PHYSICAL REVIEW A VOLUME 40, NUMBER 11 DECEMBER 1, 1989

Sliding along the interface of strongly segregated polymer melts

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(Received 22 May 1989)

Entanglements of polymer chains and deformation of polymer morphology due to shear stress in the interfacial region of segregated polymer metals are discussed. In the case of strong segregation polymer melts slide along the interface for a length scale much larger than the gyration radius of the polymer molecule.

I. INTRODUCTION

The bulk viscosity of a polymer melt is very large in proportion to $N^{3.4}$ with N being the polymerization.[1,2] Such a large viscosity is considered to come from entanglements of polymer molecules. Therefore, if the entanglements between different sorts of polymers, say, A and B polymers, at the coexistence interface are weak, the interface might slide when a shear stress is applied. In this paper we investigate the linking between A and B polymers in the interfacial region and then investigate interfacial viscosity. From a crude approximation we find that the interface between strongly segregated polymer melts is expected to slide if the system has a length scale probably less than $\sim 10^2-10^3 R_G$, where R_G is the gyration radius of a polymer molecule. This yields an important difference between polymer melts and simple liquids in the dynamics of coexisting fluids.

The typical density of a polymer is 0.01 mol/cm^3.[3] This corresponds to assuming that the diameter of the monomer is 6.8 Å. This value of the monomer diameter is approximately equal to the usually accepted typical length of a segment of a random chain for polymer, b. Therefore we shall not distinguish the monomer and the segment in the following discussion. In the case of the strong segregation the thickness of the interface is approximately 10–20 Å (Refs. 3 and 4), which is the same as the length of a few monomers. This suggests that the entanglements between different sorts of polymers at the interface are much weaker than those among like polymers in the bulk. As a result the shear stress concentrates on polymers in the interfacial region and this causes the strong deformation in the polymer morphology in the interfacial region. Such a deformation gives rise to crazes or cracks in the glassy state, and must give rise to the interfacial sliding in the fluid state as will be discussed here. We develop a phenomenological theory for the interfacial sliding in strongly segregated polymer melts. In our theory the origin of the interfacial sliding is the deformation of the polymer morphology near the interface due to the concentration of the stress at interface. The viscous flow induced by this deformation yields friction to the deformation and therefore to the surface sliding. We first present a simplified model for the linking between different sorts of polymers in the interfacial region. Then we propose a qualitative interfacial sliding mechanism of polymer melts.

In the next section we evaluate the strength of linkings between different sorts of polymer chains. In Sec. III we shall discuss the sliding mechanism at interface between polymer melts. In Sec. IV we shall discuss the effective shear viscosity at interface. Section V is devoted to remarks.

II. LINKING OF POLYMER CHAINS AT NARROW INTERFACE

The interfacial thickness λ is determined statistical mechanically.[3] In this paper we do not calculate λ, but we assume that λ is already known. Typical values of λ may be 10–20 Å. Then we present a model for the linking between different sorts of polymers in the interfacial region. We assume that the interface is narrow, so that the linking between different chains in the interfacial region is not complicated. Since the monomer diameter is equal to b, the number of layers in the interfacial region is λ/b. In each layer different sorts of polymers link at some parts. Let A' be the total area where different sorts of polymers link in a layer, and A be the total area of the layer (total area of the interface). Then the degree of the linking on the layer is defined as A'/A. Averaging this over all interfacial layers, we have the average degree of the linking, K, in the interfacial region. It is apparent that K is scaled as $K(\lambda/b)$ with $K(x)=0$ for $x \lesssim 1$ and $K(x)=1$ for $x \gg 1$. We consider only the case of $\lambda \sim b$, and shall employ a simplified model to evaluate K, as follows.

For different sorts of chains to link to each other, the thickness of the interface must be at least $\lambda=2b$. For $\lambda=2b$ we assume that the most dominant pattern of linking is such as in Fig. 1(a). This is due to the following fact. In the bulk the polymer chains are oriented in three different directions, say, x, y, and z directions, with equal

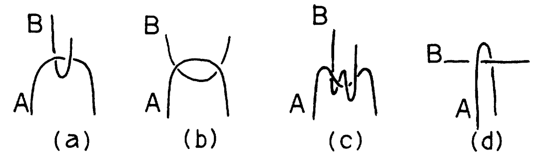

FIG. 1. Several types of linking between different sorts of polymer chains at a narrow interface.

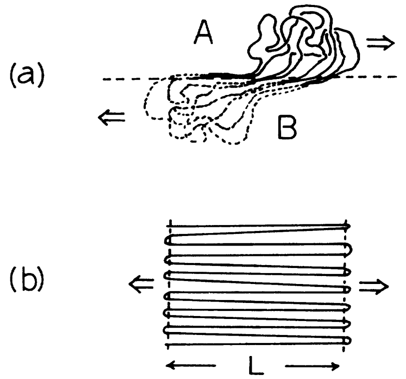

FIG. 2. Stretching of polymer molecules at the interface. Large arrows indicate applied stresses. (a) Sketch of a stretched polymer pair linked at the interface. (b) Schematic explanation of the sketch in (a) emphasizing curvilinear chain motion.

probability, $\frac{1}{3}$. Therefore, at the interface, those chains which are oriented in the direction perpendicular to the interface, should connect forming a loop in the interfacial region. The probability of finding such loops coming from one phase in the interfacial region is $\frac{1}{3}$. Thus the probability with which two loops from two phases meet with each other at the interfacial region is $\frac{1}{9}$. Halves of such meetings are parallel [Fig. 1(b)] and further halves would not link [Fig. 2(c)]. Thus the probability for such a linking as in Fig. 1(a) to occur is $\frac{1}{36}$. Thus the average degree of linking, K, is $\frac{1}{72}$. As λ becomes slightly larger, we assume that the next pattern of linking is such as in Fig. 1(d), i.e., the linking between z-directing chain (A) and x- or y-directing chains (B). Let $\lambda = 4b$. The probability for a z-directing chain to link with another x- or y-directing chain is $\frac{1}{3} \times \frac{1}{3}$ (one $\frac{1}{3}$ is for the z direction and the other $\frac{1}{3}$ is for the x or y direction). The contributions from the two phases give $\frac{2}{9}$ for finding such a linking as in Fig. 1(d) in the interfacial region. Thus the average degree of linking is $K = (\frac{2}{9} + \frac{1}{36})/4 = \frac{1}{16}$ (for $\lambda = 4b$). The present evaluation of K is rough and the accurate evaluation is left for further studies.

III. SLIDING MECHANISM OF INTERFACE

Assume that the applied shear stress is in the direction parallel to the interface between two polymer melts. The strength of the shear stress is σ per unit area. Then the tension along the chain in the bulk is $\sim \sigma b^2$. On the other hand, near the interface the stress concentrates on linked chains. The strength of the tension is $\sigma b^2 K^{-1}$. That is, the effective stress in the interfacial region is

$$\sigma_s = \sigma / K \ . \tag{1}$$

If $K < 1$, then the morphology of the chain is deformed by the effective stress (1). However, if $K = 1$, then the tension of the chain in the interfacial region is the same as that in the bulk, and there is no specific deformation in the interfacial region. Therefore the significant deformation of the chain morphology near the interface is proportional to $\sigma_s - \sigma$. In Fig. 2 we illustrate the deformation of the chain morphology in the interfacial region for small K. Figure 2(a) shows a linking of A and B chains at the interface. Molecules are stretched in opposite directions. In order to calculate the time rate of such a deformation and also to calculate the interfacial viscosity, we employ the following approximation. First, such a pair as in Fig. 2(a) is treated as isolated. Then the pair is assumed to be embedded in a liquid which has the same viscosity as the bulk polymer melt. This is a kind of mean-field-type approximation. When the pair is stretched, the pair deforms with curvilinear slidings of chains. Figure 2(b) shows the schematic explanation of molecular stretching. Here L is the average length of the chain from one linking point to the next-nearest-neighbor linking point. The sliding velocity at the interface is then given by $\dot{L} (= dL/dt)$. Even though chains move curvilinearly, this motion cannot be independent of the deformations of molecules and its surroundings. This is the main source for the friction of the deformation of the pair of chains under stretching.

There are two kinds of energy dissipation associated with this deformation of chain morphology. One is the dissipation due to the curvilinear chain motion, and the other is the dissipation due to the flow of surrounding polymer melts. It is also noted that the sliding of unlinked surfaces also contributes to the energy dissipation. The total volume of surrounding fluid which deforms with chain stretching is of the same order as the deforming linked molecules. The energy dissipation by the surrounding flow is, therefore, given by the dimensional analysis as

$$\frac{d}{dt} E \sim \eta \left[\frac{\dot{L}}{L} \right]^2 v \ , \tag{2}$$

where η is the shear viscosity of polymer melts, and v is the volume of a polymer molecule. This type of dissipation is most dominant. Others can be neglected as will be shown in the following. We now estimate the dissipation due to the curvilinear chain motion. Figure 2(b) shows a schematic model of the curvilinear motion of a polymer molecule. The velocity of middle branch is of the order $\dot{L}$. The velocity of the kth branch from the middle branch is $k\dot{L}$. The friction constant of the curvilinear motion of a chain with length L is $\eta_0 L$, where $\eta_0 = \gamma_0 b^{-1}$ with γ_0 being the friction constant of Brownian motion of a monomer. The energy dissipation due to the curvilinear motion of the kth chain is $\sim \eta_0 L (k\dot{L})^2$. Thus the total dissipation by the curvilinear motion is

$$dE'/dt \sim \eta_0 L \dot{L}^2 \sum_{-n/2}^{n/2} k^2 \sim \eta_0 (\dot{L}/L)^2 N^2 v \ .$$

Here we have used relations $n = bN/L$ and $v = n^3 N$. The first is due to the fact that $b^2 n$ is the total area of a molecule at the interface and the volume of the molecule is equal to $b^2 nL$ which is equal to $b^3 N$. Since $\eta \sim \eta_0 N^{3.4}$, we find that $dE'/dt \ll dE/dt$. The energy dissipation due to the friction by a simple contact of surfaces is estimated as follows. The total contact area per molecule at the interfacial region is nb^2K^{-1}. The friction constant per unit area is $\gamma_0 b^{-2}$, and therefore the friction constant per a molecule is $nK^{-1}\gamma_0$. This gives the frictional force $n\gamma_0 K^{-1}\dot{L}$, and the energy dissipation

$$dE_0/dt \sim n\gamma_0 \dot{L}^2/K \sim \eta_0 \frac{L}{bK}\left[\frac{\dot{L}}{L}\right]^2 v \ .$$

This is also much smaller than (2), unless n is much smaller than 1, where (2) is no longer valid. Thus the energy dissipation given by (2) is most dominant. The energy dissipation (2) is due to the viscous flow near the interface.

IV. INTERFACIAL VISCOSITY

As was discussed the effective stress needed to stretch the molecule is $\sigma_s - \sigma$. The energy input by this stress per unit time and per molecule is $(\sigma_s - \sigma)\dot{L}v/L$, where v/L is the total area of the intersection on which the stress acts. Since this energy input balances with the most dominant energy dissipation (2), we have

$$\dot{L} \sim \frac{L}{\eta}(\sigma_s - \sigma) \ . \tag{3}$$

The stress σ also acts on the bulk and gives the shear velocity σ/η per unit length. Thus the total relative velocity between two phases at the interface is

$$V_s = \lambda\frac{\sigma}{\eta} + \frac{L}{\eta}(\sigma_s - \sigma) \ . \tag{4}$$

The effective interface shear velocity η_s is defined as $\sigma \sim \lambda^{-1}\eta_s V_s$, i.e., $\eta_s \sim \sigma\lambda/V_s$. Thus we have

$$\frac{\eta_s}{\eta} = \frac{1}{1+\frac{b}{\lambda}\frac{N}{n}(K^{-1}-1)} \quad \left[\frac{L}{b} = \frac{N}{n}\right] . \tag{5}$$

We here determine an appropriate value of n in (5). If there is no stress, then n takes the equilibrium value n_{eq}. When the shear stress is applied, n changes. The time rate of the change of n due to the stretching is evaluated as $-(n/\eta)(\sigma_s - \sigma)$ with the help of (3) and the relation $nL = bN$. Only by this process n decreases indefinitely. There is also a relaxational approach of n to its equilibrium value n_{eq} due to thermal motions of polymer molecules, whose relaxational time is given as $\tau = t_0 N^{3.4}$.[1,2] The time rate of the change of n by this process is $-(1/\tau)(n - n_{\text{eq}})$. In a steady state these two processes balance with each other. The steady-state value of n is given by solving the equation

$$0 = -\frac{1}{\eta}(\sigma_s - \sigma)n - \frac{1}{\tau}(n - n_{\text{eq}}) \ . \tag{6}$$

That is, we have

$$n = n_{\text{st}} = \frac{n_{\text{eq}}}{1+(\tau\sigma/\eta)(K^{-1}-1)} \ . \tag{7}$$

Here (1) has been used. If the stress originates from the surface tension, then $\sigma \sim T/R$, where T is the interfacial tension, and R^{-1} is the curvature of interface. Thus $\tau\sigma/\eta \sim (t_0 T)/(\eta_0 R)$. The surface tension T is determined by microscopic physical quantities such as t_0 and η_0. Thus by the dimensional analysis, we have $T \sim b\eta_0/t_0$. Thus $\tau\sigma/\eta \sim b/R$. Thus if $b \ll RK$, then $n = n_{\text{eq}}$. Otherwise $n < n_{\text{eq}}$. We assume that the average polymer density at interface is the same as that in the bulk. Then the quantity n_{eq} is given as $\rho K\Omega$, where Ω is the average volume of the region covered by a molecule in the interfacial region and is scaled as $\Omega = R_G^3 g(\lambda/R_G)$, and ρ is the monomer density of the same molecule in the region of a molecule, i.e., $\rho \sim NR_G^{-3}$. Thus

$$n_{\text{eq}} \sim NR_G^{-3}R_G^3 g\left[\frac{\lambda}{R_G}\right]K \sim NKg\left[\frac{\lambda}{R_G}\right] .$$

Assuming $n \sim n_{\text{eq}}$ and $K \ll 1$, we have from (5)

$$\frac{\eta_s}{\eta} \sim \frac{1}{1+\frac{b}{\lambda g K}(K^{-1}-1)}$$
$$\sim \frac{\lambda}{b} g K^2 \quad (\text{for } n = n_{\text{eq}} \text{ and } K \ll 1) \ . \tag{8}$$

Let V be the relative velocity between two points apart from each other by a distance R in the bulk. Then $\sigma \sim \eta V/R \sim \eta_s V_s/\lambda$, which gives $V/V_s \sim (\eta_s/\eta)(R/\lambda)$. If R is the characteristic length scale of the system, then for $V/V_s < 1$, or for $R < (\eta/\eta_s)\lambda$, the sliding between two polymer melts is effective. The interfacial viscosity depends sensitively on Ω, which is also sensitive to the molecular distribution near the interface. Here we simply assume that a polymer molecule makes contact with the interface independently of other molecules and that the shape of the contact region of a polymer molecule in the interfacial region is a column. Then $g(x) \sim x$, and therefore (8) gives $\eta_s/\eta = K^2\lambda^2/(bR_G)$. Then the interface slides for the length scale less than $bR_G/(\lambda K^2)$. This critical length is $\sim 2592R_G$ for $\lambda = 2b$ and $\sim 64R_G$ for $\lambda = 4b$ using the values of K given in Sec. II. The evaluations of both K and g are not rigorous, and thus the critical length scales obtained are only qualitative.

V. REMARKS

For the strong segregation of polymer melts we have found the possibility of interfacial sliding. The origin of the interfacial sliding is the anomalous deformation of molecules in the interfacial region. The origin of the friction for the sliding is the viscous flow induced by the molecular deformation. The sliding is not a microscopic but at least a semimacroscopic effect for strongly segregated polymer melts. The present result seems to suggest the answer to the peculiar experimental observation for the phase separation in polymer blends far from the critical point (strong segregation), where the growth law of the phase-separating domain seems to slow down.[5] This can be qualitatively explained if the interface slides: The kinetic exponent for the droplet growth with the interfacial sliding is smaller than that for simple liquid where there is no sliding of the interface.[6]

ACKNOWLEDGMENTS

The author would like to thank Professor K. Kawasaki and Professor T. Hashimoto for valuable comments.

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