Amorphous–Crystalline Block Copolymer and Amorphous Homopolymer Blends. 1. A Preliminary Report

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Received October 26, 1992
Revised Manuscript Received February 23, 1993

Introduction. The particular chemical structure of a symmetrical diblock copolymer results in a lamellar microdomain morphology.[1] Adding a homopolymer to the diblock copolymer causes a morphological change from the lamellae to cylinders and finally to a disordered spherical phase.[2,3] It is interesting to extend these results to blends of diblock copolymers containing a crystallizable block. In such a blend the geometrical constraints existing because of the presence of the microphase separation may provide control over the order of the crystalline phase. The study of such a blend might lead to a fundamental understanding of molecular alignment, which is an important issue in designing new materials, such as polymer-matrix supported liquid crystalline displays or *nonlinear* optical polymers.

We recently synthesized a nearly symmetrical ethylene–propylene diblock copolymer (DEP). Since the polypropylene block is completely atactic and the polyethylene block is crystallizable, this block copolymer should be suitable for the type of investigation mentioned above. This paper presents our preliminary results from rheology, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM) measurements on this DEP diblock copolymer and its blends with atactic polypropylene (APP).

Experimental Section. The sample of poly(butadiene-*b*-2-methyl-1,3-pentadiene) was synthesized by first anionically polymerizing 1,3-butadiene by *n*-BuLi and then adding 2-methyl-1,3-pentadiene. The resulting diblock copolymer was hydrogenated using Pd/$CaCO_3$ as a catalyst to form the ethylene–propylene diblock copolymer (DEP). Two samples of atactic polypropylene (APP) with different molecular weights were prepared by hydrogenation of poly(2-methyl-1,3-pentadiene) according to the Fetters method.[4] IR and NMR measurements confirmed that the hydrogenation was complete (saturation $\approx 98\%$). Molecular weight, ethylene content, and the other molecular characteristics for these samples are listed in Table I, as well as the abbreviations used in this paper.

Two series of blends were prepared from APP190 and DEP113 and then APP15 and DEP113 by solution mixing using toluene as a solvent for DSC experiments and a mixture of toluene and 1,2,4-trichlorobenzene (1:1 in volume) for TEM work. The polymer solution was poured onto a water surface at 95 °C, and the solvent was evaporated. This procedure prevents inhomogeneity which results from the crystallization of polyethylene before the mixing of the two components. 1,2,4-Trichlorobenzene made the evaporation slower to give a smooth surface thin film necessary for TEM. All samples were dried and annealed at 150 °C for 3 days under vacuum before the measurement.

Storage (G') and loss (G'') moduli of DEP99 were measured as a function of frequency (ω) in the temperature range 100–206 °C and at 3% strain on a Rheometrics dynamic mechanical spectrometer, RDS 7700, with parallel-plate geometry. DSC measurements were carried out on a Du Pont differential calorimeter type 2000. Before the measurement the sample was annealed at 180 °C for 30 min and then cooled at 10 °C/min. The data obtained in the second cycle were used in the analysis. TEM measurement was done on a JEOL 100 CX TEMSCAN electron microscope in the bright field mode and with the filament potential of 100 kV. The specimens for TEM were quenched by liquid nitrogen after annealing at 150 °C for 3 days, so it is believed that the morphology in the melt state was "frozen". The specimens served for the measurement without staining.

Results and Discussion. It is essential to determine whether DEP forms a microdomain structure in the melt state. Small-angle X-ray scattering and TEM are not useful in this case because of the small electron density difference between the phases. Although not a direct method for determining morphology, rheological behavior has been shown to be related to the presence or absence of a microphase in block copolymers.[5]

Figure 1 presents master curves of the frequency dependence of G' and G'' for DEP99. Superposition appeared to be valid within experimental error,[6] indicating that no order–disorder transition takes place in this temperature range. The dynamic elastic and loss responses at low reduced frequencies exhibited a limiting frequency dependence of $G' \sim G'' \sim \omega^{0.5}$. This is in contrast to the typical terminal zone behavior of $G' \sim \omega^2$ and $G'' \sim \omega^1$ observed for homogeneous polymer systems. According to Bates,[5] the exponent of 0.5 for both elastic and loss moduli at the low-frequency limit is characteristic of the presence of an ordered microphase in diblock copolymers. Since the block copolymer is symmetric (see Table I), the block copolymer should form a lamellar structure. However, the rheological data only indicate the presence of microdomains. More detailed studies to determine the morphology may be provided by small-angle neutron scattering experiments from a DEP in which one of the blocks is deuterated.

Figure 2 shows a comparison of DSC cooling thermograms between two series of blends of DEP113 and APP190 and of DEP113 and APP15. DEP113 showed a relatively broad main crystallization peak with an onset temperature of 94 °C and a secondary peak near 65 °C. Upon blending APP190 with DEP113, the main peak became sharper and the onset shifted to lower temperatures. The overall changes (crystallization temperature and peak shape) were relatively small. However, for the blends of DEP113 with APP15, such changes were much more pronounced. Adding APP15 to DEP113 up to 45 wt % caused the crystallization peak to shift to lower temperature. When the composition increased to 50 from 45 wt %, the crystallization temperature abruptly decreased by about 10 °C. Above 50 wt %, by contrast, the peak shifted to higher temperatures. Although those data are not shown in this paper, DSC melting thermograms showed featureless additive behavior for this series and all the blends melted at the same temperature of about 100 °C. Consequently, the cooling thermograms suggest that the crystallization kinetics change between the region of 75–50 wt % and the one below 45 wt % of APP15 in the blends of DEP113.

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0024-9297/93/2226-3236$04.00/0

Table I

sample	abbrevn	M_w[a]	M_w/M_n[a]	polyethylene content[b] (wt %)	ethyl branch content[c] (mol %)
ethylene–propylene diblock copolymer	DEP113	113 000	1.12	48, $f = 0.48$[d]	3.0
	DEP99	99 100	1.07	50, $f = 0.50$[d]	3.0
atactic polypropylene	APP15	15 100	1.05	0	
	APP190	190 000	1.1	0	

[a] Calculated from unhydrogenated precursors' results which were measured by GPC with low-angle laser light scattering. The calibration was done by standard polybutadiene samples. [b] From ^{13}C NMR. [c] From ^{13}C NMR and FT-IR. [d] Symmetric factor defined as the polyethylene volume fraction in DEP in the melt state.

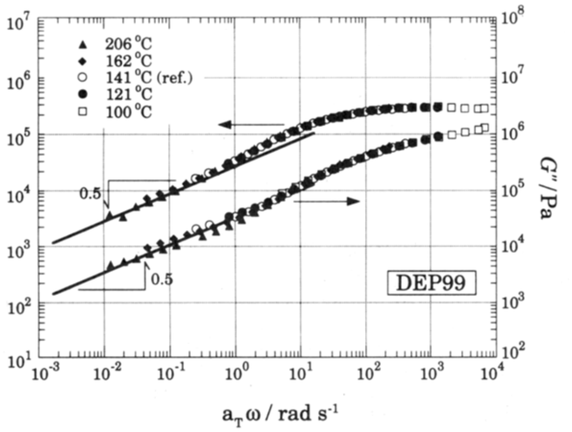

Figure 1. Master curves obtained from dynamic mechanical shear measurements for DEP99. Here a_T is the shift factor.

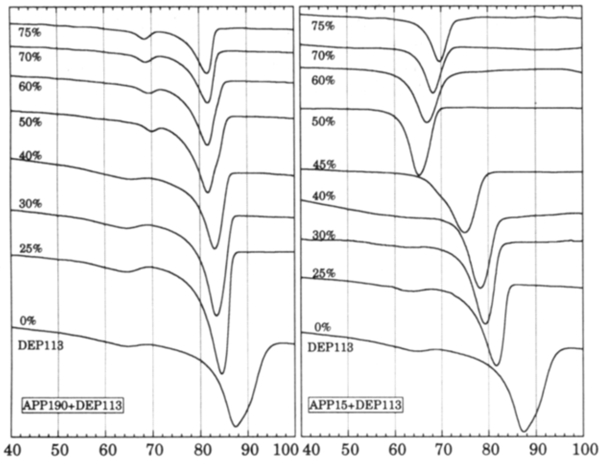

Figure 2. DSC cooling thermograms measured for two series of blends of DEP113 and APP190 and of DEP113 and APP15. The cooling rate is 10 °C/min.

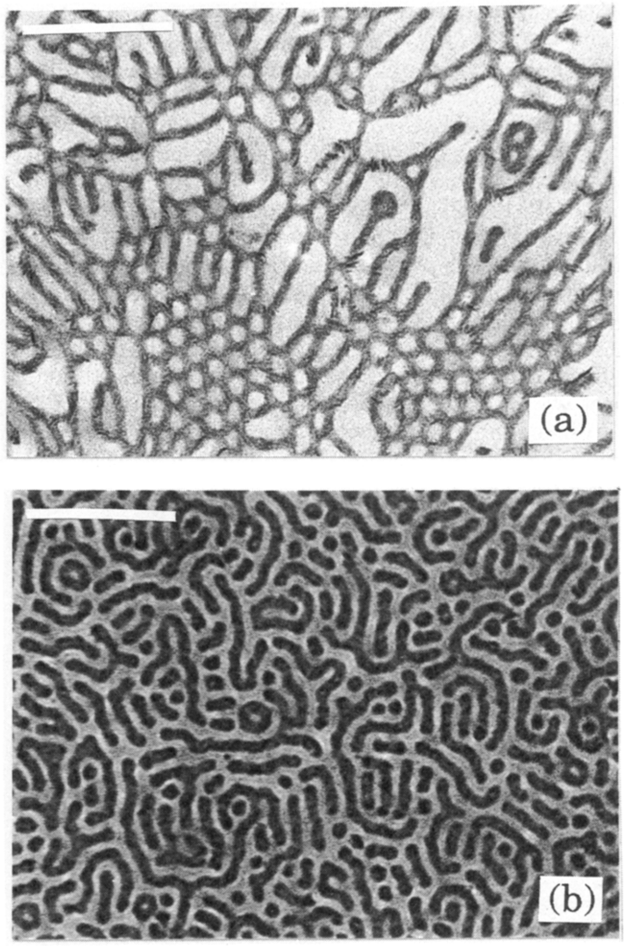

Figure 3. Bright field electron micrographs of the blends of DEP113 and APP15: (a) a bicontinuous structure obtained for 35 wt % of APP15; (b) a cylindrical structure for 65 wt % of APP15. The white bars correspond to 1 μm.

Two types of morphology were observed by TEM in the blends of DEP113 and APP. An ordered bicontinous phase was observed for 25–45 wt % of APP15 and for all compositions with APP190. On the other hand, a discrete cylindrical morphology was observed for blends with more than 50 wt % of APP15. TEM micrographs in parts a and b of Figure 3 show examples of a bicontinuous and cylindrical phase obtained for 35 and 50 wt % of APP15 in the blend, respectively. The dark area represents the polyethylene crystalline-rich phase that diffracts an electron beam. Here it should be mentioned that the micrographs represent "frozen" morphologies in the melt state of the blends because the TEM specimens were quenched from 150 °C by immersion in liquid nitrogen.

It is well-known that, for blends of a diblock copolymer (d-AB) with a corresponding homopolymer (h-A), the morphology is quite sensitive to the relative homopolymer molecular weight ($M_{\text{h-A}}/M_{\text{d-A}}$), which is defined by dividing the molecular weight of h-A by that of A in d-AB.[2,3] When $M_{\text{h-A}}/M_{\text{d-A}} > 1$, h-A cannot merge into the A-rich phase in the microdomain, resulting in macrophase separation. On the other hand, when $M_{\text{h-A}}/M_{\text{d-A}} < 1$, h-A can be solubilized in the A-rich phase and can induce morphological change, usually from lamellae to ordered cylinders and finally to a disordered spherical phase. Assuming our blends act in a similar way, this means that in the melt state macrophase separation is expected for the blend of DEP113 and APP190, while APP15 can be solubilized into the polypropylene domain in DEP113 and may create various types of morphologies depending on the composition.

Such a process can lead to interpretation of the results obtained by DSC and TEM. Since the blend of DEP113 with APP190 is macrophase separated, blending does not affect the polyethylene microdomain, which agrees with the results of TEM. The TEM observation indicates that the polyethylene phase has a bicontinuous structure for all the compositions in the melt state and blending does not change the morphology of the polyethylene phase. Consequently, crystallization kinetics of polyethylene must be the same and blending only reduces the amount of crystallinity in the overall sample. For the blends of DEP113 and APP15, the morphology of the polyethylene domain in the melt state can change upon blending. Such morphological change brings about geometrical constraints in the crystallization of polyethylene, which may depress the crystallization temperature.[7] As observed by TEM, the polyethylene crystalline phase takes on a bicontinuous phase between 25 and 45 wt % and a cylindrical morphology at more than 50 wt % of APP15 for the blend with DEP113. This feature clearly corresponds to the difference in the crystallization kinetics shown in the DSC thermograms for the APP15 blend.

Summary. The frequency dependence of G' and G'' suggests that the DEP99 forms a microdomain in the melt state. Two series of blends of DEP113 and APP190 and then DEP113 and APP15 were studied by DSC and TEM. The results of the DSC measurements can be interpreted in the framework of the currently accepted microphase-separation model for homopolymer/diblock copolymer blends.[2,3] TEM micrographs are also consistent with this interpretation. We are currently studying the isothermal crystallization kinetics of the polyethylene in these blends. Also, we are in the process of an investigation of the morphology for these blends by small-angle X-ray scattering, optical microscopy, small-angle light scattering, and additional TEM.

Acknowledgment. We thank Prof. Winter and Dr. Wedler for helping with the rheological measurements and Dr. Waddon for TEM. We also thank E. Habeeb and R. Krishnamoorti for their assistance with hydrogenation and L. J. Fetters for helpful discussions. K.S. extends his appreciation to Kanebo Ltd. for providing him the opportunity to work on this project. Support by the National Science Foundation Materials Research Laboratory, NSF DMR-9024848, is also gratefully acknowledged.

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(6) There is no theoretical basis to apply the time–temperature superposition principle to a microphase-separated system. In our case, shifting has been done on correlating the data in the plateau region on the assumption that the plateau modulus is independent of temperature. In fact, tan δ cannot be superimposed, and the maximum shifts to lower reduced frequencies with increasing temperature.

(7) It is reasonable to expect that the geometrical constraint would give a lower dimensionality to the crystallization growth process. Therefore, if the nucleation rate is the same, the lower dimensionality would provide a lower crystallization rate. In DSC thermograms, the lower crystallization rate should give a lower crystallization temperature at an infinite cooling rate. The Avrami analysis of isothermal crystallization is needed for more detailed discussion.