

# Mechanical and Rheological Properties of Styrene/Acrylic Gradient Polymers

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## SYNOPSIS

A butyl acrylate monomer with a small amount of photosensitizer was diffused into a slightly crosslinked polystyrene matrix. After a certain swelling time, the diffusion gradient was either fixed (by rapid photopolymerization *in situ*) to form a gradient polymer or changed to form an interpenetrating polymer network (IPN), once thermodynamic equilibrium was achieved. Chemical compositions were determined by FTIR. Mechanical and rheological measurements were performed using a universal testing machine and dynamic rheometer, respectively. Impact properties were evaluated with a Falling Dart Impact Tester. Compared to the IPN materials, the gradient polymers exhibit higher moduli, considerable strain, and similar impact resistance. They are also able to retain plastic properties at higher temperatures. Differences in chemical structure of equivalent layers for gradient and IPN polymers yield such differences in properties. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years, the production of about 2 billion pounds of polymer blends per year in the United States was reported.<sup>1</sup> Furthermore, while the annual growth rate of the plastics industry was 2–4%, that of the polymer alloys and blends was 9–11%.<sup>2</sup> That production and growth rate has been based mainly on research made over the last two decades on multicomponent polymers. Scientific interest and the technical importance of polymer blends is due to several reasons: First, no new polymers need to be synthesized; in addition, based on thermodynamic studies of phase equilibria in multicomponent polymer systems, blending feasibility has become less obscure.<sup>2–4</sup> Besides, because of their heterogeneous nature, polymer blends lead to systems with two or more phases whose properties depend not only on the individual characteristics of the components, but also on the method of preparation.<sup>5–7</sup> The long-term

stability of the properties of such systems can noticeably be affected if the components have the tendency to phase-separate. Blend structure stability and low birefringence can be enhanced if phase separation is restricted to the microscopic level.<sup>8</sup> Furthermore, if the phases are interconnected, the morphology leads to a synergistic performance.<sup>6,7,9–11</sup> For that reason, slightly crosslinked interpenetrated polymer networks offer a good way of making stable products of better performance than that of copolymers.<sup>7,12</sup> Even, further, if a continuous change in the composition structure of interpenetrated macromolecules is achieved throughout a polymer blend, a continuous change in individual properties would be expected.<sup>13</sup> The spatial gradient formed in that way opens up the possibility of making polymer systems with tailor-made properties for different applications.<sup>7,9,10,13–16</sup>

One method to prepare such structures is by sequential polymerization. A convenient profile throughout the sample can be reached by diffusing a monomer into a polymer matrix (polymer I) and then fixing the profile by photopolymerization “*in situ*” (forming polymer II).<sup>7,9</sup> In general, such an approach overcomes the thermodynamic incompat-

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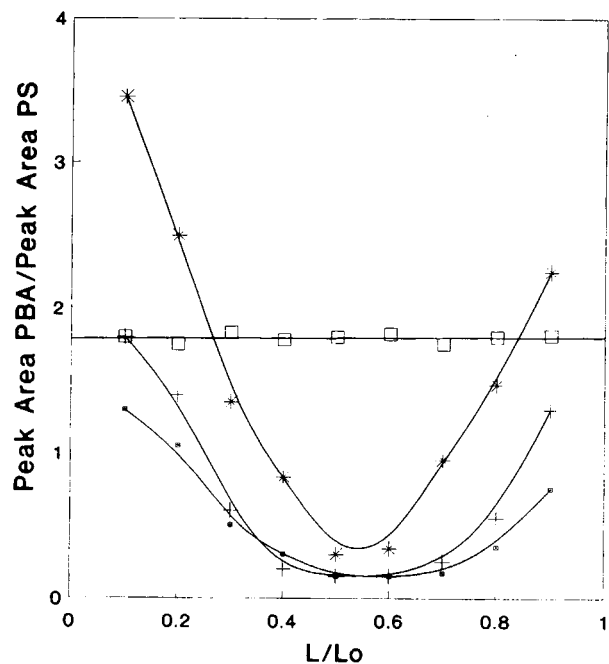
ibility of polymer blends.<sup>6</sup> In this work, the mechanical properties of samples possessing a parabolic gradient were evaluated. As a reference, a system with a constant composition of the same components (interpenetrating polymer network, IPN) was also prepared and tested. The wide difference in glass transition temperature and chemical structure of the components allows the study of the toughening effect and the chemical analysis of the second component.

## EXPERIMENTAL

Industrial-grade styrene and butyl acrylate monomers were purified by vacuum-distillation. Benzoin isobutyl ether, divinylbenzene, and ethylene glycol dimethacrylate were purchased from Aldrich Chemical Co. The benzoin derivative was used as a photosensitizer, while the other two reagents played the role of crosslinking agents for styrene and butyl acrylate monomers, respectively, having chosen each agent due to a close monomer-agent chemical composition. For each photopolymerization, the respective monomer was first mixed with 0.7 mol % of the crosslinking agent and 0.7 mol % of the sensitizer. Polystyrene plates were first prepared, using ultraviolet radiation for 48 h. After removing the unpolymerized monomer in a vacuum oven at 50°C, the plates were ready for the diffusion stage. A butyl acrylate mixture was diffused at 54°C through both sides of the matrix for different time periods to attain different global compositions. To prepare the gradient polymers, a second photopolymerization was carried out immediately after diffusion. IPNs were obtained by letting the diffused monomer equilibrate in the sample before starting the second polymerization.<sup>7,9</sup> The profiles were established by FTIR using the area ratio for the C=O absorbance peak of acrylate at about 1700 cm<sup>-1</sup> ( $A_1$ ) and the aromatic absorbance peak for the polystyrene at 1600 cm<sup>-1</sup> ( $A_2$ ). That ratio was used directly to avoid calibration errors with slightly crosslinked polymers. For the analysis, the samples were machined off layer by layer. Then, after grinding the sample, a KBr disk for each layer was prepared with a press. Figure 1 shows the gradient profiles for different butyl acrylate content, along with an IPN. Gravimetric measurements were used to obtain the average content of the second component in each blend.

Stress-strain experiments were carried out with a universal testing machine (United FM) equipped with a temperature chamber. The tests were carried out at  $4.23 \times 10^{-3}$  cm/s crosshead speed.

Rheological measurements using a dynamic



**Figure 1** Experimental profiles of IPN and gradient polymers of PS/PBA. Monomer diffused at 54°C. Nos. indicate average % of PBA content: (■) G10; (+) G20; (\*) G30; (□) IPN30.

rheometer (Rheometrics RDS II) were performed using a torsion bar fixture. Storage modulus and loss tangent were measured at 1 rad/s over a 20–140°C temperature range. Storage modulus as a function of frequency (10–100 rad/s) were evaluated at several temperatures. A falling dart impact tester (CSI) was used to characterize impact resistance of the material at room temperature.

## RESULTS AND DISCUSSION

To achieve the gradient compositions, monomer sorptions were maintained at 54°C. The diffusion curve is shown in Figure 2; initially, case II of transport behavior can be expected due to a high mass-transfer barrier; when the surface concentration in rubbery content increases, the sorption approaches Fickian diffusion.<sup>17</sup> That is why a sigmoidal curve (with slow initial diffusion) is obtained if Fick's second law is applied to estimate the amount of diffusive taken up by the polymer matrix as a function of time. Based on that equation,<sup>18</sup> using weight uptake measurements, an initial diffusion coefficient of  $1.1 \times 10^{-7}$  cm<sup>2</sup>/s was obtained, while at 1/2 of the mass equilibrium absorption, a value of  $6.43 \times 10^{-7}$  cm<sup>2</sup>/s shows how the diffusion coefficient

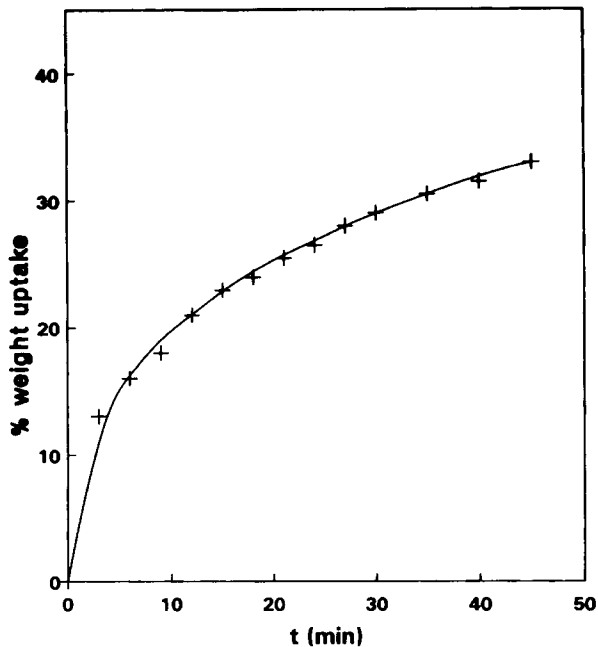


Figure 2 Experimental sorption curve for butyl acrylate in polystyrene at 54°C.

increases as the Fickian behavior is reached. For specific diffusion studies, the modeling of case II can be approximated by adding stress terms to the Fickian flux<sup>19</sup> or by taking into consideration stress relaxation in the polymer as diffusion is taking place.<sup>17</sup>

As a base line for comparison with the blends, the mechanical properties of the pure polystyrene (PS) were also evaluated. These are shown on Figures 3 and 4 where PS is seen to behave as a hard and brittle material at 40 and 60°C. The inclusion of poly(butyl acrylate) (PBA) as a rubbery component into the glassy matrix should produce a toughening effect in the material.<sup>6,20</sup> On such matter, it can be observed in Figure 3 that the (29%) IPN blend shows a plasticlike behavior, presenting a greater toughening effect than does the gradient blend of similar PBA content. However, it starts to "lose modulus" more notoriously than does the gradient polymer. In Figure 4, all the gradient materials show a toughening effect while still maintaining a high modulus at 60°C. A 1.62 value was found for the GRAD/IPN modulus ratio with similar PBA content. A sustained modulus for gradients even at "high" temperature has to be related to low rubbery content at the inner sample layers. Besides, by the "rich" rubbery content in the outer layers, the toughening effect is present even with low PBA content. That temperature response for the two types of blends studied in this work is in accordance with results reported for other systems.<sup>7,9</sup>

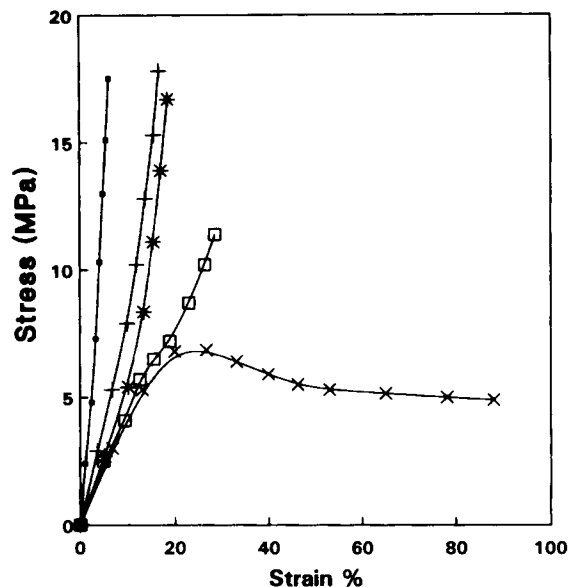


Figure 3 Stress-strain curves of IPN and gradient polymers of PS/PBA at 40°C. Nos. indicate average % of PBA content: (■) PS; (+) G12; (\*) G18; (□) G28; (×) IPN29.

In Figure 5, the variation of the Young's modulus can be observed as a function of average composition for the gradient polymers studied. Some very well known theoretical models have also been plotted to visualize the modulus behavior in terms of mor-

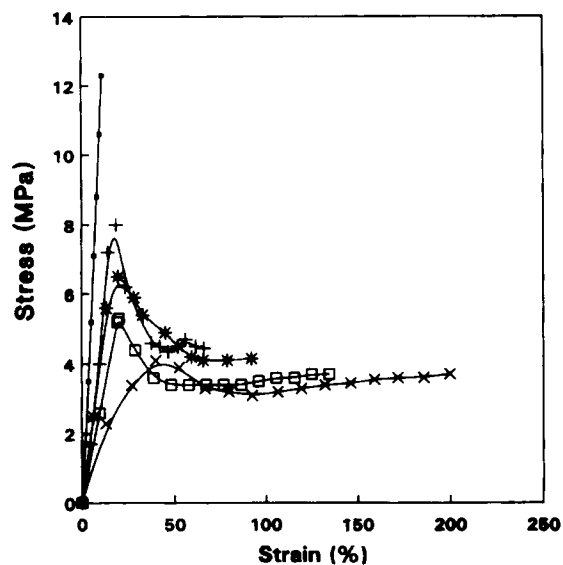
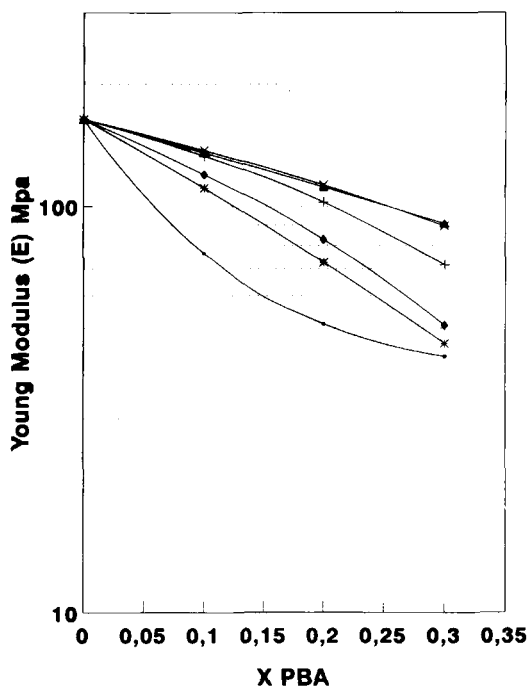


Figure 4 Stress-strain curves of IPN and gradient polymers of PS/PBA at 60°C. Nos. indicate average % of PBA content: (■) PS; (+) G12; (\*) G18; (□) G28; (×) IPN29.



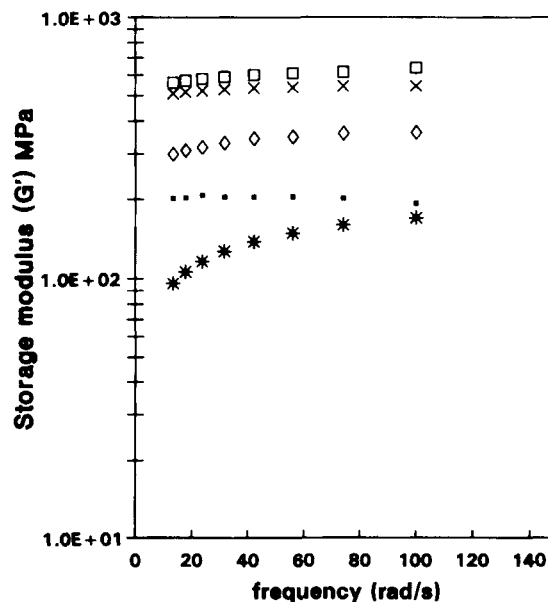
**Figure 5** Young's modulus as a function of gradient composition for the system PS/GPBA at 40°C: (×) Kerner model; (▲) Nielsen model ( $k_e = 2.5$ ); (◆) Nielsen model ( $k_e = 1.5$ ); (+) Budiansky model; (\*) Davies model; (■) experimental points.

phology. When one of the components is present at high concentration, usually there will be a continuous phase while the one at low concentration appears as a dispersed phase. For intermediate compositions, i.e., when either component has a volume fraction between 0.2 and 0.8, two continuous phases may exist. As the average compositions studied here vary between 0 and 30 wt % PBA, both of the above-mentioned cases may apply. The Kerner, Nielsen, and Budiansky models apply for the first case while the Davies model applies when two continuous phases are present. Looking at the models, it can be noticed that the ones considering dispersed PBA spheres in a continuous PS matrix produce the lines which occupy the more distant position from the experimental values. That stands for the self-consistent models, like the Kerner model,<sup>21</sup> and the Budiansky model, which considers an isotropic "composite."<sup>22</sup> That distant position also applies to the Nielsen model when using a 2.5 value for the Einstein coefficient ( $k_e$ ) which is used for dispersed spheres without slippage.<sup>23</sup> However, considering particles with a fiber geometry, being perpendicular to the tensile stress component ( $k_e = 1.5$ ), experimental data becomes closer at a 0.3 PBA weight fraction. The two-phase model (Davies model) is

the one which gives the closest value for the highest PBA content. In this model, the exponent " $n$ " equals to 1/5 indicates that the stiffer polymer carries more load than does the rubbery polymer when calculating the modulus.<sup>24</sup>

It is of interest to consider that for the gradient polymer the inhomogeneous composition throughout the samples may produce several morphological cases depending on the average composition. At low concentration of the diffused component, a sample will contain a dispersed phase near the surface and a single phase (the stiff polymer for this system) near the center. As the diffused component arrives at the center of the sample, a dispersed phase in a continuous matrix may exist and also near the surface at a "high" concentration of the second polymer (see Fig. 1) may even exist two continuous phases, as has been reported for IPNs. A microscopic study will help in clarifying the situation.<sup>25</sup>

Since mechanostatic measurements presented sample manipulation difficulties at higher temperatures, the difference in modulus at 80°C can better be observed with dynamic measurements in Figure 6. There, storage modulus as a function of frequency is shown at several temperatures for the equivalent gradient and IPN blends. At 40 and 80°C, once the curves reach a constant value, the Grad/IPN storage modulus ratio is about 3. At the low-frequency region, the moduli decrease due to higher molecular



**Figure 6** Comparison of storage modulus of IPN and gradient polymers of PS/30% PBA at different temperatures. Nos. indicate temperature (°C): (■) IPN40; (\*) IPN80; (□) G40; (×) G60; (◇) G80.

stress relaxation, especially at 80°C. In Figure 7, a 1.76 Grad/IPN loss modulus ratio can be observed at 40°C at low frequency, showing that the superiority in gradient storage modulus is not overcome by an excessive loss modulus value. Furthermore, as frequency increases, the loss modulus ratio decreases, showing both materials having similar energy losses at approximately 72 rad/s, when a dynamic load is applied. That is possible by the high rubbery content in the outer layers of the gradient polymer, as can be seen in Figure 1.

The storage modulus and tan delta at 1 rad/s for the blends of similar average composition, along with the results for the homopolymer, are presented in Figure 8. The slight crosslinking does not much affect the glass transition temperature ( $T_g$ ) of the polystyrene. Such transition for the PBA is not shown because the temperature range for the experiment is 20–135°C and the  $T_g$  of this polymer is around -40°C. The displacement of the peak to the left on both types of blends indicates some compatibility of the phases, the IPN being the one with the lower peak value. That can be explained in terms of the homogeneous composition throughout the sample. Nevertheless, to elucidate the compatibility difference between IPN and gradient materials, a further study including several concentrations and microscopic experiments is needed. Blending also gives

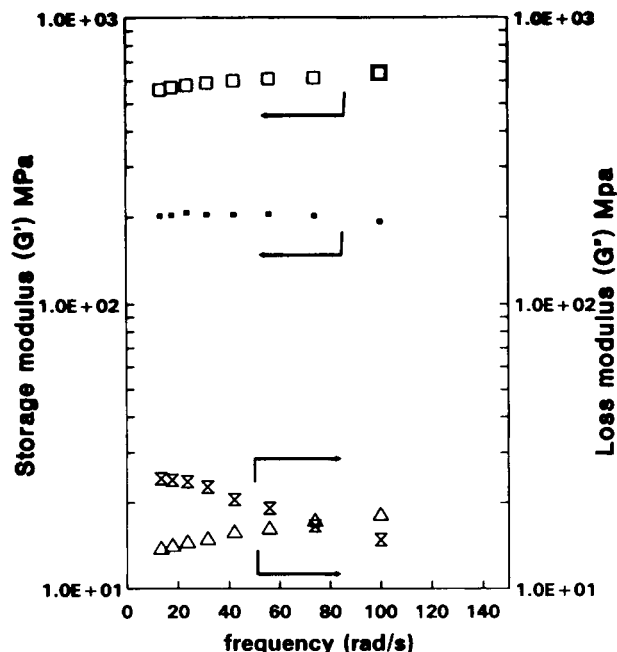


Figure 7 Comparison of storage and loss moduli of IPN and gradient polymers of PS/30% PBA as a function of frequency. Temperature 40°C. (□, ×) G; (■, △) IPN.

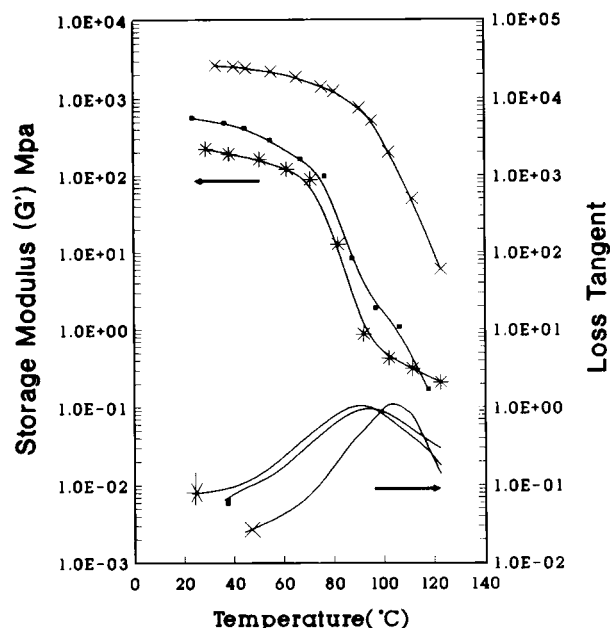


Figure 8 Comparison of storage modulus and loss tangent of PS, IPN, and gradient polymers of PS/30% PBA at 1 rad/s (×) PS; (\*) IPN; (■) G.

a wider damping region, as can be seen in the same figure. It is also important to note the lower specific loss of the gradient polymer on the plastic region, along with a higher value (compared to the IPN) on the rubbery region.

Impact results are given in Table I. There, the effect of having a high polymer concentration of a polymer possessing a very low glass transition temperature (PBA) near the surface can be noticed. The gradient material with an average of 28 wt % PBA gives a similar impact resistance to the value obtained with the IPN. It seems that such high rubbery concentration at the outer zone of the gradient material allows impact absorption, whereas the hard center layers give support to the material. A 3.8 value for the impact resistance ratio of the 10% gradient material over the homopolymer shows the synergis-

Table I Falling Dart Impact Values at 25°C

Material	Impact Resistance (J/m)
PS	4.05
G10%	15.50
G19%	19.53
G28%	21.93
IPN29%	21.40

Percentage indicates total PBA contents.

tic effect of this type of blend even with low average content of polymer with low  $T_g$ .

Since the homogeneous composition of the IPN is supposed to produce intermediate properties of the two components to a certain extent, the higher synergistic properties of the gradient polymers should be explained in terms of layer composition. As a uniform macroscopic strain was observed throughout the sample in tensile experiments, the stress has to be distributed in a nonuniform way. With the former premise, a sustained modulus would be possible if the harder layers bear greater stresses due to their higher modulus. A model for stress distribution using a stress-biased activated rate mechanism would result in an increased yielding as a result of force redistribution among the various bonds which support the load.<sup>26</sup>

## CONCLUSIONS

The gradient polymers present enhanced tensile properties, combining high modulus with considerable strains. They are able to retain high moduli at higher temperatures than can the IPN materials. They show compatibility comparable to that "obtained" by the IPN formulation. The gradient polymers are able to present an impact-resistant barrier by a high concentration of rubbery material at the surface.

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## REFERENCES

1. G. Odian, *Principles of Polymerization*, 3rd ed., Wiley-Interscience, New York, 1991.
2. L. A. Utracki, *Polymer Alloys and Blends*, Hanser, Munich, 1989.
3. P. G. de Gennes, *Scaling concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, 1979.
4. M. T. Rätzsch and H. Kehlen, *Prog. Polym. Sci.*, **14**, 1 (1989).
5. T. Inoue, H. Ishihara, H. Kawai, Y. Ito, and K. Kato, *Mechanical Behavior of Materials*, Society of Materials Science-Japan, Tokyo, 1972, Vol. 3, p. 149.
6. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*. Plenum, New York, 1976.
7. G. Akovali, K. Biliyar, and M. Shen, *J. Appl. Polym. Sci.*, **20**, 2419 (1976).
8. J. Greener, R. Kesel, and B. A. Contestable, *AIChE J.*, **35**, 449 (1989).
9. C. F. Jasso, S. D. Hong, and M. Shen, *Am. Chem. Soc. Adv. Chem. Ser. Multiphase Polym.*, **23**, 444 (1979).
10. G. C. Martin, E. Enssani, and M. Shen, *J. Appl. Polym. Sci.*, **26**, 1465 (1981).
11. T. Inoue, T. Ougizawa, O. Yasuda, and K. Miyasaka, *Macromolecules*, **18**, 57 (1985).
12. J. K. Yeo, L. H. Sperling, and D. A. Thomas, *Polym. Eng. Sci.*, **21**(11), 696 (1981).
13. M. Shen and M. B. Bever, *J. Mater. Sci.*, **7**, 741 (1972).
14. M. Dror, M. Z. Elsabee, and G. C. Berry, *J. Appl. Polym. Sci.*, **26**, 1741 (1981).
15. K. F. Mueller and S. J. Heiber, *J. Appl. Polym. Sci.*, **27**, 4043 (1982).
16. M. Pluta, P. Milczarek, and M. Kryszewski, *Colloid Polym. Sci.*, **265**, 490 (1987).
17. H. L. Frisch, *Polym. Eng. Sci.*, **20**, 1 (1980).
18. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic Press, New York, 1968.
19. R. W. Cox and D. Cohen, *J. Polym. Sci. Part B Polym. Phys. Ed.*, **27**, 589 (1989).
20. R. L. Bergen, Jr., *Appl. Polym. Symp.*, **7**, 41 (1968).
21. E. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
22. B. Budiansky, *J. Mech. Phys. Sol.*, **13**, 223 (1965).
23. L. E. Nielsen, *Predicting the Properties of Mixtures*, Marcel Dekker, New York, 1978, Chap. 3.
24. W. E. A. Davies, *J. Phys. D*, **4**, 318 (1971).
25. C. F. Jasso, E. Castellanos, N. Sánchez, and O. Laguna, to appear.
26. D. J. Matz, W. G. Guldmond, and S. L. Cooper, *J. Polym. Sci. Polym. Phys. Ed.*, **10**, 1917 (1972).

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