

## Glass Transition Behavior of Latex Interpenetrating Polymer Networks Based on Methacrylic/Acrylic Pairs

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### Synopsis

Interpenetrating polymer networks (IPN's) of poly(alkyl methacrylates) and poly(alkyl acrylates) have been synthesized in latex form. Dynamic mechanical spectroscopy studies on these materials revealed extraordinarily broad glass transition regions, illustrating the semicompatible nature of these materials. In a true synergistic effect, the value of  $\tan \delta$  remains high and nearly constant over a broad temperature range for select compositions, emphasizing their potential value in noise and vibration damping applications. Compositionally identical latex IPN pairs were prepared by slow and rapid addition of monomer. The mechanical behavior of the resulting materials was similar and can be explained in terms of the core-shell model. A 50/50 isomeric homologous series of compositions was examined. After taking into account the relative difference between the glass transition temperatures of the methacrylic/acrylic pair, no substantial change in compatibility was noted throughout the series. Because the acrylic monomer II is roughly equally solvated by both the previously formed methacrylic polymer I and the nascent acrylic polymer II, extensive polymer I/polymer II mixing is encouraged, and sharp phase separation discouraged in these materials.

### INTRODUCTION

Interpenetrating polymer networks, IPN's, a unique class of polymer blends, are synthesized by swelling network polymer I with monomer II plus crosslinker, and polymerizing in situ.<sup>1-8</sup> The resulting two-component system tends to phase separate, as do other blend-type materials,<sup>9-12</sup> but the double network structure restricts the resulting domain size and prevents gross phase separation and macroscopic layering effects. The tendency of polymer I and II to phase separate, of course, depends upon their free energy of mixing.<sup>13,14</sup> When the two polymers are similar, the special case of semicompatibility arises, where mixing is extensive but still incomplete.

Previous studies on IPN's have centered on sequential IPN's prepared as macroscopic materials in thin sheet form, employing ultraviolet light to photo-initiate the polymerizations. More recently, interest has also encompassed latex IPN's,<sup>15</sup> a microform prepared by emulsion polymerization. In the latter case, except for occasional grafting, each latex particle may be considered to be composed ideally of two molecules, and

the resulting film cast from the latex to comprise a more or less regular array of such double networks.

An important aspect of emulsion polymerization involves the so-called core-shell effect,<sup>15-17</sup> important in both homopolymer and blend emulsion<sup>18</sup> systems. The development of a core-shell morphology depends primarily on the mixing statistics arising from the semiforbidden entry of polymer loops and ends in the aqueous phase,<sup>15</sup> and also on several subtle points to be discussed below.

While semicompatible polymer blends and grafts generally are of interest for their noise and vibration damping characteristics,<sup>19-21</sup> the latex IPN's offer greater control over morphologic details important to damping. The present paper will discuss the synthesis and temperature-dependent mechanical behavior of a series of latex IPN's prepared from methacrylates and acrylates, with emphasis on their broad temperature range of damping. In addition, several of the IPN pairs to be discussed are chemically isomeric, and thus very similar chemically. By examining the homologous series of such isomeric pairs, insight can be gained into the two-phase structure apparent in all of these materials.

## EXPERIMENTAL

The methacrylate/acrylate latex IPN's were synthesized by a modified emulsion polymerization technique discussed previously.<sup>15</sup> Briefly, to 250 ml deionized, deaerated, stirred water at 60°C, 50 ml 10% (w/v) lauryl sodium sulfate solution was added, followed by 5 ml 5% (w/v) potassium persulfate solution. The calculated quantity of monomer I (to a total of 30% solids, see below) containing 0.4% tetraethylene glycol dimethacrylate (TEGDM) as a crosslinking agent was added at a rate of approximately 2 ml/min. When the first monomer was completely added, a minimum time of 1 hr was allowed for completion of the polymerization. Then a second 5 ml of the potassium persulfate solution was added, but no new soap, followed by monomer II, which also contained 0.4% TEGDM. The same reaction conditions as above were followed. This method is referred to as the dropwise addition method.

When bulk addition of monomer was used, the procedure was to add all the monomer plus crosslinking agent to the flask before adding the potassium persulfate free-radical source. Although temperature control was more difficult, the maximum deviation in temperature from 60°C was usually 2°C. Total polymer concentration of the completed latexes for both modes of polymerization was about 30% solids. In all cases, the finished latexes were cast as films and were dried for at least one week to obtain samples suitable for dynamic mechanical spectroscopy (DMS) studies.

Several pairs of polymers were formed into latex IPN's. The individual polymers and abbreviations employed are shown in Table I, along with their literature glass temperatures.<sup>22</sup> As in previous papers from this

TABLE I  
Polymers, Abbreviations, and Glass Transitions

Polymer	Abbreviation	Glass transition, °K <sup>a</sup>
Poly(ethyl acrylate)	PEA	249
Poly( <i>n</i> -propyl acrylate)	PnPA	225
Poly( <i>n</i> -butyl acrylate)	PnBA	218
Poly( <i>n</i> -amyl acrylate)	PnAmA	—
Poly( <i>n</i> -hexyl acrylate)	PnHxA	216
Poly(methyl methacrylate)	PMMA	378
Poly(ethyl methacrylate)	PEMA	333
Poly( <i>n</i> -propyl methacrylate)	PnPMA	308
Poly( <i>n</i> -butyl methacrylate)	PnBMA	293
Poly( <i>n</i> -amyl methacrylate)	PnAmMA	268

<sup>a</sup> From ref. 22.

laboratory, the first-mentioned polymer constitutes the polymer first synthesized, in this case the seed latex.

The DMS portion of the investigation employed a Rheovibron direct-reading viscoelastometer, Model DDV-II (Vibron, manufactured by the Toyo Measuring Instrument Co., Ltd., Tokyo, Japan). The temperature range investigated included from  $-100^{\circ}\text{C}$  to  $+100^{\circ}\text{C}$ , with a heating rate of approximately  $1^{\circ}\text{C}$  per minute, and the vibration frequency employed was 110 Hz. As per instrumental requirements, the sample dimensions were of the order of  $10^{-2} \times 10^{-1} \times 1.5 \text{ cm}^3$ . The quantities  $E'$  and  $E''$ , representing the storage and loss modulus, respectively, and  $\tan \delta$ , which equals  $E''/E'$ , were reported. The quantity  $\delta$  is the phase angle between  $E'$  and  $E''$ , considered as in phase and out-of-phase components, respectively,  $\tan \delta$  being a direct measure of the material damping property.

## RESULTS

The DMS behavior of the dropwise-synthesized latex IPN's will be compared with their bulk addition counterparts in Figures 1-4. The 25/75 PEMA/PnBA composition shown in Figure 1 exhibits a single broad glass transition spanning the range of  $-50^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ , with a slight suggestion of a shoulder in the  $E'$  curve. The quantity  $E''$  exhibits a nonsymmetrical maximum, while the quantity  $\tan \delta$  is found to be nearly constant over the range of  $-20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ . Figure 2 shows the bulk-addition counterpart composition. Surprisingly, the two materials exhibit very nearly identical mechanical behavior, within reasonable experimental error.

Figures 3 and 4 likewise show essentially identical results for the 75/25 PEMA/PnBA latex IPN composition. However, in Figures 3 and 4, the majority phase constitutes the less continuous phase,<sup>15</sup> resulting in a much flatter  $E'$  transition. The  $E''$  values have a low maximum near the glass

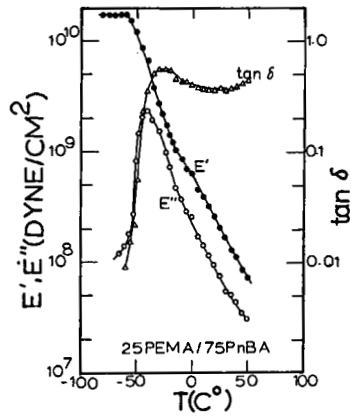


Fig. 1. Mechanical behavior of 25/75 PEMA/PnBA latex IPN. Dropwise addition of monomers I and II, consecutively. Note constancy of  $\tan \delta$  between  $-20^{\circ}\text{C}$  and  $+50^{\circ}\text{C}$ .

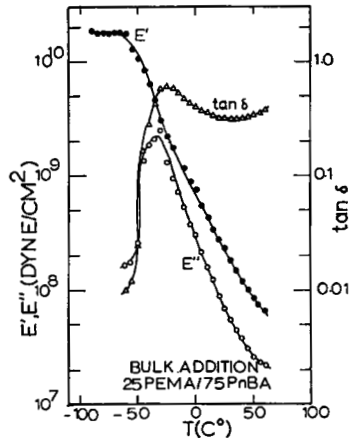


Fig. 2. Mechanical behavior of 25/75 PEMA/PnBA latex IPN. Bulk addition of monomers I and II, nonsecutively.

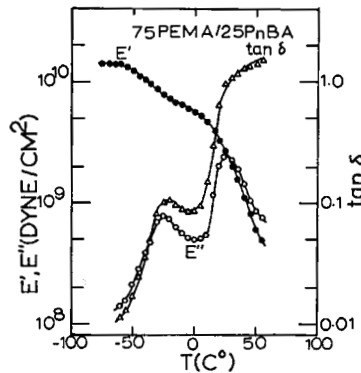


Fig. 3. Mechanical behavior of 75/25 PEMA/PnBA latex IPN, dropwise addition of monomer.

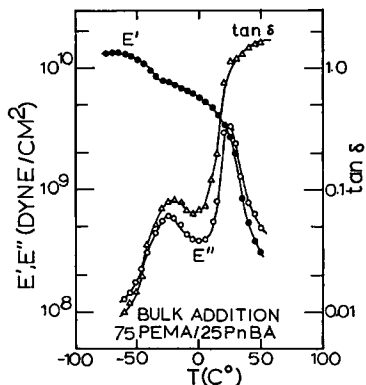


Fig. 4. The same materials as in Fig. 3, but bulk addition of monomers.

transition temperature of the PnBA material and a stronger one corresponding to the PEMA transition.  $\tan \delta$  also exhibits a low maximum near  $-20^\circ\text{C}$ , then rises off scale (1.7) at temperatures near the PEMA transition. When the quantity of the less continuous phase is small, as in the 10/90 PEMA/PnBA composition, the glass transition is relatively sharp, with a plateau in  $\tan \delta$  following a maximum, Figure 5.

The above PEMA/PnBA data illustrated the effects of compositional and synthetic detail in a nonisomeric pair. In the next several figures, we shall present a homologous series of 50/50 isomeric compositions beginning with PMMA/PEA and continuing through PnAmMA/PnHxA.

In all cases, the higher  $T_g$  methacrylate component constituted polymer I and the acrylate component, polymer II, as these products form films far easier than the inverse compositions. This qualitative result reflects the relative phase continuity of the materials, as discussed further below.

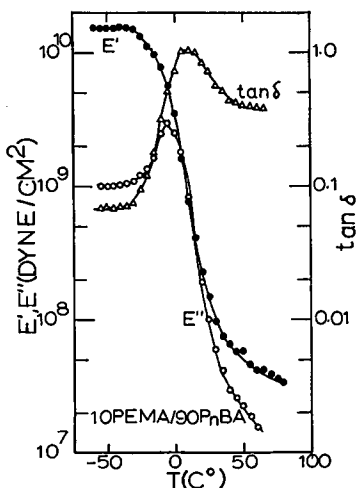


Fig. 5. This 10/90 PEMA composition yields excellent damping in the range just above  $0^\circ\text{C}$ , but poor damping elsewhere.

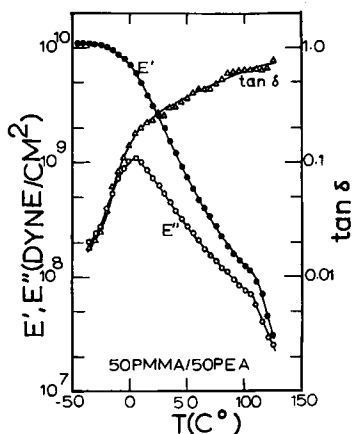


Fig. 6. With this 50/50 PEMA/PEA latex IPN isomeric pair, a broad transition is attained wherein  $\tan \delta$  probably reaches a broad maximum above  $150^\circ\text{C}$ .

The 50/50 PMMA/PEA composition in Figure 6 exhibits a single broad transition with a trace of a shoulder corresponding to the PMMA homopolymer transition.  $\tan \delta$  does not exhibit a maximum within the temperature range studied. (Although the individual latex particles are crosslinked, there is no interparticle crosslinking, and the material exhibits significant viscous flow at temperatures above the higher homopolymer glass transition temperature.)

The behavior illustrated in Figure 6 might well be compared with the sequential, sheet form IPN of the same composition, published elsewhere.<sup>7</sup> The most comparable sequential IPN (ref. 7, Fig. 4) results from swelling MMA monomer plus crosslinker and activator into crosslinked PEA. With such sequential IPN's, the first polymer, PEA, is then more continuous, whereas the second polymer is more continuous in latex IPN's.

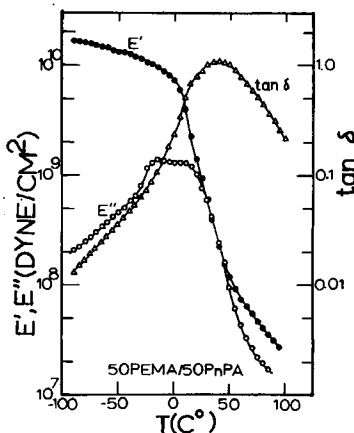


Fig. 7. Mechanical behavior of 50/50 PEMA/PnBA as a function of temperature.

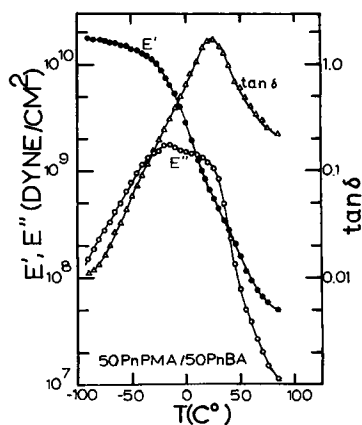


Fig. 8. Mechanical behavior of 50/50 PnPMA/PnBA.

In the present latex IPN's, PEA is the second polymer formed. The sequential form of the IPN also exhibits a single broad transition, but the shoulder is less pronounced or absent.

The next higher homolog, 50/50 PEMA/PnPA, is shown in Figure 7. A broad transition is observed, with  $\tan \delta$  exhibiting a single broad maximum and  $E''$  encompassing an unusual flat maximum. The next higher homolog, 50/50 PnPMA/PnBA, exhibits a similar behavior, Figure 8, except that the transition appears significantly sharper than that shown in Figure 7. Of course, as  $-\text{CH}_2-$  units are added to the side chains, both homopolymer glass transitions occur at lower temperatures<sup>22,23</sup>; however, the temperature difference between the transitions decreases slightly.

The trend to apparently sharper transitions continues for 50/50 PnBMA/PnAmA and 50/50 PnAmMA/PnHxA in Figures 9 and 10, respectively.  $\tan \delta$  presumably peaks above a value of 1.7, off scale of the Vibron.

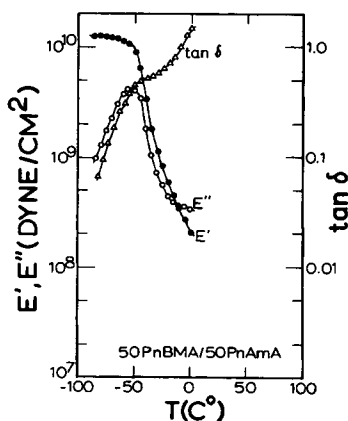


Fig. 9. Mechanical behavior of 50/50 PnBMA/PnAmA, showing  $\tan \delta$  going off scale at a value of 1.7.

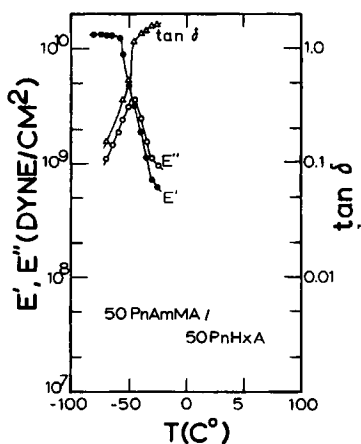


Fig. 10. Mechanical behavior of 50/50 PnAmMA/PnHxA latex IPN's as a function of temperature.

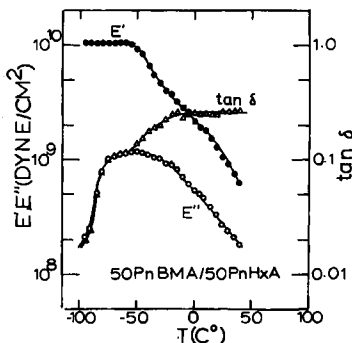


Fig. 11. The nonisomeric pair 50/50 PnBMA/PnHxA exhibits considerable incompatibility as evidenced from the broad glass transition behavior.

Through the homologous series of isomeric latex IPN pairs shown in Figures 6–10, the major point of note is that the transitions become relatively sharper for the higher homologs. However, the  $T_g$ 's of the components also drift together through the series, to be discussed below. The nonisomeric composition 50/50 PnBMA/PnHxA, Figure 11, by contrast still exhibits a very broadened glass transition behavior.

## DISCUSSION

The experimental portion of this paper included two series of experiments: (1) The damping and transition behavior of the PEMA/PnBA latex IPN's were examined as a function of composition ratio. (2) A series of isomeric homologs of 50/50 methacrylate/acrylate latex IPN's were examined as a function of increasing side chain length.



### Damping Behavior

The primary reason for examining semicompatible<sup>3,4,7</sup> latex IPN's relates to their good damping performance,<sup>24-27</sup> especially when coated onto vibrating or noise-emitting structures employing the principles of constrained layer damping. (The behavior of these materials in constrained layer damping applications will be published elsewhere.) The extensive but incomplete mixing of two polymers having widely differing glass transitions results in the only partly understood synergistic effect of good damping behavior over the entire temperature range between the two transitions. Qualitatively, the damping may be ascribed to the rubbing together of the partly mixed stiff and soft molecules.<sup>15</sup> In a broader sense, we do not believe that the broad transition observed experimentally is a single transition, but rather a continuous range of transition behavior brought about by a continuously varying range of compositions from nearly pure polymer I to nearly pure polymer II. The double network of the IPN imposes topological constraints, forcing the phases to remain small and in juxtaposition, and by not permitting extensive demixing. For example, mixtures of solutions of linear PEA and PMMA are cloudy, and eventually phase separate into two layers,<sup>28</sup> but the IPN's are clear, the phases being of the order of hundreds of ångströms in size<sup>7</sup> and very incompletely phase separated.

In Figure 1, for example, the glass transition spans the range of  $-50^{\circ}\text{C}$  to higher than  $+50^{\circ}\text{C}$ , corresponding to the published values of  $T_g$  for PEMA ( $+65^{\circ}\text{C}$ ) and PnBA ( $-55^{\circ}\text{C}$ ).<sup>22,23</sup> (Allowance should be made for frequency difference. Glass transitions are usually reported at 0.1 Hz; the present data are at 110 Hz. The quantity  $T_g$  usually increases  $6^{\circ}$  or  $7^{\circ}\text{C}$  per decade of frequency.<sup>23</sup>)  $\tan \delta$  remains relatively constant through most of this range near a value of 0.4-0.5. This value is lower than the peak values obtainable for the respective homopolymers ( $>1.0$ ), but the total area under the  $\tan \delta$ -temperature curve is significantly higher.<sup>15</sup> The constancy of  $\tan \delta$  apparently depends upon a balance of phase continuity and mass fraction. As illustrated in Figure 3, inverting the ratio of PEMA to PnBA results in very extensive  $\tan \delta$ -temperature behavioral changes. The arguments concerning continuity of both phases in IPN's, being discussed elsewhere,<sup>7,15,29</sup> will not be repeated at this time, since electron microscopy<sup>7</sup> and differential swelling techniques<sup>29,30</sup> yield more insight into this problem than DMS studies.

### Isomeric Homologs

Visual inspection of Figures 6-10 indicates a gradual sharpening of the glass transition as  $-\text{CH}_2-$  groups are added to the side chains. This sharpening is expressed in data columns 1 and 2 of Table II, where the maximum values of  $\tan \delta$  and the maximum slope ( $\log E'/T$ ) are shown for the homologous series. Also included are maximum slope values of the two crosslinked homopolymers, PEA and PMMA.<sup>31</sup> As alluded to

TABLE II  
Characterization of Glass Transition Behavior

50/50 IPN Pair	$\tan \delta$ , max	$(\log E')/T$ , max	$(\log E')/T$ , max, $\times \Delta T_g$
PMMA/PEA	0.9	0.020	2.6
PEMA/PnBA	1.0	0.038	4.1
PnPMA/PnBA	1.5	0.027	2.4
PnBMA/PnAmA	>1.7	0.055	(4.2)
PnAmMA/PnHxA	>1.7	0.042	2.2
PnBMA/PnHxA	0.25	0.015	1.2
PEA <sup>a</sup>	—	0.100	—
PMMA <sup>a</sup>	—	0.067	—

<sup>a</sup> From ref. 31.

previously, however, the glass temperatures of the homologous pairs are gradually coming together (see Table I). The maximum  $(\log E')/T$  slope can be normalized by multiplying each value by  $\Delta T_g$ , where  $\Delta T_g$  stands for the difference in glass temperatures of the two latex IPN components. The normalized values are shown in the third data column. The value for the 50/50 PnBMA/PnAmA was estimated taking 218°K as  $T_g$  for PnAmA. The values of the normalized maximum slopes now appears roughly constant, indicating no substantial change in compatibility throughout the series. However, an unexplained odd-even effect is apparent on inspection of the data. That the nonhomologous pair 50/50 PnBMA/PnHxA yields the lowest values of  $\tan \delta$  and the lowest maximum normalized slope indicates this material is less compatible than any of the homologous series. All of the latex IPN pairs have significantly lower maximum slopes than the PEA and PMMA homopolymers, suggesting the true extent of incomplete mixing in the latex IPN's.

In an earlier publication,<sup>6</sup> an expression was developed to analytically describe the extent of mixing of two incompatible polymers. The resulting incompatibility number varied between unity for no mixing and zero for the first appearance of a single broad transition. The incompatibility number, however, fails to describe the semicompatible range between the onset of one broad transition and one narrow transition indicating complete molecular mixing. The latter, rarely observed,<sup>9</sup> presumably would behave in a manner similar to a random copolymer preparation of the same overall composition.<sup>32</sup> The incompatibility number and the present analysis in Table II should be regarded as semiempirical first attempts to represent the extent of polymer blend mixing. What is still lacking is a comprehensive theory expressing the complete range of miscibility of the two polymers.

### Comparison of Dropwise and Bulk Modes of Addition

It is a widespread industrial practice to form core-shell morphologies during emulsion polymerization of graft-type polyblends by slow addition of monomer II to a polymer I seed latex.<sup>33</sup> The theory states that if diffu-

sion of monomer II within the growing latex particle is slower than the polymerization reaction, monomer II will tend to polymerize on the outer surface of the seed latex, forming a shell.<sup>34</sup> Williams pointed out<sup>34</sup> that bulk addition and slow addition methods should yield similar (but not identical!) morphologies, if for different reasons. Because loops or ends of polymer I protruding into the aqueous phase results in a thermodynamically unrealistic situation,<sup>15</sup> some type of core-shell structure may be expected in the general case. Comparison of Figure 1 with 2 and Figure 3 with 4 does substantiate the point: based on the DMS results, the morphologies are probably very similar indeed. However, in defense of industrial practice, it should be pointed out that slow addition of monomer allows better temperature control, and hence a more uniform product.

### Mixing Thermodynamics and Phase Structure

Cellular structures<sup>9,10</sup> in two-phase graft-type copolymers arise when monomer II is preferentially solvated by polymer II rather than polymer I. Then, as polymer II forms, the remaining monomer II tends to migrate out of polymer I into polymer II, resulting in large cellular domains of relatively pure homopolymer II, with cell walls comprised of polymer I.<sup>4,7,9,10</sup> Conversely, if the remaining monomer II thermodynamically preferred polymer I, more extensive molecular mixing would be encouraged. The extraordinarily broad glass transition temperature range of the methacrylate/acrylate IPN's illustrates the extensive but incomplete mixing that takes place in these systems and suggests the importance of thermodynamic quantities in determining the extent of molecular mixing and concomitant phase structures.

Table III displays the solubility parameters of the monomers and polymers examined herein.<sup>22</sup> For comparison, values for polystyrene and polybutadiene have also been included. The only complete literature data,

TABLE III  
Solubility Parameters of Monomers and Polymers<sup>22</sup>

Polymer	Solubility parameters, (cal/cm <sup>3</sup> ) <sup>1/2</sup>	
	Monomer	Polymer
PEA	8.6	9.35
PnPA	—	9.00
PnBA	8.8	8.80
PnAmA	—	—
PnHxA	—	—
PMMA	8.8	9.5
PEMA	8.3	8.95
PnPMA	—	8.8
PnBMA	8.25	8.75
PnAmMA	—	—
Polystyrene	9.3	9.10
Polybutadiene	7.1	8.5

unfortunately, are for the PMMA/PEA and PnPMA/PnBA polymer pairs. However, the available data illustrate the important point: The acrylic monomer II has no strong preference for either methacrylic polymer I or nascent acrylic polymer II. The PnPMA/PnBA solubility parameter values are identical, for example, and the other isomeric pair values are within experimental error of each other. The extensive mixing of the PEA/PMMA IPN has been previously documented by electron microscopy.<sup>7</sup>

Referring again to Table III, the complex cellular morphology in impact-resistant polystyrenes<sup>6,9,10</sup> can be explained by the relative closeness of the solubility parameters of the styrene/polystyrene pair (9.3, 9.10) compared to the styrene/polybutadiene pair (9.3, 8.5). This system exhibits the more commonly found feature of monomer II being preferentially solvated by its own polymer, favoring demixing and phase separation.

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### References

1. L. H. Sperling and D. W. Friedman, *J. Polym. Sci. A-2*, **7**, 425 (1969).
2. L. H. Sperling, D. W. Taylor, M. L. Kirkpatrick, H. F. George, and D. R. Bardman, *J. Appl. Polym. Sci.*, **14**, 73 (1970).
3. L. H. Sperling, H. F. George, Volker Huelck, and D. A. Thomas, *J. Appl. Polym. Sci.*, **14**, 2815 (1970).
4. L. H. Sperling, Volker Huelck, and D. A. Thomas, in *Polymer Networks: Structure and Mechanical Properties*, S. Newman and A. J. Chompff, Eds., Plenum, New York, 1971.
5. L. H. Sperling and R. R. Arnst, *J. Appl. Polym. Sci.*, **15**, 2317 (1971).
6. A. J. Curtius, M. J. Covitch, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, **12**, 101 (1972).
7. Volker Huelck, D. A. Thomas, and L. H. Sperling, *Macromolecules*, **5**, 340, 348 (1972).
8. L. H. Sperling and H. D. Sarge III, *J. Appl. Polym. Sci.*, **16**, 3041 (1972).
9. M. Matsuo, *Japan Plast.*, **2**, 6 (July, 1958).
10. G. E. Molau, Ed., *Colloidal and Morphological Behavior of Block and Graft Copolymers*, Plenum, New York, 1971.
11. S. L. Aggarwal, Ed., *Block Copolymers*, Plenum, New York, 1970.
12. R. F. Gould, Ed., *Multicomponent Polymer Systems*, Advances in Chemistry Series 99, American Chemical Society, 1971.
13. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
14. D. J. Meier, *J. Polym. Sci.*, **26C**, 81 (1969).
15. L. H. Sperling, Tai-Woo Chiu, C. P. Hartman, and D. A. Thomas, *Int. J. Polym. Mater.*, **1**, 331 (1972).
16. M. R. Grancio and D. J. Williams, *J. Polym. Sci. A-1*, **8**, 2617 (1970).
17. J. L. Gardon, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 241 (1973).
18. K. Kato, *Japan Plast.*, **2**, 6 (April 1968).
19. H. Mizumachi, *J. Adhesion*, **2**, 292 (1970).
20. H. Oberst, L. Bohn, and F. Lindhardt, *Kunststoffe*, **51**, 495 (1961).
21. H. Oberst et al., U.S. Pat. 3,547,757; 3,547,758; 3,547,759; 3,547,760; 3,547,755 (1970); 3,553,072; 3,554,885 (1971).
22. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1966.

23. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 23.
24. D. Ross, E. E. Ungar, and E. M. Kerwin, Jr., in *Structural Damping*, J. E. Ruzicka, Ed., ASME, New York, 1959.
25. A. G. Bodine, Jr., U.S. Pat. 3,169,881 (1965).
26. G. L. Ball and I. O. Salyer, *J. Acoust. Soc. Amer.*, **39**, 663 (1966).
27. H. Oberst et al., U.S. Pat. 3,547,759 (1970); 3,554,885 (1971).
28. L. H. Sperling, unpublished data.
29. L. H. Sperling and E. N. Mihalakis, submitted to the *J. Appl. Polym. Sci.*
30. R. E. Zapp, *Polym. Preprints*, **11**(1), 358 (1970).
31. Volker Huelck, Ph.D. Thesis, Lehigh University, 1971.
32. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960. pp. 78-83.
33. F. J. Hahn and J. F. Heaps, U.S. Pat. 3,256,233 (1966).
34. P. Keusch, J. Prince, and D. J. Williams, submitted to the *J. Macromol. Sci.*; P. Keusch and D. J. Williams, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 143 (1973); D. J. Williams, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 301 (1973).

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