calculate $Q(\mathbf{r}_1,N-n;\mathbf{r})$ was

$$Q(\mathbf{r}_1,n{=}N;\mathbf{r}) = \phi_A(\mathbf{r}_1) \qquad (14)$$

Once the Q matrices were calculated, the concentration distribution $c(\mathbf{r};z_0)$ of the chains was found with defined starting positions at various distances z_0 from the interface. To obtain the values of $c(\mathbf{r};z_0)$, it was necessary to integrate over all possible values of n and $\mathbf{r}_1$. The center of mass of these chains was then calculated using the equation

$$z_{COM}(z_0) = \frac{\sum_z z c(z;z_0)}{\sum_z c(z;z_0)} \qquad (15)$$

Because of radial symmetry of Q and c around the z-axis, we can set $x_{COM} = y_{COM} = 0$. The next step was to calculate $f(z_{COM},R_t)$, the fraction of a polymer chain that occupies a volume of the test sphere of radius R_t with the center at the center of mass of the chain. The fraction $f(z_{COM},R_t)$ was calculated for each chain with center of mass at various distances from the interface, z_{COM}. The diameter of the test sphere was chosen as an end-to-end distance of a chain with $M = M_{e,bulk}$, the entanglement molecular weight in the bulk. Specifically, for polystyrene with $M_{e,bulk} = 13\,500$ g/mol the radius of the test sphere was set to $R_t = 3.5$ nm. The calculated fractions were then normalized by the bulk value of $f(z{=}\infty,R_t) = 0.113$, obtained far from the interface to obtain f_N. The final result was obtained by plotting f_N as a function of z (really z_{COM}), the distance from the interface for various values of the χ parameter. It is worth noting that as this technique does not calculate conformations of specific chains but calculates a mean distribution for chains with a particular starting point, a mean center of mass z_{COM} close to the interface was obtained by using a starting position z_0 across the interface.

Results of the Calculations

The first stage of the calculation required solving the SCMF equations to obtain the variation of the mean

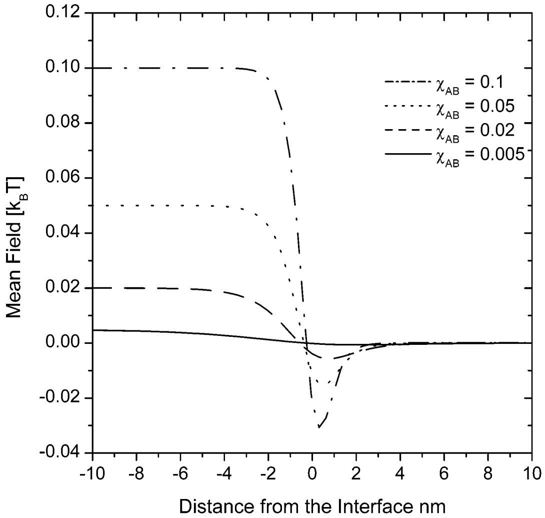

Figure 1. Variation of the mean field through the interface as a function of Flory–Huggins parameter χ.

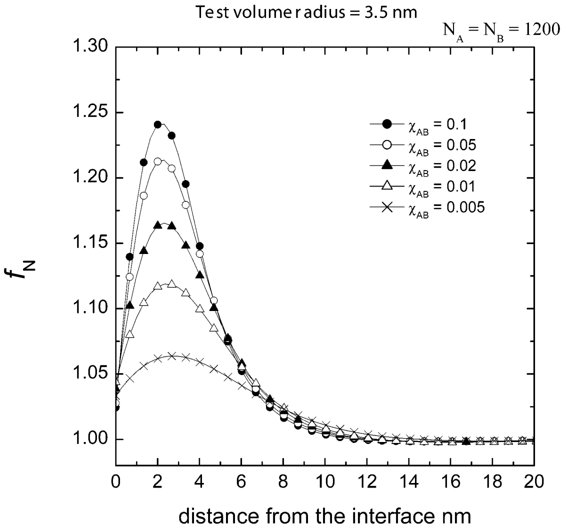

Figure 2. Variation of normalized *f* with distance from the interface as a function of χ for a test volume radius of 3.5 nm.

field through the interface $w(z)$ as a function of χ. Representative values of the mean fields are shown in Figure 1. As discussed above, the resulting volume fraction profiles agreed well with the established hyperbolic tangent predictions.

The mean-field profiles, which varied just in the z direction, were used in conjunction with the three-dimensional MDE to obtain the values of f as a function of distance from the interface, z. The results for f_N, which is f normalized by the value of f in the bulk, are shown in Figure 2. It can be seen that f_N shows a maximum close to the interface. This maximum is to be expected because, as the interface is approached from the bulk, initially the test sphere, centered on the radius of gyration of the chains, probes chains that are reflected at the interface and so more compact than in the bulk. When the z position of the center of mass of the test chain becomes significantly less than the radius of the test sphere, then much of the chain must be on the "wrong" side of the interface. This section of chain is stretched from the "wrong" to the "right" side of the interface so the value of f decreases. For the very few chains with $z < 0$ then $f_N < 1$. We take the value of f_N at maximum, which is fairly insensitive to the radius of the test sphere, to give a mean value of entanglement relevant of the particular χ value.

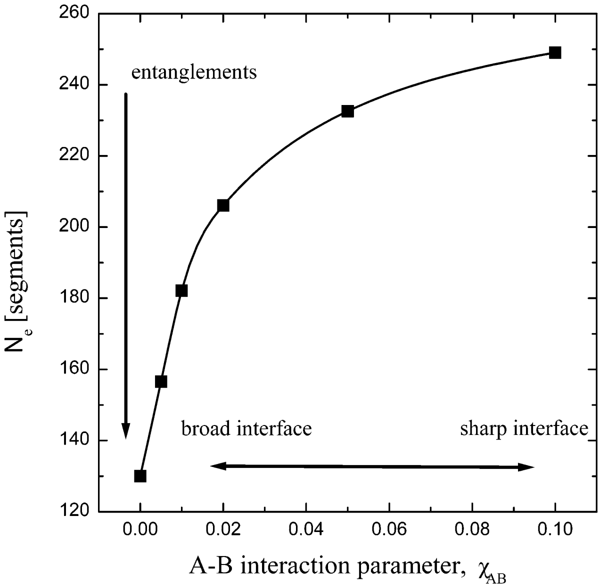

Figure 3. Calculated number of segments between entanglements as a function of χ assuming a bulk value of N_e, typical for polystyrene, of 130.

Figure 3 shows the calculated variation of interface N_e (average number of segments between entanglements) with χ. The results are scaled to the assumption that the value of N_e in the bulk equals that of polystyrene (130). It can be seen that the average interface N_e increases with χ as expected and doubles from its value in the bulk when χ reaches 0.1. From the form of Figure 3 it is clear that the calculated entanglement length asymptotes to a constant value as the interface becomes very sharp. The existence of the asymptote is expected from the arguments in the previous work,[6] where it was suggested that the entanglement length at a sharp interface was about nearly 4 times the value in the bulk. The difference between that suggestion and the results of the current calculation probably has its origin in the way entanglement density is calculated in this work. Packing is calculated over a region that has a width that is large with respect to the width of a reasonably sharp interface.

One aim of this work is to calculate the effect of reduced entanglement at the interface on the variation of toughness with the width of an interface between two polymers. Hence, we correct the previously proposed model[9] of interface coupling for the effect of the interface on the local entanglement density and spacing. The areal density of strands that couple the interface is given by

$$\Sigma \sim L_e \rho_e J(a_r) \tag{16}$$

where J is a function given in ref 9, a_r is the relative interface width, a_I/L_e, ρ_e is the entanglements density, and L_e is the mean distance between entanglements. The interface toughness is given by

$$G_c = \frac{K}{\ln\left(\left\{1 - \left[\frac{1.2\sigma_d}{\Sigma(a_r)f_b}\right]^2\right\}^{-1}\right)} \tag{17}$$

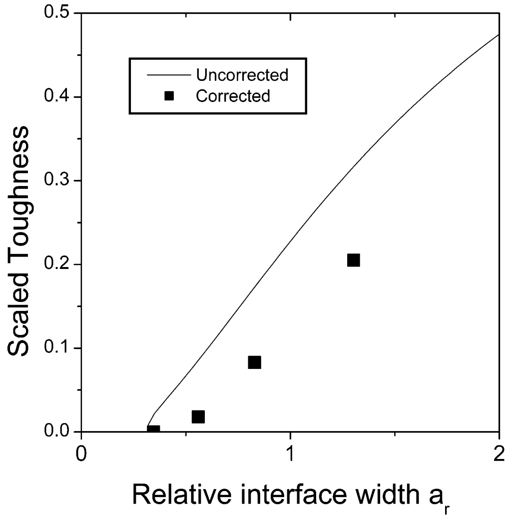

Figure 4. Calculated interface toughness as a function of interface width showing the effect of correcting for the variation of entanglement density with interface width.

where K is a constant, σ_d is the craze stress, and f_b is the force to break a chain.

Figure 4 shows the original predictions of the variation of interface toughness with relative interface width as a solid line and, as solid points, some corrected values using eqs and 10 to obtain L_e and ρ_e and hence a_r used in the calculation of G_c, but the bulk value of L_e was used to obtain the values of a_r in the abscissa. Clearly, the corrections to the entanglement density suggested in this work do reduce the calculated toughness values considerably, particularly for values of $a_r < 1$; however, the toughness is still not predicted to vary as rapidly with interface width as observed in practice.

Discussion and Conclusions

This work was the first attempt to obtain a quantitative estimate of the effect of interface sharpness on the local entanglement density. The approach is based on the concept that entanglement is entirely controlled by the packing of polymer chains. The packing density is calculated with a test sphere of radius equal to the bulk chain distance between entanglements. The choice of test sphere radius is arbitrary, but the results are not very sensitive to it. As the chain contours cease to have spherical symmetry close to the interface, it would perhaps be more logical to choose a test volume that changed shape with the chain contours but that would have been more complicated. In addition, the assumed relations between packing, f, and entanglement density or tube diameter assume spherical symmetry so could not be used simply for an anisotropic test volume.

The results demonstrate that the packing concept of entanglement implies that the entanglement density would be expected to vary significantly in inhomogeneous situations, such as near a interface or surface. Changes of entanglement density of at least a factor of 2 are to be expected. Entanglement has a profound effect on the rheological properties of a polymer melt and the high strain and failure properties of a polymer glass. It would seem likely that the entanglement properties discussed here are most likely to influence the deformation properties close to a polymer surface, particularly surface orientation and frictional processes, and also the failure properties at interfaces. There is no suggestion that the decreased entanglement might have an effect on the surface T_g, as T_g is thought to be a much more local property than entanglement; however, the decreased entanglement might contribute strongly to the rather poorly understood processes that occur during friction.

A similar approach to the calculation of entanglement at interfaces has recently been presented by Ganesan and Pryamitsyn[22] based specifically on the Kassavalis and Noolandi approach to entanglement density.[2,3] Their calculation approach is more sophisticated than the one presented here, but the results obtained are similar. They suggest that the relationship used to calculate $J(a_r)$ considerably overestimates the density of entangled strands, but this does not explain why the calculated toughness for broad interfaces is less than the measured values.

The density of entangled strands has also been calculated in a recent model presented by Benkoski et al.[23] that is based on the statistical variation of the distance between entanglements. They obtain good fit with the experimental fracture results on the PS/PMMA system while assuming that the entanglement density is constant through the interface. All these models, though complicated, are inevitably approximations to the real situation, so it seems unlikely that the fracture experiments can be used to demonstrate definitively the change of entanglement density at an interface.

In conclusion, we have demonstrated that the entanglement density close to an interface can be calculated using self-consistent mean-field techniques to obtain the local average chain packing. For polystyrene chains of degree of polymerization 1200 the packing was observed to start changing at about 10 nm from the interface. The entanglement density was found to decrease by about a factor of 2 for a fairly sharp interface with a χ of 0.1. This decrease would be expected to have a significant effect on the interface toughness.

Acknowledgment. We acknowledge valuable discussions with Ken Shull on the SCMF technique and with Ed Kramer on interface coupling. Completion of this manuscript was inspired by Venkat Ganesan and Jacob Benkoski, who sent us their papers before publication and discussed the interface-coupling problem with us.

References and Notes

(1) Lin, Y.-H. *Macromolecules* **1987**, *20*, 3080−3.
(2) Kavassalis, T. A.; Noolandi, J. *Macromolecules* **1988**, *21*, 2869−79.
(3) Kavassalis, T. A.; Noolandi, J. *Phys. Rev. Lett.* **1987**, *59*, 2674−77.
(4) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639−47.
(5) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1023−33.
(6) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798−80.
(7) Silberberg, A. *J. Colloid Interface Sci.* **1982**, *90*, 86−91.
(8) Silberberg, A. *J. Colloid Interface Sci.* **1988**, *125*, 14−22.
(9) Brown, H. R. *Macromolecules* **2001**, *34*, 3720−4.
(10) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727−36.
(11) Shull, K. R.; Kramer, E. J. *Macromolecules* **1990**, *23*, 4769−79.
(12) Shull, K. R. *J. Chem. Phys.* **1991**, *94*, 5723−38.
(13) Shull, K. R. *Macromolecules* **1992**, *25*, 2122−33.
(14) Shull, K. R. *Macromolecules* **1993**, *26*, 2346−60.
(15) Edwards, S. F. *Proc. Phys. Soc. (London)* **1965**, *85*, 613−24.
(16) DiMarzio, E. A. *J. Chem. Phys.* **1965**, *42*, 2101−6.

(17) Helfand, E. *J. Chem. Phys.* **1975**, *62*, 999−1005.
(18) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592−601.
(19) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *57*, 1812−13.
(20) Genzer, J.; Composto, R. J. *Polymer* **1999**, *40*, 4223−8.
(21) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780−7.
(22) Ganesan, V.; Pryamitsyn, V. *Macromolecules* **2002**, *35*, 9219−31.
(23) Benkoski, J. J.; Fredrickson, E. J.; Kramer, E. J. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 2377−86.

MA021044Q