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Reconsidering Random Copolymers at Interfaces

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Recent experiments[1,2] have examined the fracture strength of interfaces between two immiscible homopolymers when a thin layer of copolymer is sandwiched between the homopolymer layers. The experiment measures the force required to push a razor blade along the interface at a given speed, propagating a fracture. The measurement gives the strength of the interface, which is ultimately interpreted in terms of the number of "connections" per unit area across the interface. These connections can be provided by sufficiently long A−B diblock copolymers (one connection per diblock); A−B interfaces coated with varying amounts of diblock copolymer have been studied to confirm this picture. It is found that the known coverage of copolymer, and hence the number of connections per unit area of interface, correlates well with increased interfacial strength. The copolymers must be sufficiently long that an entangled connection is formed, which will bear load as a fracture propagates rather than simply pulling out.

In addition to studying the effect of a layer of A−B diblock copolymers on the strength of the A−B interface, Kramer et al. have placed layers of A/B random copolymers between the A and B homopolymer layers.[2] [In these experiments, the A and B monomers are polystyrene and poly(2-vinylpyridine).] Surprisingly, they found that random copolymers also strengthened the interface, if the chains were sufficiently long and symmetrical. The strengthening effect was very sensitive to the fraction f of A monomers, disappearing rapidly as f was varied away from $f = {}^1/_2$. Interpreting their results by comparing the strengthening effect to the diblock case, they conclude that for a certain thickness of random copolymer layer, each PS/PVP random copolymer of length $N = 8000$ monomers must form about 10 connections. Notably, the observed strengthening persists even when the layer of random copolymer becomes "thick", i.e., greater than the radius of gyration of the random copolymers.

This remarkable observation has been rationalized in terms of the work of Garel et al., who considered the problem of a single A/B random copolymer at a sharp A−B interface.[3] In essence, their picture was as follows. A random copolymer (RC) with $f = {}^1/_2$ has an equal number of energetically unfavorable contacts as a random coil in a phase of pure A homopolymer or pure B homopolymer; in each case, half of the monomers of the RC are in the wrong phase. But sub-sequences of the RC of s monomers will have fluctuations of order $s^{1/2}$ in the number of A monomers around the mean of $s/2$. Choose some s (to be optimized later) and consider a conformation of the RC at an A−B interface in which the sub-sequences rich in A (B) monomers are loops on the A (B) side of the interface. The entropy given up by such a conformation relative to a random walk is of order kT per loop; the enthalpy gained, again relative to a random walk conformation, is of order $\chi s^{1/2}$ per loop. Optimizing the free energy per monomer with respect to s, one obtains $s \sim 1/\chi^2$. In the PS−PVP experiments, the value of χ is about 0.1, so the loop length s is of order 100, consistent with the required number of connections formed per long RC.

Unfortunately, there is a flaw in the above theoretical picture, which spoils this apparent consistency with the experimental results. Garel et al. took as their "reference state" for the RC a Gaussian coil in either the A or the B phase. (The reference state is essentially the state that competes with those configurations in which the chain loops back and forth across the interface.) There is another possibility, which turns out to be more favorable for the RC: it can separate into a third RC-rich phase if many RC chains are present, or collapse as single coils if the RC chains are few in number but sufficiently long.

We begin by examining the phase behavior of a system containing homopolymer and RC. Consider the simple case of a mixture of A homopolymers (volume fraction ϕ) and RC (fraction f of A monomers), each of the same length N. The Flory−Huggins free energy F for a system of volume V, which assumes random mixing of the monomers and ideality of the chain conformations, is[4]

$$F/V = \chi[\phi + (1-\phi)f][(1-f)(1-\phi)] + \frac{\phi}{N}\log\frac{\phi}{N} + \frac{(1-\phi)}{N}\log\frac{(1-\phi)}{N} \qquad (1)$$

where the first term is the enthalpy per unit volume $\chi\phi_A\phi_B$ and the last terms are the entropy of mixing of the A homopolymers and the RCs. For convenience, we may add to this free energy a linear term $-\chi f(1-f)(1-\phi)$ (such linear terms do not change the phase behavior); this amounts to subtracting the enthalpy of the pure RC phase. We then obtain

$$\tilde{F}/V = \chi(1-f)^2\phi(1-\phi) + \frac{\phi}{N}\log\frac{\phi}{N} + \frac{(1-\phi)}{N}\log\frac{(1-\phi)}{N} \qquad (2)$$

Equation 2 is exactly the same result as for a mixture of A and B homopolymers, with an effective χ parameter $\chi_{\text{eff}} = (1-f)^2\chi$. (Note that as f approaches unity and the RC chain is pure A, the interaction vanishes.) Thus the phase behavior, and the interfacial widths and surface tensions, are as for a homopolymer blend with a χ parameter χ_{eff}. In particular, the critical point for the blend is $\phi = {}^1/_2$, $\chi N = 2/(1-f)^2$ ($\chi N = 8$ for the case $f = {}^1/_2$). The Helfand results[5] for the interfacial width Δ and tension γ in the strongly segregated regime become $\gamma \sim \Delta^{-1} \sim (1-f)\chi^{1/2}$. The surface tension is reduced by a factor of 2 for $f = {}^1/_2$.

In the experiments of ref 2, the RC chains are many times longer than the homopolymer chains, which were themselves incompatible. At sufficient concentration, the RCs would then certainly phase-separate from either the pure-A or the pure-B phases into a phase of essentially pure RC. Thus if there are many RC chains present in the experiment, the Garel analysis is not applicable, because it assumes a reference state of a

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Gaussian coil in either the pure-A or the pure-B phase, when in fact the reference state should be a RC chain in a pure-RC phase. This makes a big difference, as we shall see in detail below, because now to put a single RC chain on the A–B interface we must first pay the enthalpy cost of bringing a Gaussian RC coil from the RC-rich phase to the A-rich phase. To compute this cost, imagine destroying s monomers of pure-RC phase and then creating s RC monomers in the pure homopolymer A phase. The cost of these two operations is

$$\Delta H_{\mathrm{RC}\to\mathrm{A}} = -s\chi f(1-f) + s\chi(1-f) = s\chi(1-f)^2 \quad (3)$$

or $\chi(1-f)^2$ per RC monomer.

Now we consider a single RC chain immersed in the pure-A phase and ask what its conformation should be. If the chain were together with some other RC chains, we would expect a droplet of RC-rich phase, with some interface with the A-rich phase; what happens as the droplet becomes smaller and smaller? Does it make sense to think of a "droplet" consisting of a single collapsed chain? To answer these questions, we argue as follows. For a droplet to be well-defined, its interfacial width Δ must be small compared to the droplet radius R. Since the interfacial width goes as $\chi^{-1/2}$ and the radius of a collapsed chain is of order $N^{1/3}$, we must have

$$N > \chi^{-3/2} \quad (4)$$

Equivalently, we could ask if the bulk condensation energy, of order χN, is larger than the surface energy, $\chi^{1/2}N^{2/3}$, which gives the same criterion.[6] The inequality (4) will be satisfied for sufficiently large N; for the experimental case $\chi = 0.1$, the threshold value of N is of order $10^{3/2}$, and the RCs used experimentally are much longer than this. We conclude from this criterion that a sufficiently long isolated RC chain in a homopolymer-rich phase will adopt a collapsed configuration, which is then the reference state to be compared to configurations in which the chain loops back and forth across an A–B interface. The free energy of this collapsed configuration is the same as that of a RC chain in a bulk RC-rich phase, plus the interfacial-tension contribution $4\pi N^{2/3}\gamma$.

Note that one need not worry that we have neglected some loss of conformational entropy upon collapse of a single chain from a Gaussian coil into a compact droplet. Such a term is in fact part of the interfacial tension. To see this, consider first a region of melt bounded by a sharp interface. Each bond right at the interface is prohibited from crossing the interface, which amounts to a loss of conformational entropy of order kT per bond at the interface. The conformations of the chains in this finite region of melt are ideal in every other respect—that is, the conformations are Gaussian random walks with reflecting boundary conditions at the surface of the droplet. Thus the loss of conformational entropy of the surface bonds amounts to a surface tension of order kT/a^2.[7] This is the same situation as for a melt confined in a slab, for which there is no force induced between the parallel surfaces defining the slab until the thickness becomes comparable to the presistence length.

Now consider a more diffuse interface between immiscible homopolymers. The Helfand argument tells us that the interface consists of intermixed A and B loops of length s of order $1/\chi$. These loops are nearly random walks, "excursions" of A chains onto the B-rich side and back again; hence the interfacial width Δ goes as $s^{1/2}$ or $\chi^{-1/2}$. The interfacial tension can be estimated from the enthalpy of the A–B contacts in this region as $\chi\Delta$ per area. Or we may estimate the interfacial tension from the entropy loss of the loops as kT per loop, with Δ/s loops per unit area (the interface of width Δ is dense in loops, each of which displace volume s). Each of these estimates gives the interfacial tension of order $\chi^{1/2}$. The point is that the interfacial tension includes the loss of entropy of those chains constrained not to cross the interface, just as when the interface was sharp.

Having established that the correct reference state is a collapsed or phase-separated RC chain and not a random-walk configuration in one of the homopolymer-rich phases, we reconsider the argument of Garel et al. summarized above. Recall that the enthalpy gain per loop from the Garel argument of $\chi s^{1/2}$ (with s optimized to $s \sim \chi^{-2}$, an enthalpy of order kT per loop) is relative to the state of half the monomers being in a pure-A phase and half in a pure-B phase. Now consider the enthalpy cost per loop of bringing the RC from the pure-RC phase to this state; again, we may imagine destroying s monomers from a pure-RC phase and creating $s/2$ monomers each in a pure-A and a pure-B phase, at a cost

$$\Delta H_{\mathrm{RC}\to\mathrm{A\&B}} = -s\chi f(1-f) + (s/2)\chi[(1-f) + f] \quad (5)$$

$$= s[\chi/2 - \chi f(1-f)] \quad (6)$$

Clearly, the gain of kT per loop is negligible compared to the cost per loop $[\chi/2 - \chi f(1-f)]s$ to take the RC from the RC-rich phase to the reference state of the Garel argument.

So what can serve as an explanation of the experimental results of ref 2, that RC chains on an A–B interface interpenetrate the homopolymer enough to form connections that strengthen the interface? Our simple Flory–Huggins picture predicts that the bulk RC–A interface is broader by a factor of $1/(1-f)$ than the bulk A–B interface, because of the reduced magnitude of χ. If the interfacial width becomes of order the distance between entanglements in the melt, the interface will be strengthened by interpenetration of the immiscible chains. For the case $f = 1/2$, this effect is the same as reducing χ by a factor of 4, from 0.1 to 0.025, and such a value of χ is still too large to afford much interfacial strength.

Next, we consider the possibility that for a few RCs, there exist highly unlikely sequences along the RC so rich in A or B monomers that these chains are enthalpically favorable to be placed at the A–B interface. To be effective at strengthening the interface, such a sequence should contain an entanglement segment, of N_e monomers. Consider now a sequence of s monomers with $n > fs$ A monomers. The enthalpy cost of removing this sequence from the RC-rich phase and placing it in the A-rich phase is computed as before, by subtracting the cost of creating s monomers of RC in the pure-RC phase with fs A monomers and then converting $\delta n = n - fs$ monomers from B to A from the cost of creating those same monomers in the pure-A phase:

$$\Delta H_{\mathrm{RC}\to\mathrm{A}}(\delta n) = -\chi f(1-f)s - \chi(1-2f)\delta n + \chi((1-f)s - \delta n) \quad (7)$$

$$= \chi[s(1-f)^2 - 2(1-f)\delta n] \quad (8)$$

If the sequence is so rich in A monomers that $n > s(1 +$

$f)/2$, *i.e.*, the sequence is closer in composition to pure A than to the RC phase, this is enthalpically favorable.

The probability of a given loop of length s having n A monomers is

$$p(n;s) = (2\pi f(1-f)s)^{1/2}\exp[-(n-fs)^2/(2f(1-f)s)] \quad (9)$$

The fraction ψ of chains with one such unlikely loop of $n > fs$ monomers is approximately $\psi = (N/s)p(n;s)$ (N/s independent chances to have such a loop).

These chains are so rare that their translational entropy is enough to prevent adsorption at the interface. To see this, estimate the translational entropy per chain of these rare chains as $\log(\psi/N) = -(1/2)\log s - (n - fs)^2/(2f(1-f)s)$. Even neglecting the first term, consider the free energy change upon adsorption of such a chain, which we estimate as

$$\Delta F_{\mathrm{RC}\to\mathrm{A}}(\delta n) = (\delta n)^2/(2f(1-f)s) + \chi[s(1-f)^2 - 2(1-f)\delta n] \quad (10)$$

$$= \chi s(1-f)^2[1-2\chi(1-f)] + (\delta n - 2\chi f(1-f)^2 s)^2/(2f(1-f)s) \quad (11)$$

in which we have completed the square to show that the optimum value of δn is $\delta n = 2\chi f(1-f)^2 s$, at which value ΔF is still quite large, $\chi s(1-f)^2[1-2\chi(1-f)]$, or $\chi(1-\chi)s/4$ for $f = {}^1/_2$. Recall we expect that s must be greater than the entanglement molecular weight N_e for the loop to strengthen the interface. For $s = N_e \approx 100$ for polystyrene and $\chi = 0.1$, $\Delta F = +2.25kT$.

Finally, we explore the possibility that a loop with fewer than N_e monomers may sometimes result in an entanglement, which strengthens the interface. After all, N_e is only the characteristic number of monomers per entanglement. What is the probability $P_{\mathrm{ent}}(s)$ with which one or more entanglements are created if we place a loop of s monomers across a sharp A–B interface?

For $s \gg N_e$, we can estimate how often an entanglement is *not* created, by considering a loop of s monomers extending into and back out of a lattice of obstacles. To avoid entanglement with any of the obstacles, the path of the loop must completely retrace its steps; that is, its conformation must be that of a "lattice animal" of total bond length $s/2$. Retracing steps is exponentially unlikely, so that the number of such paths which fail to entangle should scale as $\exp(-cs/N_e)$, where c is some constant of order unity.

Less clear is how $P_{\mathrm{ent}}(s)$ becomes small for $s < N_e$. One possible route to estimating $P_{\mathrm{ent}}(s)$ in this limit is to try to extend the Lin–Noolandi argument for the entanglement length N_e.[8,10] In brief, this argument is as follows. A chain segment of s monomers displaces a volume $V = sv$ and sweeps out a volume R^3 ($R^2 = sa^2$). The volume fraction of the segment's own monomers in the swept-out volume is $\phi = V/R^3$, which scales as $s^{-1/2}$. When ϕ becomes sufficiently small, less than some ϕ^*, the rest of the monomers in the volume R^3 must come from other chains, which are likely to entangle with the given segment. Thus $R^* = (V/R^2)/\phi^*$ is the radius of an entanglement segment, which is a useful formula since the ratio $V/R^2 \equiv p$ is in fact the "packing length", a material parameter independent of s.

Such an entanglement segment then displaces a volume $V^* = (V/R^2)^3/\phi^{*2}$, so that the plateau modulus is $G \equiv (4/5)kT/V^* = (4/5)\phi^{*2}kT/p^3$. This relationship between chain dimensions (radius and displaced volume through p) and the entanglement volume has recently been demonstrated for a wide variety of polymers,[10] and the value of $\phi^* = 0.0565$ determined experimentally.

If s is less than N_e, then the concentration of monomers belonging to chains other than the given segment becomes smaller, and entanglements less likely. All we really know is that $P_{\mathrm{ent}}(N_e) \approx {}^1/_2$. We might speculate that the chance of entanglement is proportional to the fraction of monomers belonging to other chains inside the sphere containing our loop. That is, perhaps P_{ent} goes as $1 - \phi$ for $s < N_e$, down to such small s that ϕ approaches unity and the given segment can no longer be a random walk. We have $(s/N_e)^{1/2} = R/R^* = \phi^*/\phi$, so the minimum s is $s_{\min} = N_e\phi^{*2} \ll N_e$.

$$P_{\mathrm{ent}}(s) \approx 1 - \phi^*(N_e/s)^{1/2}, \qquad s > s_{\min} \quad (12)$$

The behavior of $P_{\mathrm{ent}}(s)$ could be explored experimentally by spreading ABA triblock copolymers on an A–B homopolymer interface and performing experiments as in ref 2 to see how the interface weakens as the B block is made progressively shorter. For now, we shall examine the consequences of short loops occasionally giving entanglements that strengthen the interface. Note that we must be careful not to "explain too much"—we had best not conclude that the short loops at the interface between immiscible homopolymers are enough to strengthen such interfaces. We seek to compare, then, the likelihood of a loop forming an entanglement for the two cases of homopolymer–homopolymer and RC–homopolymer interfaces with the same effective χ.

In the case of homopolymer–homopolymer interfaces, the sum over Boltzmann weights for a loop of length s to penetrate the interface times the probability $P_{\mathrm{ent}}(s)$ of forming an entanglement is

$$P^{\mathrm{homo}}_{\mathrm{ent}} = \int_0^N \mathrm{d}s\, e^{\chi s} P_{\mathrm{ent}}(s) \quad (13)$$

For the RC–homopolymer interface, we have the additional stochastic variable n, the number of A monomers on the RC loop penetrating into the A-homopolymer phase. We find (for $f = {}^1/_2$)

$$P^{\mathrm{RC}}_{\mathrm{ent}} = \int_0^N \mathrm{d}s \int_0^s \mathrm{d}n\, e^{\chi(3s/4-n)} e^{-2(n-s/2)^2/s} P_{\mathrm{ent}}(s) \quad (14)$$

which expresses the double sum over the loop length and the number of A monomers on the loop with appropriate Boltzmann weights. At the most likely number of A monomers $n = s/2$ this integrand is the same as for the homopolymer but with the χ parameter replaced by $\chi_{\mathrm{eff}} = \chi/4$, as we found above from eq 2 with $f = {}^1/_2$. However, the enthalpy cost is less for larger n. From eqs 11 we see that integration over n gives a saddle-point value of $n = (s/2)(1 + \chi/2)$ and

$$P^{\mathrm{RC}}_{\mathrm{ent}} = \int_0^N \mathrm{d}s\, e^{\chi(1-\chi)s/4} P_{\mathrm{ent}}(s) \quad (15)$$

which again looks like the case of homopolymer–homopolymer penetration, but with χ replaced by $\chi(1-\chi)/4$, a slightly smaller value of χ_{eff}.

We conclude, then, that the probability of loops penetrating from a RC phase into an A-homopolymer phase, including the effect of fluctuations in the number of A monomers on a sub-sequence of the RC chain, is the same as for a homopolymer–homopolymer interface with an effective χ parameter given by $\chi_{\text{eff}} = \chi(1 - \chi)/4$. We do not need to say what $P_{\text{ent}}(s)$ is; if a homopolymer–homopolymer interface with $\chi = \chi_{\text{eff}}$ is sufficiently diffuse that interpenetration of loops strengthens the interface, then the RC–homopolymer interface will likewise be strengthened. For the experiments of ref 2, it appears that this reduction in χ, from 0.1 to 0.0225, is not a strong enough effect to explain the strengthening of the interface; hence the results of ref 2 remain mysterious within our picture at present. It is perhaps possible that the random copolymers studied by Kramer et al. are either (1) slightly "tapered", i.e., A-rich at one end and B-rich at the other, leading to some tendency to behave as diblocks, or (2) polydisperse in composition, permitting a compositionally diffuse interface, leading to increased strength.

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