Stress Relaxation in the Lamellar Copolymer Mesophase

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ABSTRACT: When diblock copolymers organize into a lamellar mesophase, the interpenetration between like blocks from opposing interfaces is inhibited at high molecular weight. For layers of height h and polymerization index N we show that interpenetration is confined to distances ξ of order $(h/N^2)^{-1/3}$, which becomes much smaller than h itself. We show by self-consistent field methods that the concentration of penetrating monomers falls off with penetration depth y as $\exp(-(y/\xi)^{3/2})$. We argue that the relaxation time for sliding stress grows exponentially as a fractional power of the molecular weight because of this small interpenetration. A numerical example calculation suggests that interpenetration is significantly inhibited in real copolymers and that the predicted slow-relaxation regime should be accessible.

I. Introduction

Block copolymers made with incompatible blocks form equilibrium domain structures of various types.[1] These structures and their distinctive properties have attracted steadily increasing interest.[2] These copolymers have great practical utility in improving properties of homopolymer blends[3] and of adhesives.[4] Thus it is important to understand how the rheology of these materials differs from that of simpler polymer fluids. Empirically,[5] this rheology is marked by high viscosity, leading to difficulty in processing. It is also observed that the domains may be aligned by shear; the domain walls tend to line up along the stream lines.[6] Our aim here is to explore the distinctive rheological features expected for copolymer domain phases. Distinctive features are expected because of the unusual state of the polymers in the domains. These polymers are stretched[6-9] out to lengths indefinitely greater than their ideal random-walk dimensions. Moreover the junction points in these copolymers are confined to the domain interfaces, thus strongly limiting their motion.

Rheological behavior in weak flow may be described in terms of the stress response to a small step strain. This response is characterized by the initial stress and by the relaxation time required for this stress to decay. We consider two cases: a shear tending to slide the layers past one another and a compression of the layers.

As anticipated, we calculate a distinctive behavior of the relaxation time for these two types of stress. A common feature of the two is an exponential growth of time with molecular weight, owing to the end confinement of the copolymer chains. More remarkable is the behavior of the sliding response time. This grows exponentially in a fractional power of the molecular weight and thus becomes much shorter than the compressional time. This relatively fast response arises from the distinctive small interpenetration of chains from opposing layers.

We consider chiefly the case of a neat phase of symmetric diblock lamellae where both blocks are in the melt state. Since we are interested in scaling behavior at high molecular weight, it suffices to use schematic models of the polymer coils.[10] Since the effects important here are at length scales longer than the distance between these coils, it suffices to treat their interactions with self-consistent field methods.[10,11] The relaxation processes we treat arise from the topology and connectivity of the chains, so that the motions may be described at a schematic level.[12] Our estimates deal with the asymptotic behavior for high molecular weight,[7] where the recent conformational theory of Semenov[13,14] is applicable. In order to discuss the stress relaxation we first describe the interpenetration zone, where chains from opposing interfaces may coexist. We then discuss the chain motions required for the relaxation of sliding stress and estimate the corresponding relaxation time. We next deal with the case of compressional stress. Finally, we estimate the various times and moduli for a specific example taken from recent structural studies.

II. Interpenetration Zone

The copolymer blocks in a mesophase domain may be treated[15] as statistically independent random walks in a nonuniform external potential. For our purpose we may treat each polymer as a chain of N beads connected by harmonic springs of zero unstretched length. In a lamella each bead has a height-dependent free energy denoted $\mu(z)$, measured in units of k_BT. This μ is the free energy cost of bringing that bead to the height z from some reference position. The probability $G(r,r',k)$ that a subchain of k beads starting at r' ends at r obeys[11]

$$\partial G/\partial k = (1/2)a^2\nabla^2 G - \mu(z)G \qquad (1)$$

where the microscopic length a^2 is related to the size of the free chain (without μ): $\langle (r-r')^2\rangle = 3a^2k$.

From this G the bead density ρ at any height z may be inferred.[15] For diblocks in a lamella, each block, of N beads, has one end confined within the narrow phase boundary between the blocks. The other end is free. We denote the number of chains per unit area of the interface as σ. The potential $\mu(z)$ arises from the interaction of a given chain with others. In an incompressible melt $\mu(z)$ must be such as to achieve a constant, predetermined density of beads ρ everywhere. Once this μ is determined, the chain conformational statistics can be readily found from eq 1.

As shown in ref 14 the problem of finding the potential profile $\mu(z)$ simplifies greatly at high molecular weight N. Then each chain ending at z_0 may be regarded as a stretched-out line of beads which fluctuates only narrowly in position, as shown in Figure 1. Each bead is in mechanical equilibrium under the tensions from its successor and predecessor, together with the external force $-\nabla\mu$ from the other chains. The only important randomness in the ensemble of chains is then the distribution

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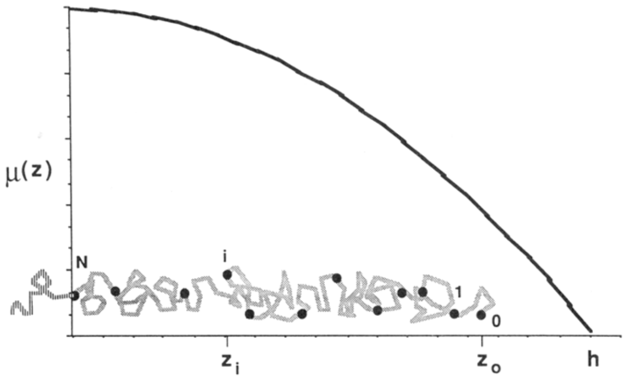

Figure 1. Sketch of the asymptotic[14] monomer free energy $\mu(z)$ in a lamella of height h with schematic representation of a copolymer block of N beads with its free end at height z_0. The numbering of the "beads" is shown.

$\epsilon(z_0)$ of starting heights. The potential $\mu(z)$ must be parabolic—$\mu(z) = A - Bz^2$—in this limit, for this is the only form that takes a chain starting from any height z_0 to the $z = 0$ interface in exactly N beads. The coefficient B is given by $B = a^{-2}\pi^2/(8N^2)$. The A coefficient depends on the coverage σ: $A = Bh^2$, so that $\mu = 0$ at the height h that accommodates all $N\sigma$ beads per unit area at the required bead density ρ, viz., $h = \sigma N/\rho$.

In this large-N limit the grafted layer becomes impenetrable to outside chains. The reduction in penetration for increasing N has been observed numerically[16] and experimentally.[9] Because our copolymers are stretched, it is rather difficult to find the amount of penetration analytically. To get some insight on the extent of the interpenetration zone we consider first the sample system of a grafted-chain layer in contact with a melt of long, free homopolymers. The penetration of homopolymer into the grafted layer is quite important in itself for understanding certain aspects of adhesion[4] and compatibilization[3] of polymer blends. Having analyzed this simple penetration problem, we turn to our central question: viz., the interpenetration of chains across a lamella.

Qualitatively, the extent of penetration by an outside chain of length k is controlled by the competition between the translational entropy to be gained by penetration and the energetic cost of penetration.[17] Thus, penetration into a region of potential μ is inhibited whenever $\mu k \gtrsim 1$. For the majority of the layer, $\mu \simeq Bh^2 \simeq 1/N(h/R)^2$, where $R = 3a^2N$ is the root-mean-square end-to-end distance of the unperturbed chain. Thus penetration throughout the layer is only possible for small chains of length $k < N(R/h)^2$. Chains much longer than this k may only penetrate into the outer fringe of the copolymer layer, where the potential is much smaller than its maximum value: $\mu \simeq Bh(z-h) \simeq h(z-h)/(R^2N)$. A penetrating segment of length k may penetrate a distance $z - h$ of order $ak^{1/2}$, since any potential that allows substantial penetration cannot distort the random-walk statistics drastically. Penetration into the outer fringe is allowed when $\mu k \simeq 1$, as above. This leads to a condition for penetration $k^{3/2} \lesssim N^{3/2}(R/h)$. The chains penetrate to distance $(h - z)$ of order $ak^{1/2}$, i.e. $(h-z)^3 \simeq R^3(R/h) \sim N^2/h$. Even this fringe penetration is inhibited whenever the copolymers are stretched so that $h > R$.

Of course, some outside chains penetrate further than the characteristic distance $(R^4/h)^{1/3}$. We may understand these deeply penetrating chains by the same scaling arguments used above. A chain penetrating far beyond the typical distance necessarily pays a high price in free energy. Such energies are capable of distorting the penetrating segment away from its random-walk configuration. For a penetrating section of k beads, the interaction energy cost of penetration is $\mu k \simeq h(z-h)k/(R^2N)$. The stretch energy of such a section is roughly $[(z-h)/R]^2(N/k)$. The sum of these is minimal when $k^2 \simeq N^2(z-h)/h$. The net energy cost $\Delta S(z)$ is then roughly $h^{1/2}(z-h)^{3/2}/R^2$. The concentration of chain ends penetrating to a height z is $[\text{const} \times \exp(-\Delta S(z))]$, so that the number of chain ends falls off exponentially with the 3/2 power of the penetration depth.

We now corroborate these qualitative expectations using more systematic calculations. We consider first the penetration of homopolymers into the grafted layer. The local concentration $\phi(z)$ of the penetrating chains may be found by using Edward's ground-state dominance method.[10,11] Here, the concentration ϕ becomes the square of an amplitude ψ, which satisfies

$$(1/2)a^2\nabla^2\psi - \mu\psi = 0 \qquad (2)$$

with $\psi^2 = \phi = \rho$ outside the grafted layer. The constant a is the microscopic length introduced in eq 1. Evidently ϕ decays to zero within the layer with some characteristic length ξ. For the purpose of determining the potential μ this interpenetration may be neglected, so that we may use the asymptotic parabolic form of $\mu(z)$. Thus near the extremity of the layer, $\mu(z) = (z-h)F$, with $F = a^{-2}\pi^2h/(4N^2)$. In view of eq 2 one expects on dimensional grounds $\xi^{-2} \sim F\xi$, or $\xi = F^{-1/3}$. More concretely, the assumed form $\phi(z) = \rho\exp(f([h-z]/\xi))$ yields for $h - z \gg \xi$

$$\phi(z) = \rho\exp[-(4/3)((h-z)^{3/2}F^{1/2})] \qquad (3)$$

up to a constant numerical factor. (For later use we note that the amplitude ψ behaves the same, with the 4/3 replaced by a 2/3.)

Since $\xi \sim F^{-1/3} \sim h^{-1/3}N^{2/3}$, the interpenetration region grows more slowly than the height, as claimed. The thickness ξ agrees with our qualitative estimate for $(z - h)$ above. If the coverage σ is fixed, then $h \sim N$ and $\xi \sim N^{1/3}$. If instead $h \sim N^{2/3}$, as in block-copolymer lamellae,[8] then $\xi \sim N^{4/9}$. The penetrating chains alter the potential μ from its parabolic form—indeed[18] the potential is altered in this region by corrections to the asymptotic classical behavior, even without the homopolymer. Still, the potential is only slightly altered in the deep region described by eq 3, so that this equation remains valid. Since this limit of the penetration zone is correct, we expect the formula to be qualitatively correct for the bulk of the zone, so that our conclusions about scaling behavior remain valid.

The same decrease in penetration occurs if the penetrating chains come from the opposing layer in a pure diblock system. Interpenetration arises because a given end may move slightly above a height h without much cost in its (free) energy $S(z)$. In the strongly stretched limit appropriate for long chains[13,14] this energy has the form

$$S(z_0) = \sum_k (1/2)a^{-2}(\mathrm{d}z/\mathrm{d}k)^2 + \mu(z(k))$$

where $z(k)$ is the height of the kth bead of the chain and a, defined above, is a microscopic length. Using the parabolic $\mu(z)$ cited above $S(z_0)$ is independent of z_0 for all $z_0 < h$.[14] But if z_0 is raised above h and into the opposing layer, S begins to increase. (The exact, self-consistent $\mu(z)$ is not parabolic, but we assume for the moment that the deviations from the parabola may be neglected.) A straightforward classical-mechanics calculation, reported in the Appendix, gives

$$\Delta S = (2/3)[8F/3]^{1/2}a^{-1}(h - z)^{3/2} \qquad (4)$$

As noted above, we expect chain ends to extend above the height h if the energy cost ΔS is of order kT or less. From eq 4 this amounts to $y \equiv (z - h) \simeq a^{2/3}F^{-1/3}$. In the parabolic potential the force F is $a^{-2}\pi^2h/(4N^2)$. Thus ends from one parabola are to be found in the opposing parabola over distances y of order $(ha^{-4}/N^2)^{-1/3}$. This y is the width of the interpenetration region.

A chain beginning near the height h is not strongly stretched over the distance y. If the first k beads of a chain were unperturbed by stretching effects, their mean-squared displacement $\langle(\delta z)^2\rangle$ would be of order a^2k. The stretching induced by the force F gives rise to a net displacement $\langle\Delta z\rangle$ of order $k\ \mathrm{d}z/\mathrm{d}k \simeq (Fa^2k^2)$. Evidently the stretching contribution to Δz becomes dominant for $(Fa^2k^2)^2 \gtrsim a^2k$, i.e., for $\Delta z \gtrsim (Fa)^{-1/3} \sim (h/N^2)^{-1/3}$. This Δz is evidently on the order of y above. Thus the chain sections in the interpenetration region, unlike the chains as a whole, are only weakly stretched. Qualitatively, these sections may be treated as random walks; a chain in the interpenetration zone y has roughly $(y/a)^2$ beads there, as anticipated above.

The occurrence of interpenetration alters the potential μ from the parabolic form assumed here. Thus, our estimates of the zone width y are not obviously self-consistent. The true self-consistent potential for two opposing grafted layers is softer than the two abutting parabolas assumed above. Still, the true potential can be perturbed but little at the extremes of the interpenetration zone, so that $\mathrm{d}\mu/\mathrm{d}z$ at $z = h - y$ must still be of the order F assumed above. Thus, our estimate of y should not be altered importantly by the corrections to the potential. However, such corrections would be necessary in calculating the shape of the interpenetration zone in any detail.

The explicit scaling of the zone width y with chain length N depends on the case. For copolymer chains in a lamellar phase, the layer thickness h varies[8,13,19] as $N^{2/3}$. Accordingly, $y \sim N^{4/9}$. For chains end grafted to a surface in a solvent, the height h depends on the number of chains per unit area σ and on the strength of the excluded-volume interaction between the beads. For fixed coverage σ the height h is proportional to N, so that $y \sim N^{1/3}$.

III. Relaxation of Sliding Stress

The limited interpenetration of chains in opposing layers leads to limited entanglement. Thus we expect that stress held by these entanglements should relax in a distinctive way. For comparison we recall the behavior of a melt of homopolymer chains of length N.

If a step strain is imposed on an entangled homopolymer melt at time $t = 0$, the resulting stress resembles that in a rubber network. The associated "plateau modulus" arises[20] from the distortion of the mutually entangled chains in the melt. The stress relaxes from this rubberlike plateau in a time τ that increases strongly with the chain length N. The viscosity of the melt is proportional to this τ. The relaxation time is believed[12] to be the time required for a typical chain to escape from its initial entanglements. The chains are believed to escape by "reptation", a Brownian motion of a chain along its contour length. Asymptotically, this escape requires a time τ of order N^3.

We may apply a similar step strain to a lamellar domain structure. We consider here a transverse shear strain tending to slide each lamella along its neighbors. For simplicity we suppose that the two blocks are symmetric and that both are in a melt state above any glass transition temperature.

As in the homopolymer melt, the initial shear distorts the entangled copolymer chains. The number of entanglements per unit volume is a local property of the melt; thus the associated modulus should be the same as in the homopolymer melt discussed above. But these chains cannot escape from their entanglements in the same way as homopolymer chains. On the other hand, they each have one end anchored at the domain interface, so that reptation is impossible. On the other hand, they are stretched substantially beyond their equilibrium size. This could produce a driving force for relaxation. Further, as noted above, only a limited escape is required. Only chains entangled with *opposing* chains transmit stress between layers. Thus we assert that the time τ_s for stress to relax is the time for a chain in the interpenetration zone to disengage from that zone.

A chain end in the interpenetration zone may over time retract into its own layer. Indeed, chain ends are distributed[14] throughout the layer, so that a given end spends only a minority of its time in the interpenetration zone. As in an ordinary polymer melt, a chain may move along its own contour without violating entanglement constraints. This motion results from independent Brownian forces on the beads of the chain, i.e., Rouse dynamics.[12] The motion may be described in terms of local elements of stored length—"reptons"—along the contour.[21] These reptons diffuse along the chain independently. Their diffusivity depends only on the local structure of the chain and its environment; thus it is the same as in the homopolymer melt. Whenever a repton enters or leaves the end of a chain, that end advances or retracts a small distance. As with homopolymers, this local distance, or "tube diameter" is on the order of a monomer length.

The curvilinear displacement of an end is subdiffusive at short times, as with homopolymers. Specifically, the root-mean-square curvilinear displacement $k(t)$ over time t varies as $t^{1/4}$ for times $t \ll O(N^2)$. In this time regime the reptons can only diffuse over a small fraction of the chain; the resulting motion is uncorrelated with the bulk of the chain and is independent of its length.

At times t of order N^2, the displacement k is of order $N^{1/2}$. At this point the anchored end influences the motion of the free end. Further displacements k must involve shortening of the curvilinear path of the chain. As in a star polymer melt,[10,22] such shortening carries a high statistical penalty. Thus, e.g., for k to grow as large as $N/2$, half of the chain would have to retrace the path of the other half, by means of small side excursions along the original path. The retracing costs an entropy of order N and is exponentially improbable. Thus the displacement k remains confined to excursions of order $N^{1/2}$. These excursions are smaller than the amount of chain in the interpenetration zone, as discussed above. This zone involves chain sections of roughly $(y/a)^2$ beads; this grows as $N^{2/3}$ or $N^{8/9}$ in the cases considered above.

Evidently the reptation of a chain along its confining path is not sufficient to relax the stress. Some other means of escape from these entanglements is required. One such means is that proposed for star polymer melts.[10,22] This process requires the free end of a chain to contract along its path despite the high entropic cost noted above. Without this cost, the time $\tau(k)$ would be that for brownian motion along the tube: viz., $N^2(k^2/N)$. The free-energy cost multiplies this time by a factor exponential in that cost, so that $\tau(k) \sim Nk^2 \exp(k^2/N)$. Thus a displacement $k \simeq N^{2/3}$ would require a time τ of order $N^{7/3}$ exp(const $\times N^{1/3}$).[23] This displacement is that required for grafted chains at fixed coverage σ. For copolymer domains with $h \sim N^{2/3}$, we have $\tau \sim N^{25/9}$ exp(const $\times N^{7/9}$).

Other more cooperative mechanisms may be important in disentangling the chains. One possibility is the tube renewal or constraint-release[24] mechanism. Here a chain becomes disentangled because the others move to let it pass. A second possibility is the unbraiding or disentwining motion[25] postulated for single star polymers in a good solvent. Both of these motions could occur in the stretched polymer melts considered here. The stretching could have a strong effect on the disentanglement process. To understand the role of these motions would require a careful analysis, which we do not pursue here. These motions occur in tandem with the retraction motion discussed above; thus, they can only increase the relaxation rate.

IV. Compressional Stress

If the lamellar copolymer domain structure is subjected to a step compression, the chains are initially distorted as in a rubber, and the stress is essentially that of the homopolymers in the same conditions. The associated modulus is independent of molecular weight. Over time the chains disentangle, and the associated distortion disappears. But even then the system is not in equilibrium, for the lamellar spacing is still at its compressed value. The modulus is on the order of the interfacial energy per unit volume and hence varies as $N^{-2/3}$. Thus over the disentanglement time, the stress falls to a small fraction of its initial rubbery value.

The disentanglement process required to relieve this compressional stress is more difficult than for a sliding stress. The compression has stretched out each lamella to a larger area and increased the area per chain. To adjust to this larger area per chain, each chain must disentangle from its neighbors grafted to the same interface, as well as those from the opposing interface. As with a star polymer melt, each chain must retrace its path to the confined end if it is to disengage. The curvilinear displacement k of the end needed for disengagement is the whole chain length N. Accordingly, the relaxation time τ is exponentially long in molecular weight, as discussed above: $\tau \sim N^3$ exp(const $\times N$).

In principle the stress in the compressed lamellae may relax completely if the lamellar spacing can be restored to its equilibrium value. But this requires polymers to redistribute themselves so as to reduce the total number of layers in the sample. The reduction might occur by diffusion of individual copolymers across to another lamella. This would entail drawing an entire block of the copolymer through the layer occupied by the incompatible blocks. Alternatively, the number of layers can be reduced by certain dislocation motions. In any case, we assume that the time required for this final stress relaxation to be longer than the disentanglement time discussed above.

V. Discussion

As described above, the relaxation of stress in these lamellar structures is quite slow in comparison with that in a homopolymer melt. Further, the effect is strongly anisotropic. At high molecular weight, sliding stress relaxes much faster than compressional stress. The latter requires a time exponential in molecular weight, while the former requires a time exponential in a fractional power of molecular weight. The overall slowness of the relaxation means that this domain material should become very viscous as molecular weight is increased. Thus it should become difficult to anneal or process copolymers in this phase-separated state. Such difficulties are often encountered in these systems.[5] To estimate how strong these effects are in practice, we consider a specific example: viz., a polystyrene/polyisoprene diblock whose layer thickness has been well measured.[8] This copolymer was one of a series that showed the predicted 2/3 power scaling between thickness and molecular weight. It has a styrene molecular weight of 49 000 and an isoprene molecular weight of 48 000. The measured half-height h_s for the styrene layer is 110 Å and the half-height h_i of the isoprene is 120 Å at 30 °C.[26] The homopolymer root-mean-square end-to-end distances are[8] $R_s = 150$ Å for the styrene block and $R_i = 160$ Å for the isoprene block.

We first estimate the width y of the interpenetration region. We assume that the potential $\mu(z)$ has its asymptotic form and is unperturbed by the interpenetration effects. Thus our estimate is only a rough one. As discussed above, a free end extending beyond height h by a distance y has a lower probability relative to one at height h by the Boltzmann factor $\exp(-\Delta S/kT)$ with ΔS given by eq 4. We recall that the root-mean-square end-to-end distance R is $(3Na^2)^{1/2}$ in our notation. Thus from eq 4 the Boltzmann factor is e^{-1} for $y = (3/2)^{1/3}(2\pi)^{-2/3}(R^4/h)^{1/3}$. Thus for the styrene and isoprene sides we have $y_s \simeq 55$ Å and $y_i \simeq 60$ Å.

The expected relaxation times depend strongly on the degree of entanglement of the polymers. For our polystyrene blocks the entanglement molecular weight M_s is[27] 13 500, so that each styrene block has about four entanglements. For the isoprene blocks the entanglement molecular weight M_i is 4000, so that each isoprene block has about 12 entanglements. The molecular weight K in the interpenetration zone can be found by assuming ideal-chain behavior: $3y^2/K = R^2/M$. The factor 3 occurs because y^2 is the mean-squared displacement in the single direction perpendicular to the layer, while R^2 is a mean-squared *vector* displacement. Using y_s, R_s, y_i, and R_i, we infer $K_s \simeq K_i \simeq 20\,000$. Evidently the styrene blocks are barely entangled with the opposing layer.

Though the copolymers in this example would not be expected to show the asymptotic relaxation behavior, this asymptotic regime appears easy to achieve. What is required is some degree of entanglement in the interpenetration zone. In the example, entanglement is already achieved on the isoprene side. Thus it seems sufficient to replace the styrene blocks by a polymer having lower entanglement molecular weight. Alternatively, one may freeze out the polystyrene's relaxation by operating below its glass transition temperature.

VI. Conclusion

The stress relaxation processes discussed here are both unusual and important. It appears that stress in diblock domain structures can be expected to relax much differently than in a homopolymer melt. For high molecular weight the relaxation should be very slow and anisotropic. To observe this distinctive behavior experimentally would be of great interest. Although our calculations were done explicitly only for the lamellar morphology, the same scaling laws are expected for the other domain morphologies. Our scaling predictions are also valid if the layers are expanded by solvent, as they are when polymers are densely grafted to a surface immersed in solvent.[28] Thus the ideas presented here should enable understanding of the relaxation of transverse forces between these grafted

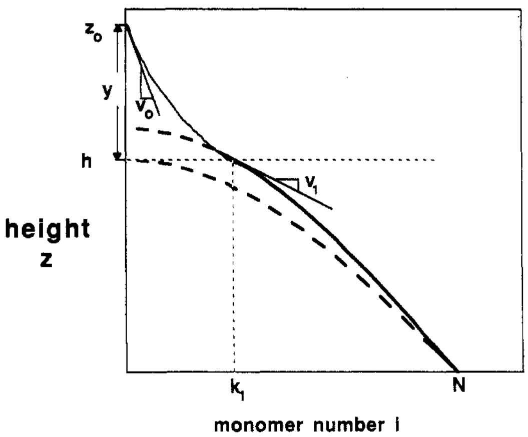

Figure 2. Sketch of height z versus bead number i for chains ending near the outer limit of the layer. Dashed line: a chain ending at the outer limit. Solid line: a chain ending slightly beyond the outer limit. The quantities v_0, v_1, k_1, and y, defined in the text, are shown.

layers. Such forces may be important in understanding the tribology of solid surfaces immersed in surfactant fluids.

Our rough calculations for diblocks show that the molecular weights used in practice approach the small interpenetration expected asymptotically but are not sufficiently entangled to show the expected asymptotic slow relaxation. This intermediate regime of weak interpenetration without entanglement appears important and accessible. By increasing the height h without increasing the unperturbed chain radius R, one could attain this intermediate regime to an arbitrarily good approximation. The relaxation of stress in this regime would be of interest to work out theoretically.

A potentially important effect is the mixing region at the interface between the two blocks. This region has a significant influence on the chain configurations and on dynamic relaxation unless the chains are very long. For real chains these effects could obscure the relaxation processes described here.

Another theoretical improvement appears promising. Our estimates of interpenetration used the simplest perturbation approach. More systematic approximations to the concentration profile in the interpenetration zone should be possible in our limit of high molecular weight. Along with this, there is much room for improvement in our treatment of the stress relaxation, using recent refinements in reptation theory.

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Appendix

In order to calculate $S(z_0)$ we consider in Figure 2 the trajectory $z(k)$ of an interpenetrating chain. The chain must cover the distance from its starting height $z_0 \equiv h + y$ with exactly N beads. The force equilibrium of each bead along the chain amounts to Newton's equation of motion: $a^{-2}\,\mathrm{d}^2z/\mathrm{d}k^2 = \mathrm{d}\mu/\mathrm{d}z$. We note that the tension $a^{-2}\,\mathrm{d}z/\mathrm{d}k$ plays the role of a velocity; accordingly, it is related to the potential energy μ via conservation of Newtonian energy:

$$(1/2)a^{-2}[\mathrm{d}z/\mathrm{d}k]_z^{\,2} + \mu(z) = (1/2)a^{-2}[\mathrm{d}z/\mathrm{d}k]_{z_0}^{\,2} + \mu(z_0)$$

By construction, the parabolic potential μ is such that chains starting at $z_0 \leq h$ (dashed line in the figure) use the required N beads with no tension in the chain end: $\mathrm{d}z/\mathrm{d}k_{z=z_0} = 0$. But raising the end above h produces a tension $\mathrm{d}z/\mathrm{d}k \equiv v_0$ at the end. The change $S(z_0) - S(h)$ in energy is simply the work $\int_h^{z_0} a^{-2}\,\mathrm{d}z\, v_0(z)$ done against this tension in raising a chain end from h to the desired height.

The number of beads N in the chain, equivalent to the transit time for the corresponding Newtonian trajectory, may be expressed[14] in terms of the potential μ:

$$N = \int_{z_0}^{0}\mathrm{d}z\,(\mathrm{d}z/\mathrm{d}k)^{-1} = \int_{\mu_0}^{\mu}\mathrm{d}\mu'\,\mathrm{d}z/\mathrm{d}\mu\,[2a^{-2}(\mu' - \mu_0)]^{-1/2}$$

For a chain pulled out of an equilibrium layer of height h, this integral consists of two parts: an initial part beyond h, with k_1 beads, and the remainder. Thus, if we recall that $\mu(h) = 0$ and $\mu(0) = A$

$$N = k_1 + \int_0^A \frac{\mathrm{d}\mu}{[v_1^{\,2} + 2a^{-2}\mu]^{1/2}}\frac{\mathrm{d}z}{\mathrm{d}\mu} \tag{A1}$$

Here v_1 is the tension $\mathrm{d}z/\mathrm{d}k$ at height h.

Since the number of beads N is fixed, this equation implicitly determines v_1 in terms of the initial k_1. Evidently, if k_1 is zero, so that the entire chain is within the equilibrium layer, then v_1 is also 0. The initial increase of v_1 depends only on the region around $\mu = 0$, as we now show. We separate $\mathrm{d}z/\mathrm{d}\mu$ into its value at $\mu = 0$ plus a remainder: $\mathrm{d}z/\mathrm{d}\mu = F^{-1} + \mu R(\mu)$, where the remainder R is finite as $\mu \to 0$. The contribution of these two terms to the integral of eq A1 may be readily found. The integral in $R(\mu)$ has a finite derivative with respect to $v_1^{\,2}$ at $v_1 = 0$. Thus the R contribution has the form const + $O(v_1^{\,2})$. The F^{-1} contribution may be found explicitly; for small v_1 it is dominated by the small-μ region and is of order v_1. Specifically, eq A1 now reads

$$N = k_1 - F^{-1}a^2v_1 + \text{const} + O(v_1^{\,2}) \tag{A2}$$

Thus, since $k_1 = 0$ when $v_1 = 0$

$$k_1 = F^{-1}a^2v_1 + O(v_1^{\,2}) \tag{A3}$$

Now, the initial section of the chain, beyond height h, imposes a second relation between k_1 and v_1:

$$v_1 = v_0 + a^2\tilde{F}k_1 + O(k_1^{\,2})$$

Here $\tilde{F}$ is $\mathrm{d}\mu/\mathrm{d}z$ in the small region where the k_1 beads lie, and v_0 is the desired end tension. Combining this result with eq A3 determines v_1 in terms of v_0: $v_1 = v_0/(1 - \tilde{F}/F)$. Finally, the displacement y is related to v_1 and v_0 via $v_1^{\,2} = v_0^{\,2} + 2\tilde{F}y$. Combining, we find

$$v_0^{\,2} = \frac{2ya^2(F - \tilde{F})^2}{2F - \tilde{F}} \tag{A4}$$

The work ΔS required to produce the displacement y is given by

$$\Delta S = \int_h^{h+y} a^{-2}v_0\,\mathrm{d}z = \frac{2}{3}\left[\frac{2(F - \tilde{F})^2}{2F - \tilde{F}}\right]^{1/2} a^{-1}y^{3/2} \tag{A5}$$

We observe that if the external force $\tilde{F}$ is zero, this ΔS is exactly that found below eq 3 for the amplitude ψ in the case of homopolymer penetration. Taking $\tilde{F} = -F$, as appropriate for opposing copolymer layers, we obtain the result quoted in eq 4.

Registry No. (Isoprene)(styrene) (block copolymer), 105729-79-1.

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Molecular Dynamics in Bulk *cis*-Polyisoprene As Studied by Dielectric Spectroscopy

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ABSTRACT: Dielectric spectroscopy from 10^{-1} to 10^9 Hz was used to investigate bulk amorphous *cis*-polyisoprenes with different molecular weights having narrow molecular weight distributions. A molecular weight dependent normal-mode relaxation process due to reorientation of the end-to-end vector as well as a molecular weight independent segmental-mode process caused by local chain motions were observed. The relaxation time for the normal-mode process exhibits a molecular weight dependence that can be described below a critical molecular weight, M_c ($=10^4$), according to the Rouse theory; but above M_c the relaxation time follows the 3.7 power of M_w, which is explicable with the reptation theory. Both processes were analyzed in terms of dipole–dipole correlation functions and reveal a Kohlrausch–Williams–Watts (KWW) type of relaxation behavior. The nonexponential decay is explained with the cooperative nature of motions in the bulk amorphous state. The stretched exponential β_{KWW} for the normal-mode process depends on the chain length whereas it remains constant for the segmental process. The results are in agreement with new theoretical and computational approaches.

I. Introduction

It is well established[1,2] that most dipolar amorphous polymers give rise of multiple dielectric relaxation processes. Among them, the well-known α and β processes are often found. Their frequency–temperature locations are essentially independent of molecular weight.[3]

From a variety of macromolecules only a few reveal a low-frequency relaxation, which is strongly dependent on molecular weight.[4] The first dielectric investigation in the bulk amorphous state for poly(propylene oxide), which contains both a "fast" α process and a "slow" molecular weight dependent process, was carried out by Baur and Stockmayer.[5,6] The latter process was interpreted with the Rouse–Zimm theory for unentangled polymer chains.[7,8] For the entangled state of poly(propylene oxide), the experimental results of Beevers et al.[9] were compared with the predictions of the models for reptational motions of chains, as proposed by de Gennes[10] and Doi and Edwards.[11] Adachi and Kotaka[12–16] studied *cis*-polyisoprene in its undiluted state and observed two relaxation regions, as in the case for poly(propylene oxide). Because of the asymmetry in the chemical structure of *cis*-polyisoprene, the polymer has components of the dipole moment both parallel and perpendicular to the chain contour (Figure 1). Therefore, *cis*-polyisoprene exhibits a

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