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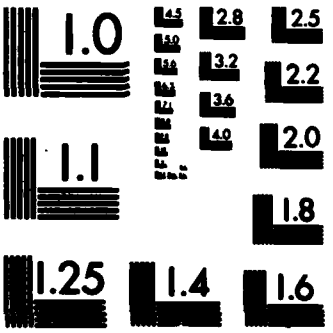

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Homopolymer-Induced Microphase Separation of a Homogeneous Diblock Copolymer

by

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August 29, 1983

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Binary polymer blends were prepared from a homogeneous diblock copolymer (1,2 polybutadiene-1,4 polybutadiene) and either of the corresponding homopolymers. Using dynamic mechanical testing and transmission electron microscopy it was shown that the 1,4B homopolymer and the copolymer form homogeneous blends; however, addition of 1,2B homopolymer induces a heterogeneous morphology when present in sufficient proportions. The nature of this homopolymer-induced microphase separation is compared to predictions of a recent theory of Hong and Noolandi.

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NOTE

Homopolymer-Induced Microphase Separation of a Homogeneous Diblock Copolymer

by

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In a series of recent papers, Hong & 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 comrpised 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 1 gives the locations of the loss tangent (3.5 Hz) peaks for the two homopolymers, the diblock copolymer and for 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 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 coworkers[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 90,000; the proportion of copolymer is 25 weight percent. 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.

Acknowledgement

This research is supported by the Office of Naval Research.

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Figure Legends

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.

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.

Table 1

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 (tanδmax) °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

FIG 1

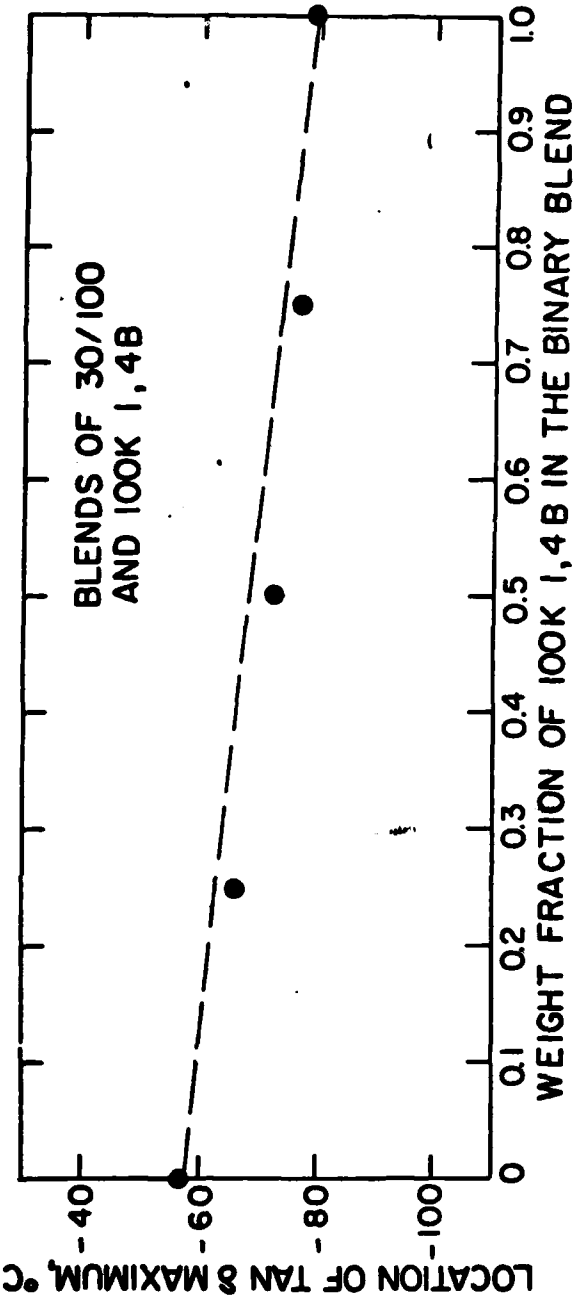
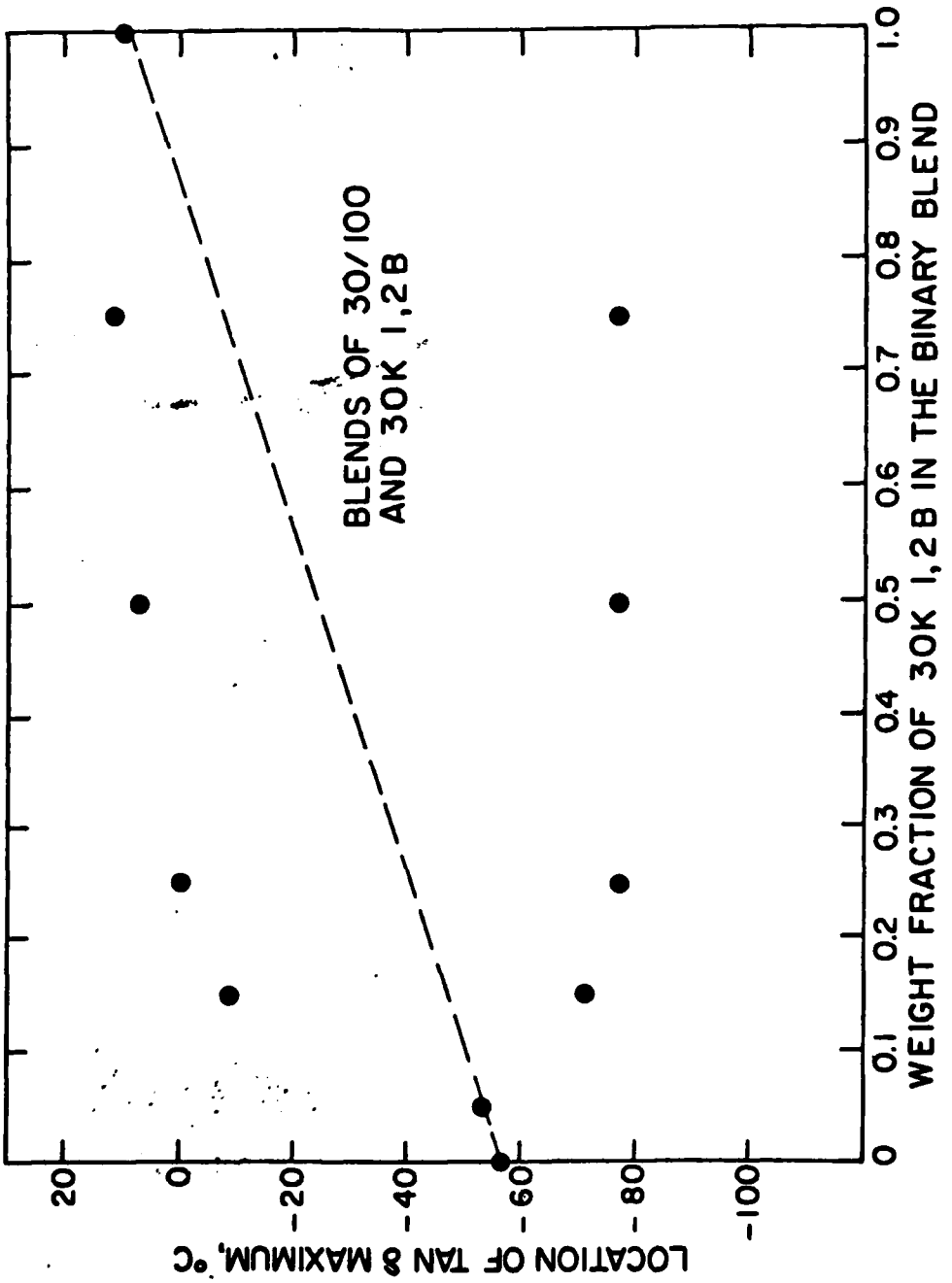
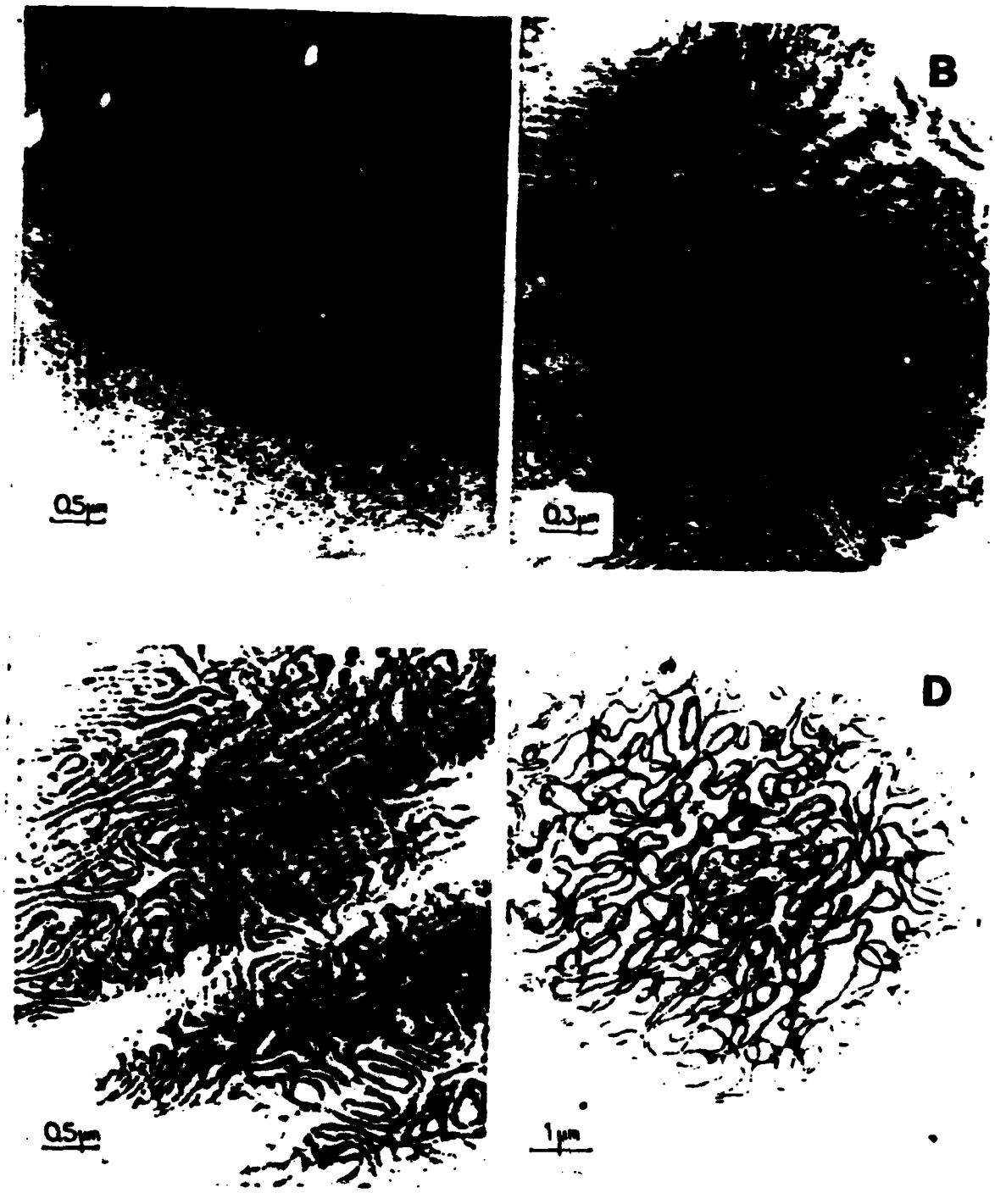

BLENDS OF 30/100
AND 100K 1,4B
LOCATION OF TAN δ MAXIMUM, °C
-40
-60
-80
-100
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
WEIGHT FRACTION OF 100K 1,4 B IN THE BINARY BLEND

FIG. 2


LOCATION OF TAN δ MAXIMUM, °C
20
0
-20
-40
-60
-80
-100
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
WEIGHT FRACTION OF 30K 1,2 B IN THE BINARY BLEND
BLENDS OF 30/100
AND 30K 1,2 B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