Importance of a Broad Composition Distribution in Polymeric Interfacial Modifiers

M. D. Dadmun

Chemistry Department, The University of Tennessee, Knoxville, Tennessee 37996-1600

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ABSTRACT: The importance of the sequence distribution in a copolymer that is used as an interfacial modifier relative to the importance of its composition polydispersity is examined. Using Monte Carlo simulation, the microstructure of a copolymer is shown to have a greater influence on the ability of a copolymer to effectively strengthen a biphasic blend than the compositional polydispersity. Correlation to experimental studies and implications of these results on the design of polymeric surfactants are also noted.

Mixtures of surfactants are encountered in almost all applications of interfacial modifiers.[1] Heterogeneity in composition that results from the manufacturing process or deliberate formulation of various surfactant types to exploit synergistic behavior are two possible mechanisms by which mixed surfactants can be utilized in practical applications.[1−6] One area where the use of an interfacial modifier has been shown to be useful, but not completely understood, is the addition of a copolymer to a biphasic polymer mixture to improve the properties of a two-phase system.[7−39] There exist contradictory experimental results regarding the ability of a random copolymer to effectively compatibilize an immiscible polymer blend.[17−19,31,35−39] Explanations that have been proffered to explain this discrepancy have included the difference in the sequence distributions[40−43] or the compositional distributions[31] of the copolymers that were used in the experimental studies. Clearly, both types of polydispersity exist in the experimental systems; thus, it is difficult to ascertain the relative importance of both factors from an experimental viewpoint. We present in this paper results from a Monte Carlo simulation study that provide insight into the relative importance of the polydispersity of composition and the sequence distribution that exists in a copolymer on its ability to act as an interfacial modifier in a polymer blend.

It is well-known that two long chain molecules will rarely mix on a thermodynamic level due to their low entropy of mixing. The resultant two-phase structure will often have inferior properties to the initial components, primarily due to the presence of a sharp biphasic interface between the phases that does not provide entanglement between the polymers in the separate phases. This lack of entanglement across the interface results in poor transfer of stress, which in turn degrades the macroscopic properties of the mixture.

Because of the importance of the presence of a biphasic interface on the macroscopic properties of a polymer blend, substantial work has been completed toward improving the interface of blends by addition of a random copolymer to act as an interfacial modifier. Experimental results suggest that some random copolymers are efficient compatibilizers while others are not. These results include studies on mixtures of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with random copolymers of PS and PMMA as compatibilizer which show that the random copolymer does not improve the strength of the biphasic interface as well as a block copolymer.[18,19] Nor does it inhibit droplet coalescence in the blend after shear cessation,[34] an important mechanism in the compatibilization process.[44−47] Alternatively, if the strength of a biphasic interface is determined on mixtures of PS and poly(2-vinylpyridine) (P2VP) with a PS/P2VP random copolymer as an interfacial modifier, the random copolymer substantially improves the interfacial strength between the two homopolymers[17,31] Additionally, seminal work by Fayt et al.[35−39] showed that addition of tapered (which can also be thought of as a type of random) copolymers of PS/PE (polyethylene) to a blend of PS and PE improved the elongation and ultimate strength of that blend *more* than the addition of a similar diblock copolymer.

Recently, we have presented simulation results that suggest that these seemingly contradictory experimental results may be explained by considering the specific sequence distribution of the copolymers that are utilized in these experimental results.[40−43] These results suggest that the random copolymer must be blocky in nature to be an effective compatibilizer, which is true for PS/P2VP and PS/PE copolymers, but not PS/PMMA. Alternatively, Kramer et al. have suggested that the distribution in the composition of the copolymer chains that results from the copolymerization process may explain the different experimental response for the various random copolymers.[31]

The simulation model and technique utilized in this study is very similar to one that has been used previously;[40−43] thus, only new and pertinent information will be provided here. The simulation is completed on a three-dimensional lattice model with 2504 chains, each of length 10, using periodic boundary conditions. One-half of the homopolymers are of type A and half are type B. The percentage of copolymer present is kept at 7.5%, and the copolymer system has a composition of 50% A and 50% B. The sequence distribution of the copolymer system is parametrized by the parameter Px, which is equal to

$$\mathrm{Px} = P_{AB}/(P_A P_B) \tag{1}$$

In this equation, P_{AB} is the percentage of AB diads in the copolymers, P_A is the percent of A monomers in the

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copolymers, and P_B is the percentage of B monomers in the copolymers. Px is essentially a normalized probability that two neighboring monomers on a copolymer chain are different types.

The simulation proceeds by allowing the homopolymers and copolymers to mix at high temperature and then quenching to a lower temperature in the two-phase regime. In this process the system equilibrates as a two-phase system, and the copolymer migrates to the interface. It is fairly well understood that a copolymer that is acting as a compatibilizer in a polymer blend will strengthen the biphasic interface,[16−33] lower interfacial tension (to create a finer dispersion),[7−15] and inhibit coalescence during processing.[44−47] Each of these mechanisms contributes to the improvement of the macroscopic properties of biphasic polymer blends upon addition of a copolymer; the importance of each has been the subject of some debate in the literature. Thus, the copolymer must, at a minimum, entangle with the homopolymer to be an efficient interfacial modifier. This fact is utilized in the analysis of the simulation data. The ability of a given copolymer system to compatibilize an immiscible polymer blend is correlated to the average number, per copolymer chain, of nonbonded nearest neighbors on the lattice that are also copolymers. In order for the copolymer to entangle with the homopolymer, the homopolymer must displace neighboring copolymer chains, and thus, a minimum in the number of neighboring copolymer chains correlates to better compatibilizing ability.

The copolymer systems that are examined in this paper include three samples that are compositionally monodisperse (every chain is 50% A and 50% B) but differ in their sequence distribution. The three sequence distributions are a blocky copolymer structure (Px = 0.5), a statistically random copolymer (Px = 0.0), and a random copolymer with alternating tendencies (Px = 1.5). Also examined are five copolymer systems that are compositionally polydisperse. These include the same three sequence distributions as above (Px = 0.5, 0.0, and 1.5) and ones that mimic PS−P2VP and PS−PMMA random copolymers. The compositionally polydisperse random copolymers are created by modeling the copolymerization process; a pool of monomers (50% A and 50% B) are polymerized by choosing a monomer at random and then adding subsequent monomers to create the copolymer. The identity of the monomer that is added to the growing polymer chain is weighted by the reactivity ratios of the monomers and the composition of the remaining monomer pool. In this manner, the overall composition of the copolymer system remains 50/50; however, the composition of individual chains may deviate from this average.

Figure 1 is a plot of the average number of nonbonded next-nearest neighbors that are part of a copolymer, N, as a function of reduced temperature, $\tau = k_B T/\epsilon$ where k_B is Boltzmann's constant, T is the temperature, and ϵ is the interaction parameter between A and B monomers. For this system, the mixing/demixing transition occurs at $\tau_c = 6.69$. Interestingly, inspection of this plot shows that utilizing N as a measure of the ability of a copolymer to act as an efficient interfacial modifier agrees with previous results that utilized the conformation and shape of the copolymer for the same analysis.[40−43] Both show that, as a random copolymer becomes more blocky, it becomes a more effective compatibilizer.

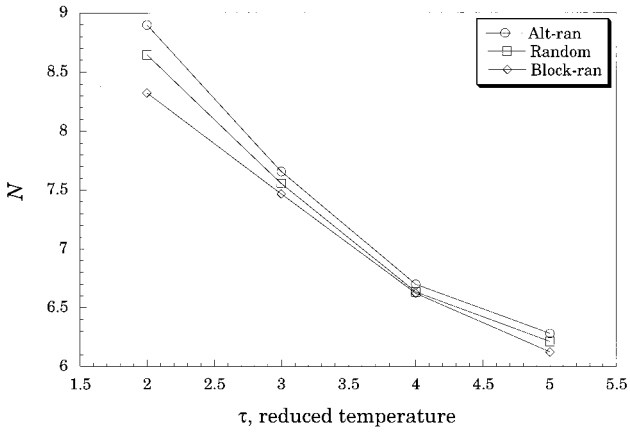

Figure 1. Plot of the average number of nonbonded next-nearest neighbors that are part of a copolymer, N, vs reduced temperature for the three types of random copolymer structures of interest in this study.

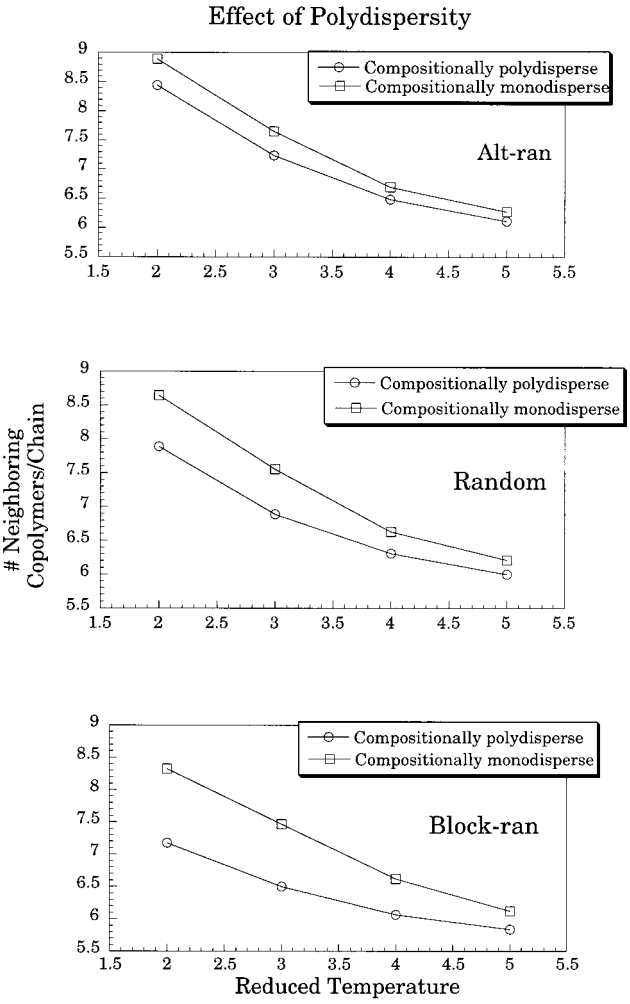

Figure 2. Average number of neighboring copolymer monomers per chain for the three different sequence distributions of the copolymer. Note the large difference in the block-ran structure that does not exist in the alt-ran copolymer.

Figure 2 provides the first insight into the effect of compositional polydispersity on the ability of a copolymer to compatibilize a polymer blend. This figure shows plots of N versus reduced temperature for a compositionally monodisperse copolymer and a similar compositionally polydisperse sample for each sequence distribution, block-ran (Px = 0.5), random (Px = 0.0), and

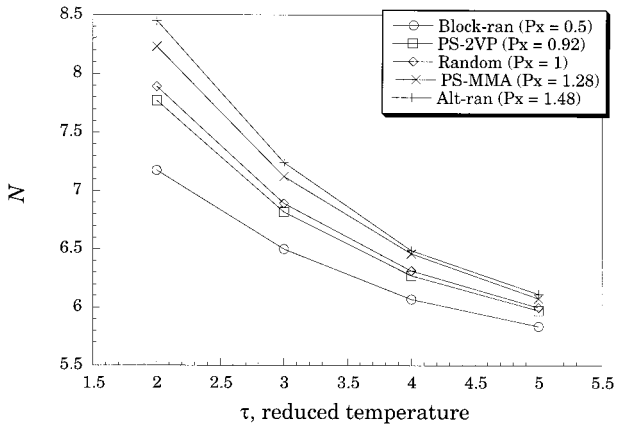

Figure 3. *N* vs reduced temperature for the copolymers with compositional polydispersity. The trend with sequence distribution verifies that sequence distribution is more important than compositional polydispersity in determining the ability of a copolymer to compatibilize a polymer blend.

alt-ran (Px = 1.5). These plots show that, regardless of sequence distribution, increasing the polydispersity of composition in the copolymer improves the ability of that copolymer to modify the interface. However, the extent of modification is dependent on the sequence distribution. The alt-ran copolymer, which was classified as a poor compatibilizer from previous results and Figure 1, increases the number of neighboring polymers that are homopolymers only slightly (<0.5 monomers per chain at $\tau = 2.0$). However, the addition of compositional polydispersity allows the blocky copolymer to more substantially mix with the homopolymer, to the extent that there are 1.2 more neighboring homopolymer monomers per chain at $\tau = 2.0$. Thus, the increase in the extent of mixing due to compositional polydispersity is more than 100% greater for the blocky copolymer than for the more alternating structure.

Figure 3 also provides insight into the relative importance of the sequence distribution and compositional distribution in this process. Figure 3 shows a plot of N versus τ for all of the compositionally polydisperse samples. Inspection of this plot shows two important trends: first that the sequence distribution effect that is observed in the monodisperse samples is also observable in the polydisperse sample; to wit that the lower the Px of the copolymer, the better compatibilizer it is. This includes the two samples that mimic the experimental systems of poly(styrene-*ran*-2-vinylpyridine) and poly(styrene-*ran*- methyl methacrylate) in the model polydisperse systems. Second, the data of this plot predicts that a random PS-2VP copolymer will be a better compatibilizer than PS-MMA, in agreement with the experimental evidence.[17−19,31]

Thus, the Monte Carlo simulation results indicate that incorporating compositional polydispersity into a compatibilizer improves its efficiency at compatibilization. However, the results presented above imply that sequence distribution effects in copolymers are more important than compositional distribution effects. This conclusion is supported by the observation that the poor adherents (alt-ran copolymers) do not improve much with an increase in compositional polydispersity while those that have shown promise, blocky copolymers, substantially improve with an increase in the compositional polydispersity of the sample. Additionally, a clear dependence on the sequence distribution of the copolymer's ability to compatibilize an interface is seen in the polydisperse samples. Thus, to compatibilize a biphasic polymer blend effectively, a blocky copolymer should be utilized as an interfacial modifier. Additional compositional polydispersity will further improve the interfacial modification process.

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References and Notes

(1) Mixed Surfactant Systems; Holland, P. M., Rubingh, D. N., Eds.; ACS Books: Washington, DC, 1992; Vol. 501.
(2) Rodriguez, C. H.; Scamehorn, J. F. *J. Surfactants Deterg.* **1999**, *2*, 17.
(3) Schulz, P. C.; Minardi, R. M. *Colloid Polym. Sci.* **1998**, *276*, 278.
(4) Morgan, M. E.; Uchiyama, H.; Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *Langmuir* **1994**, *10*, 2170.
(5) Abe, M.; Mizuguchi, K.; Kondo, Y.; Ogino, K.; Uchiyama, H.; Scamehorn, J. F.; Tucker, E. E.; Christian, S. D. *J. Colloid Interface Sci.* **1993**, *160*, 16.
(6) Abe, M.; Tokuoka, Y.; Uchiyama, H.; Ogino, K.; Scamehorn, J. F.; Christian, S. D. *Colloids Surf.* **1992**, *67*, 37.
(7) Isreals, R.; Jasnow, D.; Balazs, A. C.; Guo, L.; Sokolov, J.; Rafailovich, M. J. *J. Chem. Phys.* **1995**, *102*, 8149.
(8) Lyatskaya, Y.; Gersappe, D.; Balazs, A. C. *Macromolecules* **1995**, *28*, 6278.
(9) Lyatskaya, Y.; Jacobson, S. H.; Balazs, A. C. *Macromolecules* **1996**, *29*, 1059.
(10) Lyatskaya, Y.; Balazs, A. C. *Macromolecules* **1996**, *29*, 7581.
(11) Lyatskaya, Y.; Gersappe, D.; Gross, N. A.; Balazs, A. C. *J. Chem. Phys.* **1996**, *100*, 1449.
(12) Pickett, G. T.; Jasnow, D.; Balazs, A. C. *Phys. Rev. Lett.* **1996**, *77*, 671.
(13) Gersappe, D.; Irvine, D.; Balazs, A. C.; Guo, L.; Rafailovich, M.; Sokolov, J.; Schwarz, S.; Peiffer, D. *Science* **1994**, *265*, 1072.
(14) Gersappe, D.; Balazs, A. C. *Phys. Rev. E* **1995**, *52*, 5061.
(15) Yeung, C.; Balazs, A. C.; Jasnow, D. *Macromolecules* **1992**, *25*, 1357.
(16) Brown, H. *Annu. Rev. Mater. Sci.* **1991**, *21*, 463.
(17) Dai, C.-A.; Dair, B. J.; Dai, K. H.; Ober, C. K.; Kramer, E. J.; Hui, C.-Y.; Jelinski, L. W. *Phys. Rev. Lett.* **1994**, *73*, 2472.
(18) Sikka, M.; Pellegrini, N. N.; Schmitt, E. A.; Winey, K. I. *Macromolecules* **1997**, *30*, 445.
(19) Kulasekere, R.; Kaiser, H.; Ankner, J. F.; Russell, T. P.; Brown, H. R.; Hawker, C. J.; Mayes, A. M. *Macromolecules* **1996**, *29*, 5493.
(20) Creton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. *Macromolecules* **1992**, *25*, 3075.
(21) Washiyama, J.; Kramer, E. J.; Creton, C. F.; Hui, C.-H. *Macromolecules* **1994**, *27*, 2019.
(22) Lee, Y.; Char, K. *Macromolecules* **1994**, *27*, 2603.
(23) Kramer, E. J.; Norton, L. J.; Dai, C.-A.; Sha, Y.; Hui, C.-Y. *Faraday Discuss.* **1994**, *98*, 31.
(24) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.
(25) Brown, H. *J. Mater. Sci.* **1990**, *25*, 2791.
(26) Creton, C.; Brown, H. R.; Deline, V. R. *Macromolecules* **1994**, *27*, 1774.
(27) Sha, Y.; Hui, C.-Y.; Ruina, A.; Kramer, E. J. *Macromolecules* **1995**, *28*, 2450.
(28) Brown, H. R. *Macromolecules* **1989**, *22*, 2859.
(29) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, *26*, 4164.
(30) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* **1991**, *24*, 1864.
(31) Dai, C.-A.; Osuji, C. O.; Jandt, K. D.; Dair, B. J.; Ober, C. K.; Kramer, E. J.; Hui, C.-Y. *Macromolecules* **1997**, *30*, 6727.
(32) Shull, K. R.; Kramer, E. J.; Hadziioannu, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(33) Dai, K. H.; Kramer, E. J.; Shull, K. R. *Macromolecules* **1992**, *25*, 220.
(34) Lee, M. S.; Lodge, T. P.; Macosko, C. W. *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 2835.
(35) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 79.

(36) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1269.
(37) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2209.
(38) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 775.
(39) Fayt, R.; Jérôme, R.; Teyssié, Ph. *Makromol. Chem.* **1986**, *187*, 837.
(40) Dadmun, M. D. *Macromolecules* **1996**, *29*, 3868.
(41) Dadmun, M. D. In *Computational Studies, Nanotechnology, and Solution Thermodynamics of Polymer Systems*; Dadmun, M. D., Noid, D. W., Sumpter, R. G., Van Hook, W. A., Melnichenko, Y., Eds.; Kluwer Academic: New York, 2000.
(42) Waldow, D.; Dadmun, M. D. *Phys. Rev. E* **1999**, *60*, 4545.
(43) Dadmun, M. D. *Mater. Res. Soc. Symp. Ser.* **1997**, *461*, 123.
(44) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(45) Macosko, C. W.; Guegan, P.; Khandpur, A.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(46) Guegan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993.
(47) Milner, S. T.; Xi, H. *J. Rheol.* **1996**, *40*, 663.

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