mixing process associated with the melting of the α-crystals. In this way the convex curve associated with the plot $(T_m^\circ - T_b)/T_m^\circ$ vs. ϕ_1^2 is transformed into a straight line with a slope nearly the same as that of the low-temperature data. Moreover, one can derive from eq 2 the renormalization factor for each composition and therefore predict the $\gamma + \gamma'$ crystalline function, which is found to increase with PVF_2 content, in qualitative agreement with the DSC observations of the same author.[3]

Conclusions

In conclusion, when applying eq 1 to multicrystalline blends, one should renormalize the volume fractions by excluding the volume associated with crystals not involved in the melting and mixing processes under consideration. Otherwise one can erroneously interpret the results and obtain an apparent composition dependence for the interaction parameter. These arguments offer a plausible explanation for the melting point depression effects observed by Morra et al.[3] in PVF_2/PMMA blends.

Registry No. Poly(vinylidene fluoride) (homopolymer), 24937-79-9; poly(methyl methacrylate) (homopolymer), 9011-14-7.

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Homopolymer-Induced Microphase Separation of a Homogeneous Diblock Copolymer

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Received September 19, 1983

In a series of recent papers, Hong and Noolandi[1] developed a theory for the phase behavior of various multicomponent polymer systems containing block copolymers. One of the novel features of the theory was the fact that it predicted a particular range (temperature and molecular weight) where a block copolymer by itself can be in a homogeneous state but the addition of a homopolymer will cause the mixture to form a heterogeneous morphology containing microdomains. The purpose of the present Note is to provide experimental verification of this predicted behavior.

Details of the synthesis and characterization of the polymers described here can be found in previous publications from this laboratory[2,3] and in the doctoral thesis of Torradas.[4] The homogeneous diblock copolymer was comprised of a 30 000 molecular weight block of 1,2-polybutadiene (>99% 1,2 addition) and a 100 000 molecular weight block of 1,4-polybutadiene (36% cis 1,4; 51% trans 1,4; 13% 1,2); this copolymer will be referred to by the code 30/100. The two homopolymers employed here were matched in microstructure with the individual block moieties of the copolymer; thus homopolymers are designated 30K 1,2B and 100K 1,4B. As in previous work, specimens of these polymers and various blends were prepared by spin casting[5] from cyclohexane. Specimens were lightly cross-linked with high-energy electrons to facilitate handling. Methods of contrast enhancement for transmission microscopy and techniques employed on our Rheovibron dynamic viscoelastometer have been reported in detail elsewhere.[2,6-8]

Table I
Location of Loss Tangent (3.5 Hz) Maxima for Homopolymers, Binary Homopolymer Blends, and the 30/100 Block Copolymer

specimen	% 30K 1,2B	% 100K 1,4B	% 30/100	$T(\tan\delta_{max})$, °C
30K 1,2B	100	0	0	9.1
blend 1	75	25	0	9.8 and −82.2
blend 2	50	50	0	13.6 and −77.3
blend 3	23	77	0	14.8 and −76.5
100K 1,4B	0	100	0	−79.1
30/100	0	0	100	−57.0

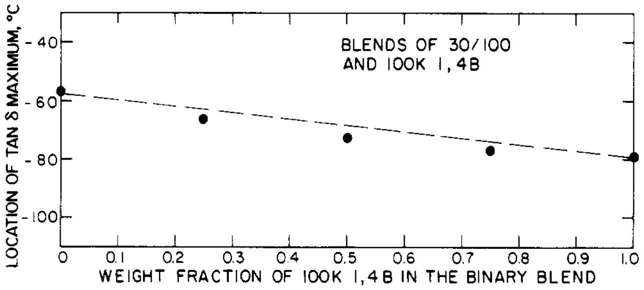

Figure 1. Temperature of the maximum in the loss tangent (3.5 Hz) for blends of 30/100 and 100K 1,4B.

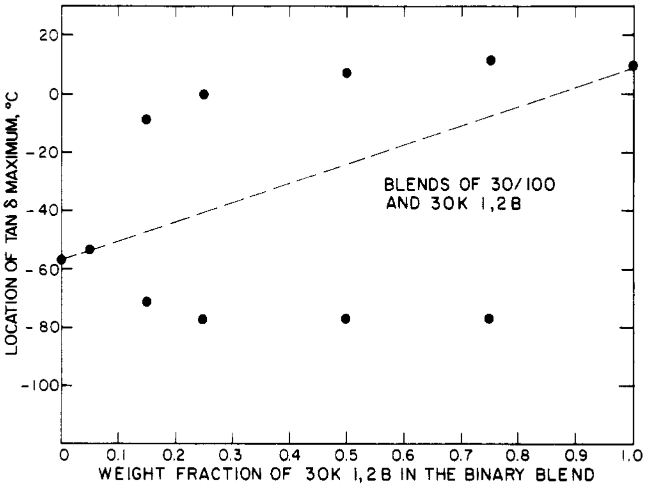

Figure 2. Temperature of the maximum in the loss tangent (3.5 Hz) for blends of 30/100 and 30K 1,2B.

Table I gives the locations of the loss tangent (3.5 Hz) peaks for the two homopolymers, the diblock copolymer, and the homopolymer blends. As discussed in more detail elsewhere,[2,4] the two homopolymers form two-phase blends (two damping peaks) over the entire range examined whereas the 30/100 block copolymer is homogeneous (a single, intermediate transition). When the 30/100 copolymer is blended with 100K 1,4B, homogeneous blends are obtained as indicated in the loss tangent data shown in Figure 1 and in the featureless transmission electron micrographs[4] not shown here. Thus the 100K 1,4B homopolymer does not induce microphase separation of the 30/100 diblock. In Figure 2, however, there is clear evidence that addition of an appropriate amount (around 10%) of the 30K 1,2B homopolymer results in the appearance of two loss tangent maxima. Transmission

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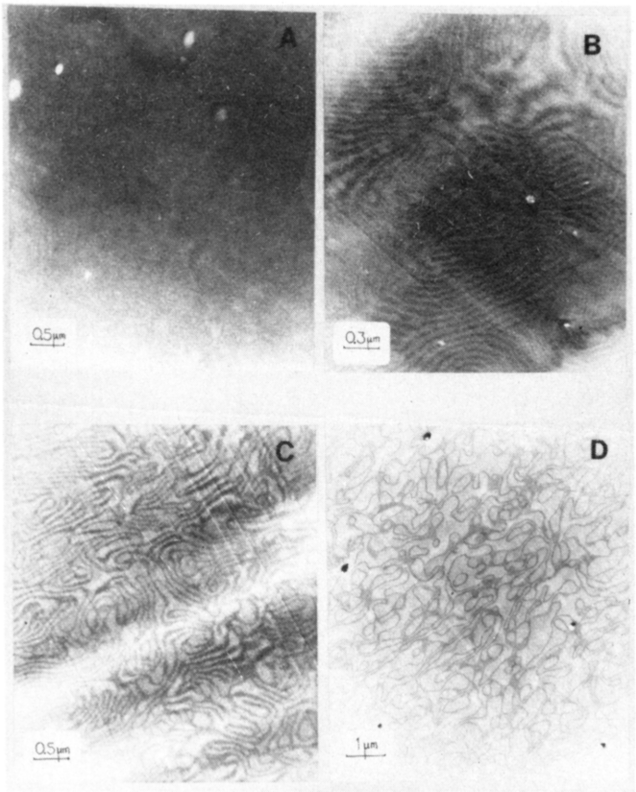

Figure 3. Transmission electron micrographs of (A) 30/100 copolymer; (B) blend of 75% 30/100 copolymer and 25% 30K 1,2B; (C) blend of 50% 30/100 copolymer and 50% 30K 1,2B; (D) blend of 25% 30/100 and 75% 30K, 1,2B.

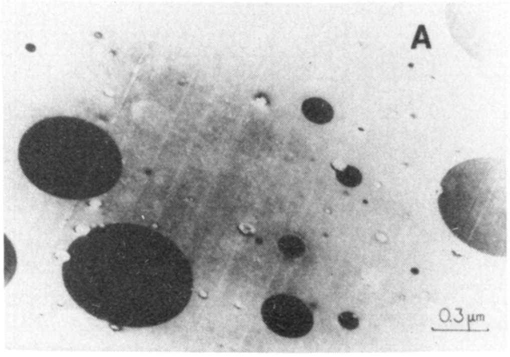

Figure 4. Transmission electron micrograph of a blend of 25% of the 30/100 copolymer and 75% of the high molecular weight 90K 1,2B.

electron micrographs of some of these blends are shown in Figure 3, showing clearly the homopolymer-induced microphase separation.

Although we have focused our attention here on the appearance of the heterogeneous morphology at low homopolymer contents, Hong and Noolandi[1] point out that continued addition of homopolymer should lead once again to homogeneous materials as the pure homopolymer composition is approached. At 75% homopolymer content this reversal had not yet occurred for the system examined here. We have no data at present in the region between 75 and 100% homopolymer. This region may be particularly interesting to study in the future since Leibler and co-workers[9] have predicted that phenomena similar to a critical micelle concentration should be seen in the region of very low diblock copolymer contents.

As a final point we note that the homopolymer-induced microphase separation documented above does not occur when the added homopolymer molecules are very much longer than the corresponding block of the copolymer. In this case two homogeneous phases are formed; the copolymer separates from the high molecular weight homopolymer but does not undergo microphase separation itself. Figure 4 shows an example of this type of behavior for a blend of the 30/100 copolymer with a 1,2-polybutadiene of molecular weight of 90000; the proportion of copolymer is 25 wt %. Hong and Noolandi[1] point out the possibility of this type of phase separation into two homogeneous phases in some of the many phase diagrams which they are able to construct from their general theory.

Acknowledgment. This research is supported by the Office of Naval Research.

Registry No. Poly(butadiene) (homopolymer), 9003-17-2.

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Glass Transition of Poly(tetrafluoroethylene)

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The glass transition of poly(tetrafluoroethylene) has been a subject of long controversy. Figure 1 shows a histogram of the various reported glass transition temperatures.[1–41] The temperatures 400, 260, 230, and 170 K were cited most often. A similar histogram was prepared earlier for polyethylene by Davis and Eby.[42] The latter also showed a broad scatter, indicating that different relaxations can confuse the assignment of the glass transition. In the last years we have been collecting a data bank on heat capacities of linear macromolecules.[43] On the basis of these heat capacity data it was possible to resolve the question of the glass transition of polyethylene. Polyethylene has a specifically broad transition, reaching from about 120 to 250 K, with a temperature of half-freezing of 237 K.[44] For poly(tetrafluoroethylene), not enough data were available at that time to do a similar analysis.

We report here about T_g of a low CF_2–CF_3 content copolymer as a model of poly(tetrafluoroethylene). DSC experiments at low temperature are described and interpreted together with literature data on crystalline poly(tetrafluoroethylene). It will be shown that the glass transition is quite broad. It reaches from about 160 to 240 K, with a midpoint of about 200 K. This agrees with most calorimetry data in Figure 1 and covers the suggested 170 and 230 K T_g's.

The measurements were carried out with a Standard Mettler TA 2000B low-temperature differential scanning calorimeter in the temperature range from 110 to 350 K at a heating rate of 10 K/min. The sample mass was about 30 mg. Calibration of the amplitude was done with aluminum oxide (sapphire). The sample was a slightly copolymerized poly(tetrafluoroethylene) [poly(tetrafluoro-

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