Macromolecules **1987**, *20*, 1033–1041

Morphological Properties of Ultrahigh Molecular Weight Polyethylene–Polypropylene Blend Films Produced by Gelation/Crystallization from Solutions

Chie Sawatari, Shuka Shimogiri, and Masaru Matsuo*

Department of Clothing Science, Faculty of Home Economics, Nara Women's University, Nara 630, Japan. *Received September 8, 1986*

ABSTRACT: Films of a polyethylene–polypropylene blend were prepared by gelation/crystallization from semidilute solutions by using ultrahigh molecular weight polyethylene (6×10^6) and polypropylene (4.4×10^6). The polyethylene/polypropylene compositions studied were 75/25, 50/50, and 25/75. The elongation was carried out in a hot poly(ethylene glycol) oil bath at 140 °C. The maximum drawability was affected by the compositions. This interesting phenomenon is discussed in terms of the morphology of the blend films as studied by wide-angle X-ray diffraction, small-angle X-ray scattering, small-angle light scattering, optical microscopy, and scanning electron microscopy. The facile drawability of the blend gel films with draw ratios in excess of 50 is thought to be due to the existence of a suitable level of entanglement between the polyethylene and polypropylene chains in spite of their incompatibility in solution.

Introduction

It is well-known that the theoretical Young's modulus and tensile strength of polymeric materials can only be realized if the chains are fully aligned and extended and if the specimen is almost completely crystalline. In an attempt to produce such an ideal sample, chain alignment induced by deformation or flow has been investigated extensively. The ultimate value of the Young's modulus is close to the crystal lattice modulus in the direction of the polymer chain axes. In previous work,[1,2] the crystal lattice modulus of polyethylene and isotactic polypropylene was measured by X-ray diffraction using ultradrawn films which were produced by gelation/crystallization from dilute solutions. The measured crystal lattice modulus of polyethylene was in the range 213–229 GPa,[1] while that of polypropylene was 39–43 GPa.[2] Furthermore, efforts were made to produce polyethylene and polypropylene specimens whose Young's modulus is almost equal to their crystal lattice modulus. Thus, it was found that the Young's moduli of polyethylene and polypropylene approached 216[1] and 40.4 GPa,[2] respectively, when the dry gel films of polyethylene and polypropylene could be consistently elongated to the remarkably high draw ratios of 400 and 100, respectively. The considerable difference in the value of crystal lattice modulus between polyethylene and polypropylene is due to the fact that the polyethylene chain has a fully extended (all trans) planar zigzag conformation, while the isotactic polypropylene chain crystallizes in a helical form in which alternate bonds have trans and gauche conformations.

The thermal properties of ultradrawn polyethylene and polypropylene films are better than those of commercial films. DSC measurements indicated that the melting point of polyethylene with draw ratios in excess of 100 is 155 °C[3] which is higher than the equilibrium melting point of 145.5 °C estimated by Flory and Vrij;[4] this effect is associated with the strong superheating behavior of the specimens. Similarly for polypropylene with a draw ratio of 100, the melting point was 178 °C, which is close to the equilibrium value reported by Krigbaum and Uematsu.[5] Here it should be emphasized that the mechanical properties of ultrarawn polyethylene are much better than those of ultradrawn polypropylene but the thermal properties are poor. Thus, this paper deals with the ultradrawing of blend gel films of polyethylene and polypropylene to produce films with improved mechanical and thermal properties.

Blends of polyethylene and polypropylene have previously been investigated in terms of their morphological and mechanical properties, in order to improve the high-impact strength and low-temperature toughness.[6-10] Lovinger et al.[6] studied the mechanical properties and morphology of blends that were prepared in a two-roll mixer at 200 °C for 15 min with different polyethylene/polypropylene (PE/PP) compositions and molded to a nominal thickness of 1.25 mm. According to their results, the stress increased monotonically with increasing polypropylene content, while strength is much lower in all blends than in the pure polymer. A distinct maximum in tensile strength and Young's modulus occurred at a composition of 80% polypropylene. They pointed out that the blends fail at low elongation because of their two-phase structure, consisting of interpenetrating networks or of isolated polyethylene domains in a polypropylene matrix.

Keller et al.[7] proposed a potentially new method for blend production. They used the "surface growth" method of Zuijenburg and Pennings[11] for producing blend films from mixed solutions of polyethylene and polypropylene. They reported that with mixed solutions entanglements between polyethylene and polypropylene chains occur despite their incompatibility both in solution and in the adsorbed layer on the rotor surface and that in the growth process both constituents are incorporated into the fiber or film that is formed. The resultant blend films contained intimately mixed crystalline regions of each pure component and combined the thermal and mechanical properties of both.

In the present work, our focus is on the ultradrawing of blend films produced by gelation/crystallization from semidilute solutions according to the method of Smith and Lemstra.[12,13] Gel films are prepared with different compositions. The deformation mechanism of the gel films with different compositions was investigated in terms of their morphological aspects by small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), small-angle light scattering (SALS), scanning electron microscopy, and polarizing microscopy.

Experimental Section

The samples used in these experiments were linear polyethylene and isotactic polypropylene with molecular weights of 6×10^6 and 4.4×10^6, respectively. The solvent was decalin. The polyethylene/polypropylene compositions chosen were 75/25, 50/50, and 25/75. The solutions were stabilized with 0.1% (w/w) antioxidant, di-*tert*-butyl-*p*-cresol. Decalin solutions were prepared by heating the well-blended polymer/solvent mixture at 150 °C for 40 min under nitrogen. The hot homogenized solution was quenched by pouring it into an aluminum tray which was sur-

0024-9297/87/2220-1033$01.50/0

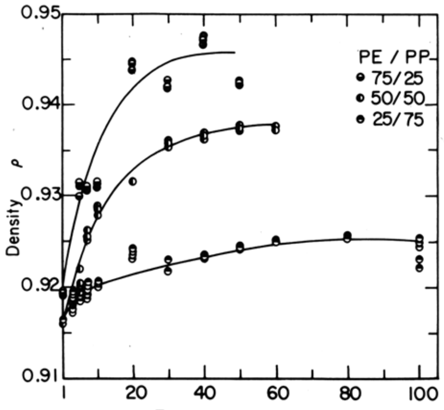

Figure 1. Change in densities of the 75/25, 50/50, and 25/75 blends against draw ratio λ.

rounded by ice water, thus generating a gel. The decalin was allowed to evaporate from the gel under ambient conditions. The resulting dry gel, which had a thickness of 300 μm, was vacuum-dried for 1 day to remove residual traces of decalin.

The dry gel film was cut into strips of length 30 mm and width 10 mm. The strips were clamped in a manual stretching device in such a way that the length to be drawn was 10 mm. The specimens were placed in a poly(ethylene glycol) (PEG) bath at 140 °C and immediately elongated manually to the desired draw ratio λ. The elongation condition was determined on the basis of two preexperiments. One is that the undrawn polyethylene gel films were partially melted in a hot PEG bath at 140 °C but specimens drawn beyond λ = 10 could be held even in a bath at 140 °C. The other is that the drawing of polypropylene could be realized to λ = 60 in a hot PEG bath at 140 °C but it was impossible to realize elongation beyond λ = 20 in a hot oven at 140 °C. Then the elongation of the blends was carried out in a PEG bath at 140 °C. After the samples were stretched, the stretcher with the sample was annealed at 140 °C for 2 h and quenched to room temperature. The stretcher with the sample was immersed in hot water at 80 °C for several minutes to remove PEG. The drawn films were immersed in ethanol for 1 week and vacuum-dried to remove residual traces of antioxidant and PEG completely.

The density of the films was measured by pycnometry with chlorobenzene–toluene as the medium. Since the density was very dependent on the presence of residual antioxidant and PEG in the films, great care was taken to remove them. For this reason, the drawn specimen was cut into fragments and immersed in ethanol for 30 days and subsequently vacuum-dried for 1-day prior to measuring the density. Figure 1 shows the result. The density increases with increasing draw ratio λ and tends to level off beyond λ = 30. This tendency is related to the oriented crystallization of the blend films.

The thermal behavior was estimated from the melting endotherm in differential scanning calorimetry (DSC) curves. Dried gels, weighting about 5 mg, were placed in standard aluminum sample pans. Samples were heated at a constant rate of 10 °C/min.

Scanning electron micrographs and optical micrographs were obtained with a JSM-T300 and a Nikon optical polarizer (XTP-11), respectively.

SALS patterns were obtained with a 3-mW He–Ne gas laser as a light source. Diffuse scattering was avoided by sandwiching the specimen between cover glasses with silicone oil as an immersion fluid.

The X-ray measurements were carried out with a 12-kW rotating-anode X-ray generator (Rigaku RAD-rA). WAXD patterns were obtained with a flat camera using Cu Kα radiation at 200 mA and 40 kV. The X-ray beam was monochromatized with a curved graphite monochromator. SAXS intensity distribution in the meridional direction was detected with a position-sensitive proportional counter (PSPC). The measurement was carried out by point focus with a three-pin hole collimator system. The corrected intensity was obtained by subtracting the contribution of the background (corresponding to air scattering) from the total intensity. The counting interval exposure times was 4 × 10^5 s both for total intensity and air scattering.

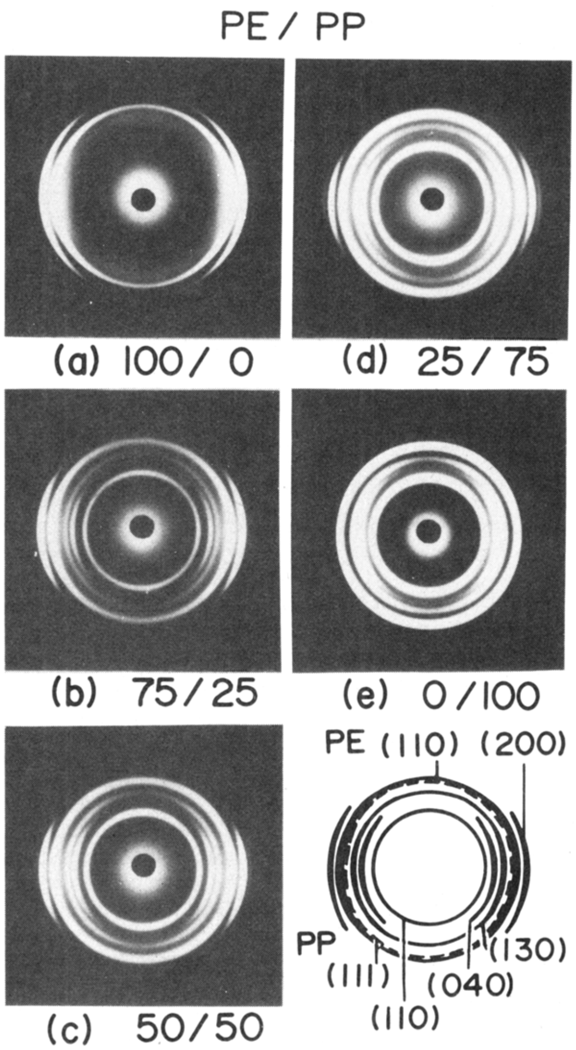

Figure 2. WAXD patterns (end view) from original blended gel films and the individual homopolymers: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100.

Results and Discussions

It has previously been shown that for a sufficiently high molecular weight the maximum achievable draw ratio depends principally on the concentration of the solution from which the gel is made.[12,13] This phenomenon was attributed to a reduced number of entanglements per molecule in solution-cast/spun polymers in comparison with those obtained from the melt. Quantitative theoretical considerations led to the expection that an optimum level of entanglements can be realized by a proper choice of the solution concentration. Thus, in the present work gel films were prepared from solutions of various concentrations and their drawability was assessed in order to establish the optimum concentration for maximum drawability. In this way it was found that the best results were obtained for gels prepared from solutions of a concentration of about 0.45 g/(100 mL). It is assumed that this optimum concentration is appropriate to ensure the existence of a suitable level of entanglement between polyethylene and polypropylene chains. In fact this is supported by the experimental observation that in the gelation/crystallization process both constituents were intimately mixed, so that separate phases corresponding to each component could not be defected. The resultant film could be elongated to draw ratios in excess of 50.

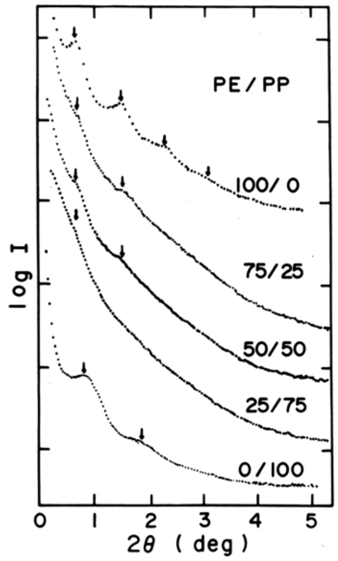

Figure 3. SAXS intensity distributions (end view) from the blends (100/0, 75/25, 50/50, 25/75, and 0/100).

Figure 2 shows WAXD patterns (end view) from original blend films with three PE/PP compositions and the individual homopolymers, when the incident beam was directed parallel to the film surface. The WAXD patterns exhibit the preferential orientation of the crystal *c* axes of polyethylene and polypropylene perpendicular to the film surface.

Figure 3 shows SAXS intensity distributions (end view) from the original (undrawn) blends and the individual homopolymers, in the meridional direction. The intensity distributions of the 75/25 and 50/50 blends shows scattering maxima corresponding to long periods of 118 and 115 Å, respectively. In contrast, the profile of the intensity distribution for the 25/75 blend shows a monotonic curve having an indistinct scattering maximum. Considering the intensity distributions in the WAXD patterns, it is obvious that the original (undrawn) blend films are composed of crystal lamellae that are more or less oriented with their large flat faces parallel to the film surface but the orientational fluctuation of the lamellae and the fluctuation in size increase with increasing content of polypropylene.[17-19] Here it should be noted that the fluctuations for the blends are larger than those of the individual homopolymers. This result presumably indicates that the entanglement between polyethylene and polypropylene chains hampers the formation of large lamellae that can become highly oriented parallel to the film surface. The peak positions corresponding to scattering from the polyethylene and polypropylene lamellae are very close to each other, and their long periods could be estimated as 119 and 105 Å, respectively. Accordingly, it is very difficult to recognize whether the scattering peaks from the blends are due to the scattering from polyethylene or polypropylene lamellae. These peaks are probably only due to the distribution from the average scattering from the lamellae of the individual homopolymers. In any case, both the WAXD and SAXS results indicate that the structure of the blend gel films is similar to that of single crystal mats, i.e., within the lamellar crystals constituting the gel the crystal *c* axes are oriented perpendicular to the large flat faces. Thus, when as-cast blend films are dried by slow evaporation of solvent, the constituent lamellar crystals become oriented parallel to the film surface.

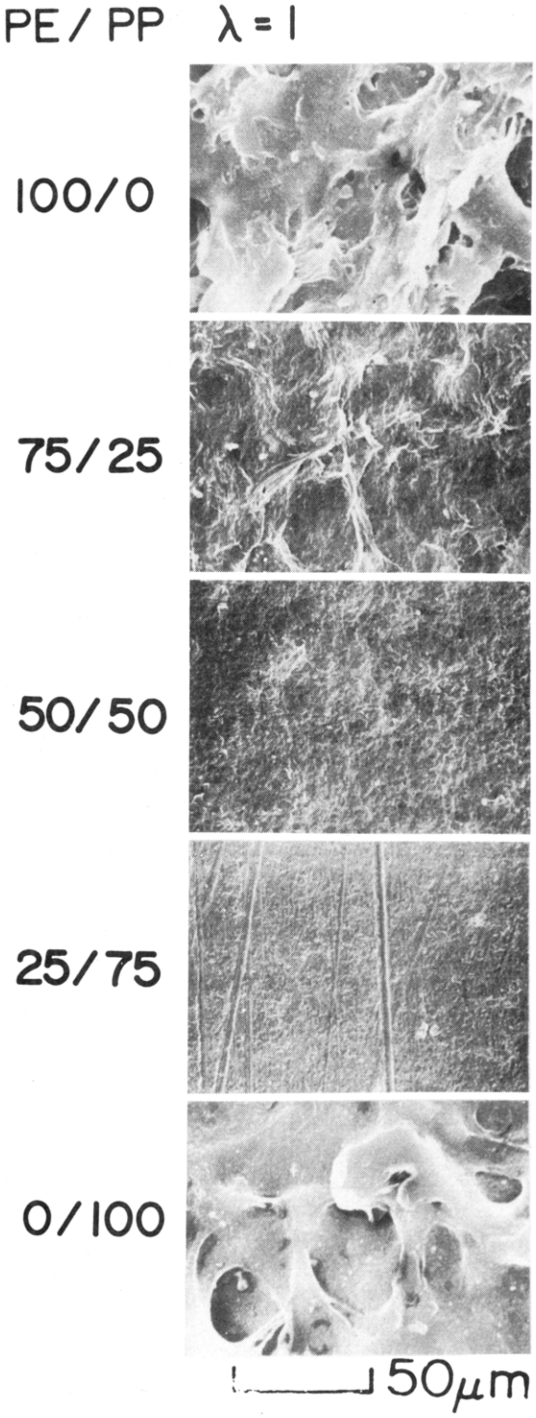

Figure 4. Scanning electron micrographs of dry gel films in an undeformed state: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100.

Figure 4 shows the change in the appearance of the specimens with different PE/PP compositions under scanning electron microscopy. The texture of polyethylene and polypropylene blend films is apparently composed of fibrillar interconnected lamellar crystals seen edgewise. With increasing content of polypropylene, the fibrillar texture become extremely fine, rather like the smooth surface of a melt film. More important, however, is the fact that distinct domains, corresponding to the polyethylene and polypropylene components, cannot be recognized. Thus, it may be concluded that the two components become intimately mixed in the gelation/crystallization process in spite of their incompatibility in solution. These scanning electron micrographs are different from those reported by Lovinger et al.[6] for the films blended in a two-roll mixer. According to their report,[6] very short lamellae (1 μm or less) were observed in polyethylene, while

Table I
Values of the Maximum Draw Ratio at Various PE/PP Compositions

PE/PP compn	100/0	75/25	50/50	25/75	0/100
max draw ratio	400[a]	50	60	100	100[b]

[a] Reference 1. [b] Reference 18.

those in polypropylene were very broad and many micrometers in length. Their 50/50 blend incorporated both these features and also showed clearly a two-phase structure of the sample with islands of polyethylene of the order of 2–10 μm dispersed within the continuous matrix of polypropylene. The islands of polyethylene become smaller as the polypropylene content increases. They confirmed that the polypropylene lamellae are also smaller than those in the pure polymer, since the rapidly crystallizing polyethylene regions promote nucleation of polypropylene lamellae. In contrast in the present work, as already indicated above, a two-phase structure is not observed in the blend films and the fibrillar texture of the blends is smaller than that in the individual homopolymers (see Figure 4). This suggests that the level of entanglement between polyethylene and polypropylene chains hampers the formation of large lamellae of the individual components.

Table I shows the relationship between the maximum draw ratio and PE/PP compositions for the gel films. This result indicates that the maximum draw ratio for the blend film increases as the polyethylene content increases. This tendency is in contradiction to the drawability of individual homopolymers. In, Figure 4, it is obvious that the lamellar size becomes smaller as the polypropylene content increases. This indicates that lamellar size has significant effect on the maximum draw ratio of the blend films. Therefore it may be expected that there exists an effective entanglement between polyethylene and polypropylene chains in the 25/75 blend film to assure high drawability, and this entanglement hampers the growth of large lamellae. However, this point is still not clearly resolved.

Figure 5 shows the optical (cross-polarized) micrographs corresponding to Figure 4. At this scale of magnification, it was confirmed that the most obvious morphological features observed under the scanning electron microscope are not spherulites but have a rodlike texture. This will be discussed in detail in relation to SALS experiments.

In Figure 5 it is further seen that the size of the rods of polyethylene and polypropylene is larger than that of the blends and that the size of the rods in the blend films decreases with increasing content of polypropylene. This is in good agreement with the observed results by scanning electron microscopy in Figure 4.

Figure 6 shows the change in the appearance of the 25/75 and 75/25 blends with increasing draw ratio λ under scanning electron microscopy. The deformation modes are of similar morphology and they are independent of the PE/PP compositions. Already at low elongation, such as λ = 5, the filaments are highly oriented parallel to the draw direction, as in the deformation of the individual homopolymers in the lower micrographs in Figure 5. As λ increases, the width of the filaments is gradually decreased. At λ = 40, the fine filaments seem to be disruptively deformed and the observations at this magnification reveal a relatively smooth surface rather like a drawn melt film. The development of the fine filaments could be readily followed in the polarizing microscope. As can be seen in Figure 7, the elongated birefringent regions are predominantly oriented in the direction of stretching. This deformation mode is very similar to that of the 50/50 blend gel film, although the photographs for the 50/50 film are not shown in this paper.

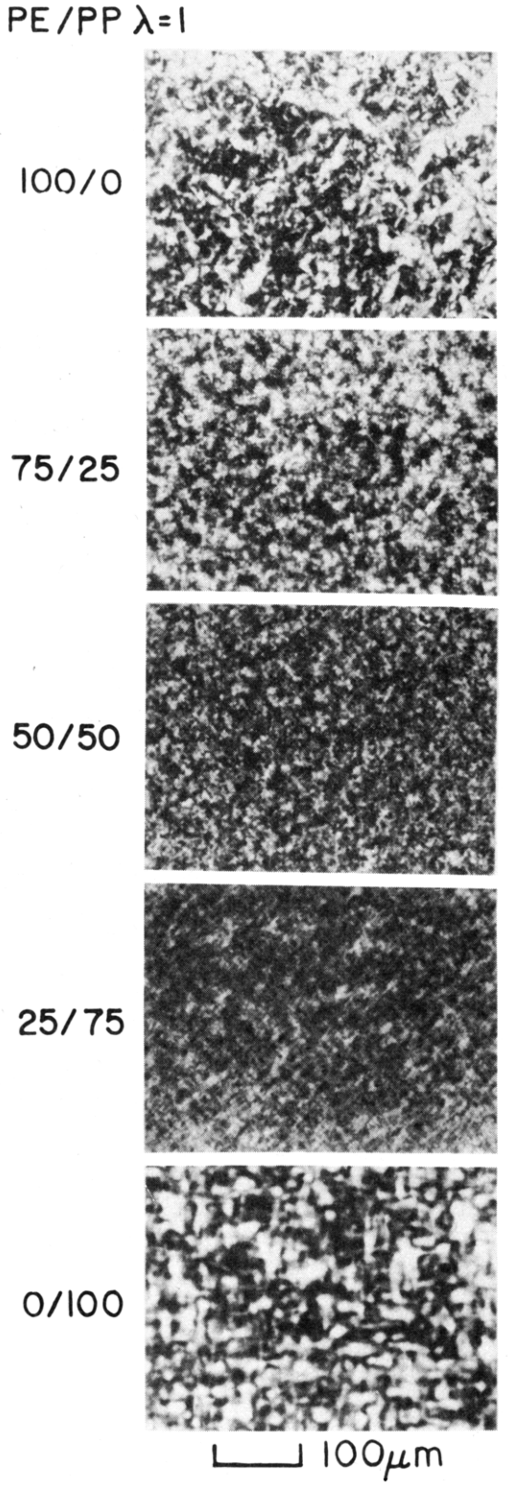

Figure 5. Optical micrographs (crossed-polarized) of dry gel films in an deformed state: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100.

Figures 8–10 show SALS patterns under the Hv polarization condition as a function of elongation ratio. The patterns from the undrawn blend films show a diffuse X-type characterizing the scattering from rodlike textures. This suggests that in localized areas of the sample the lamellae are organized into a large rodlike texture. The scattering pattern appears at a wider scattering angle in comparison with that reported previously for the polyethylene[15,17] and polypropylene[18] gel films. Such patterns presumably indicate the existence of smaller size rods in

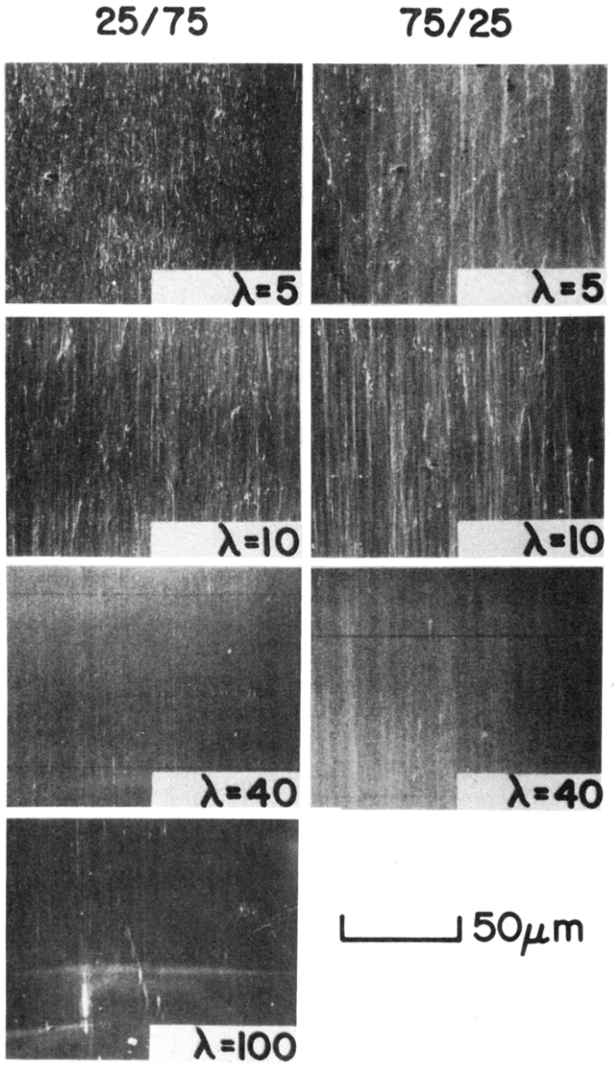

Figure 6. Scanning electron micrographs of the 75/25 and 25/75 polyethylene/polypropylene blends at various draw ratios λ.

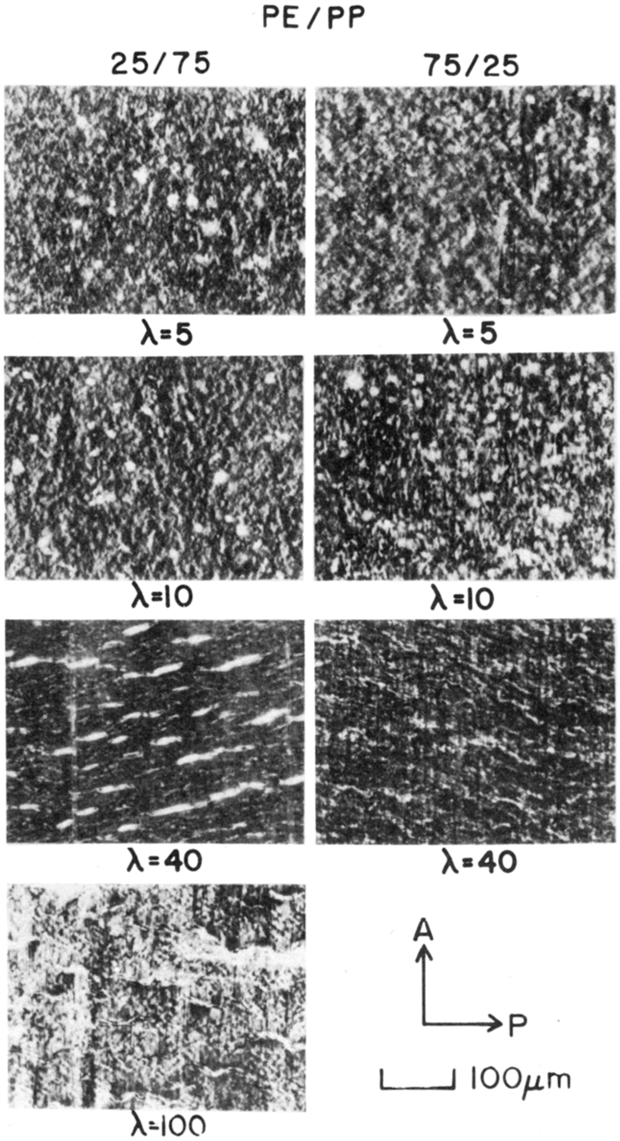

Figure 7. Optical micrographs (crossed-polarized) of the 75/25 and 25/75 blends at various draw ratios λ. In a drawn film (at λ = 40) with the 25/75 composition, the white domains along the horizontal direction are cracks.

comparison with rods within the individual homopolymer films. This result supports the microscopic results in Figures 4 and 5. Furthermore, the notches of the four lobes are less clearly defined. This indicates that the optical axes are oriented normal to the film surface but show orientation disorder with respect to the rod axis. This confirms the conclusion arrived at in the WAXD (Figure 2) and SAXS (Figure 3) investigations that the structure of the blend gel films comprises lamellar crystals.

Upon drawing up to a ratio of 10, the scattering lobes are extended in the horizontal direction. This deformation mode has a similar profile for the three kinds of blend films. The profiles exhibit scattering characteristic of rodlike textures oriented in the stretching direction. Beyond λ = 20, in contrast, the scattering lobes are extended in the vertical direction. Such patterns have already been observed for polyethylene and polypropylene gel films drawn in PEG baths at 135 and 140 °C, respectively, although they are not shown in this paper. Beyond λ = 40, the scattering from the blends (except the 75/25 blend) showed indistinct patterns whose lobes become like sharp streaks. These streaks correspond to the scattering from fine filaments oriented in the stretching direction, observed in the optical (cross-polarized) microscopy in Figure 7.

Figure 11 shows WAXD patterns from the specimen with λ = 20. The patterns exhibit a high degree of orientation of the crystal *c* axes of the individual homopolymers with respect to the stretching direction. The detailed observations reveal that the degree of orientation of polyethylene (as measured by the anglar width of the arcs) is independent of the PE/PP composition while that of polypropylene is affected by it, i.e., with increasing content of polypropylene, the degree of orientation decreases. This problem will be analyzed quantitatively in a subsequent paper[19] in terms of the relationship between the mechanical properties and the PE/PP compositions.

Figure 12 shows the WAXD patterns for the blend films corresponding to the maximum draw ratio of each composition. In comparison with the patterns in Figure 11, the further decreasing angular spread of the strong equatorial (130), (040), and (110) polypropylene reflections indicates an extremely high orientation of the crystal *c* axes with respect to the stretching direction.

Figures 13–15 show the change in the profile of the DSC curves with increasing draw ratio λ for the 75/25, 50/50, and 25/75 blends respectively. To check the reproducibility of the profiles, DSC measurements about a given draw ratio were carried out several times. As illustrated in Figures 13 and 14, the DSC curves exhibit separated endotherms corresponding to the individual homopolymers. The peak and shoulder at the lower temperature

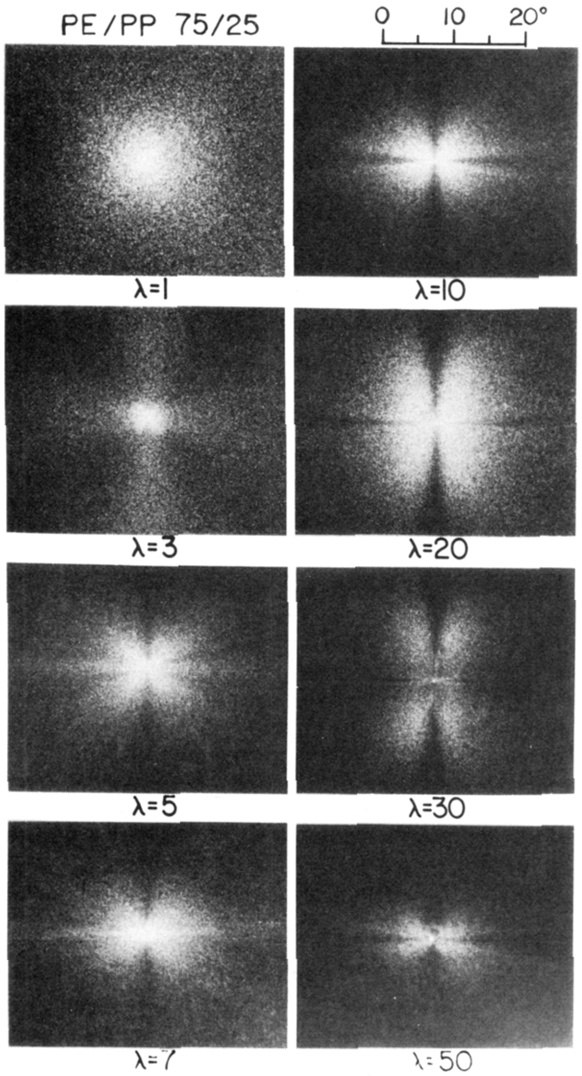

Figure 8. Hv light scattering patterns from the 75/25 blend at various draw ratios λ.

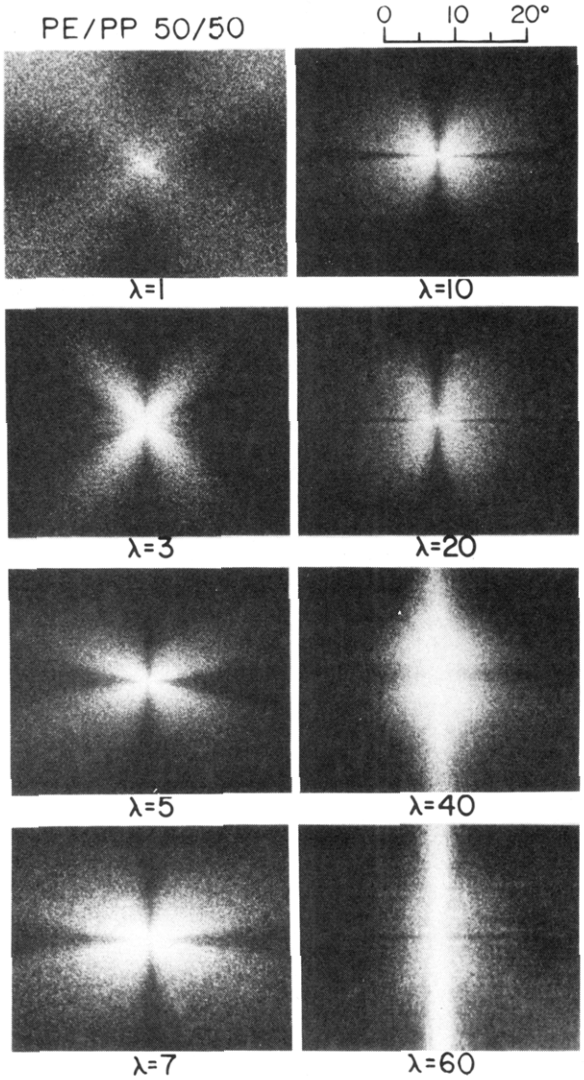

Figure 9. Hv light scattering patterns from the 50/50 blend at various draw ratios λ.

are due to polyethylene and the other peaks are due to polypropylene. At $\lambda = 1$, the melting point of polyethylene within the blends appears around 130 °C, which is lower than that of the polyethylene homopolymer (140 °C). This is probably due to a decrease in crystallinity, as shown in Figure 16.

Figure 16 shows the change in density of undrawn films with increasing annealing time in a PEG bath at 140 °C. The density decreased drastically within 10 s but the specimens could be kept without any partial melt in a macroscopic sense for more than 2 h. This is probably due to the blended effect of polypropylene whose melting point is higher than 140 °C.

In Figures 13 and 14, and $\lambda = 5$ a shoulder appears at the high-temperature side of the polyethylene large peak and becomes a new peak at the expense of the large peak. Beyond $\lambda = 10$, the melting point of the new peak increases gradually as λ increases. Beyond $\lambda = 20$, it becomes higher than the equilibrium melting point reported by Flory and Vrij.[4] This phenomenon is well-known as a superheating effect which has been observed for highly oriented polyethylene.[20] Therefore the observed melting points are probably not the true equilibrium values. The observed abnormaly high apparent melting temperatures may be explained by assuming that polymer chains in the melt retained the extended-chain arrangement and therefore the entropy of fusion would obviously be smaller than the value calculated for random coils in the melt. The melting point of polypropylene increases with increasing content and in the 50/50 blend at $\lambda = 60$ it reached 177 °C, which is close to the value that has been observed for polypropylene with $\lambda = 100$.[18]

As illustrated in Figure 15, the DSC curves show the complicated profile of the 25/75 blend films. The profiles are representative results obtained on the basis of several measurements at a given draw ratio. It was found that the reproducibility was much poorer than for the 75/25 and 50/50 blend films beause of the shrinkage of the drawn specimens during the heating process, especially for the specimens with draw ratios beyond 20. Beyond $\lambda = 10$, superheating effects are observed for the melting point of polyethylene.

The endotherm of polypropylene is composed of multiple peaks for the specimens beyond $\lambda = 20$. The peak appearing around 178 °C for the specimen with $\lambda = 40$ shifts to higher temperatures and the peak height increases with increasing λ. The peak reached 187 °C, which is almost equal to the equilibrium melting point.[5] Such a high melting point has never been observed for ultradrawn polypropylene homopolymer. This is an interesting phenomenon.

It was of interest to ascertain whether the polyethylene crystallites within the blend films are transformed beyond the normal melting point (145.5 °C) of polyethylene. In

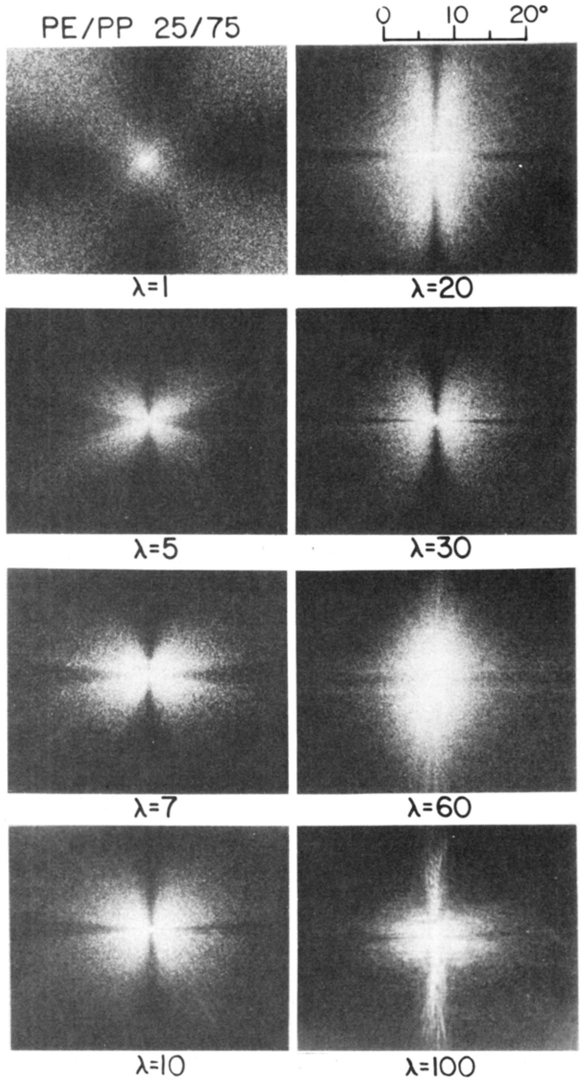

Figure 10. Hv light scattering patterns from the 25/75 blend at various draw ratios λ.

order to study the problem, WAXD patterns were observed in the horizontal direction with increasing temperature.

Figure 17 shows the result for the 25/75 blend film with λ = 60, when the sample was fixed at a constant stress of 0.018 GPa to avoid shrinkage of the film. The specimens were annealed for 20 min at the indicated temperatures prior to photographing. As can be seen in the series of patterns, the strong equatorial reflections from the (110) and (200) crystal planes shift to smaller scattering angles and their intensities become weaker as the temperature increases to 160 °C. This tendency becomes considerable for the crystal (200) plane associated with the thermal expansion of the crystal a axis. At 170 °C, the reflections from the (110) and (200) crystal planes disappeared due to melting. This behavior is quite different from that of cross-linked polyethylene, where a transformation to the hexagonal rotator phase is observed.[21] This difference can be understood on the basis of the assumption that the extended polyethylene chains in a polypropylene matrix have higher mobility than those in an amorphous cross-linked polyethylene matrix.

Here it should be noted that the polyethylene crystallites within the polypropylene matrix are evidently not free to allow a random orientation in the melt state. This is indicated by the WAXD patterns at 20 and 100 °C which do not show diffraction rings but show the equatorial reflections of the (110) and (200) crystal planes, indicating that the crystal c axes are highly oriented with respect to the stretching direction. This type of intensity distribution is attributed to the existence of entanglement between polyethylene and polypropylene chains, which hampers the random orientation of polyethylene chains in the melt state.

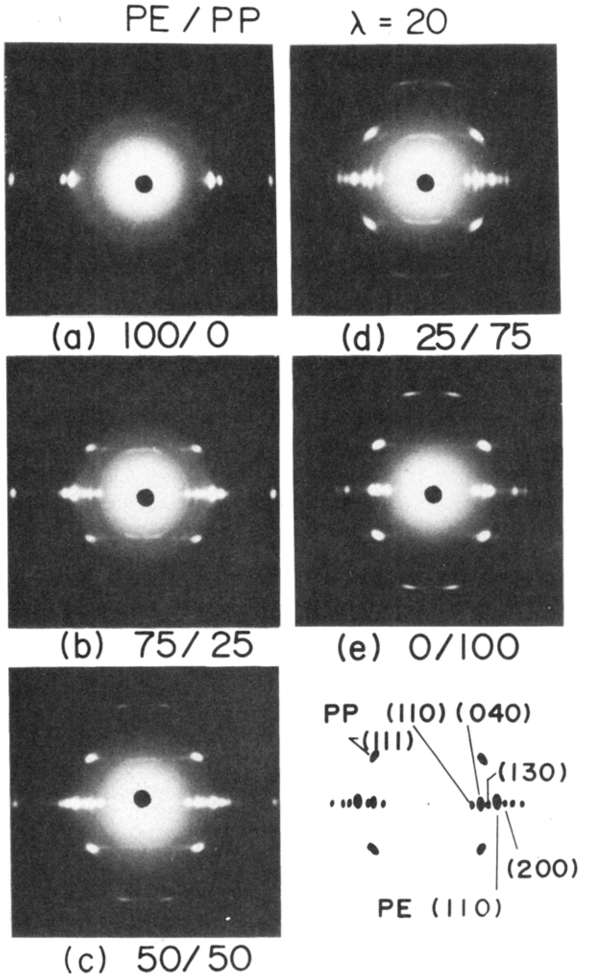

Figure 11. WAXD patterns (through view) from the blend films and the individual homopolymers at λ = 20.

In order to study the recrystallization process, the intensity distribution for the (002) crystal plane was observed by the step-scanning method. The measurement was carried out with point focusing using a system in which the incident beam was collimated by a collimator 2 mm in diameter, and the diffraction beam was measured by a square slit of 0.9 mm × 0.9 mm. The intensity distribution was measured at a step interval of 0.1° with a time interval of 10 s, in the range 71–79° (twice the Bragg angle). Figures 18 and 19 show the changes in the intensity distribution corresponding to the heating and cooling processes in Figure 17. The diagrams in Figure 18 show that the intensity becomes weaker with increasing temperature and it disappeares altogether around 170 °C, as a result of the melting of polyethylene crystallites. The diagram in Figure 19 shows that on cooling the peak reappears around 130 °C, as a result of recrystallization, and its intensity becomes stronger with decreasing temperature. Comparing the profiles at 20 °C in Figures 18 and 19, one can see that the intensity from polyethylene crystallites within the specimen heated beyond 160 °C is lower than that within the original specimen, indicating a decrease in crystallinity. This is due to the fact that the polyethylene crystallites within the blend gel film become similar to those within a melt film by recrystallization after

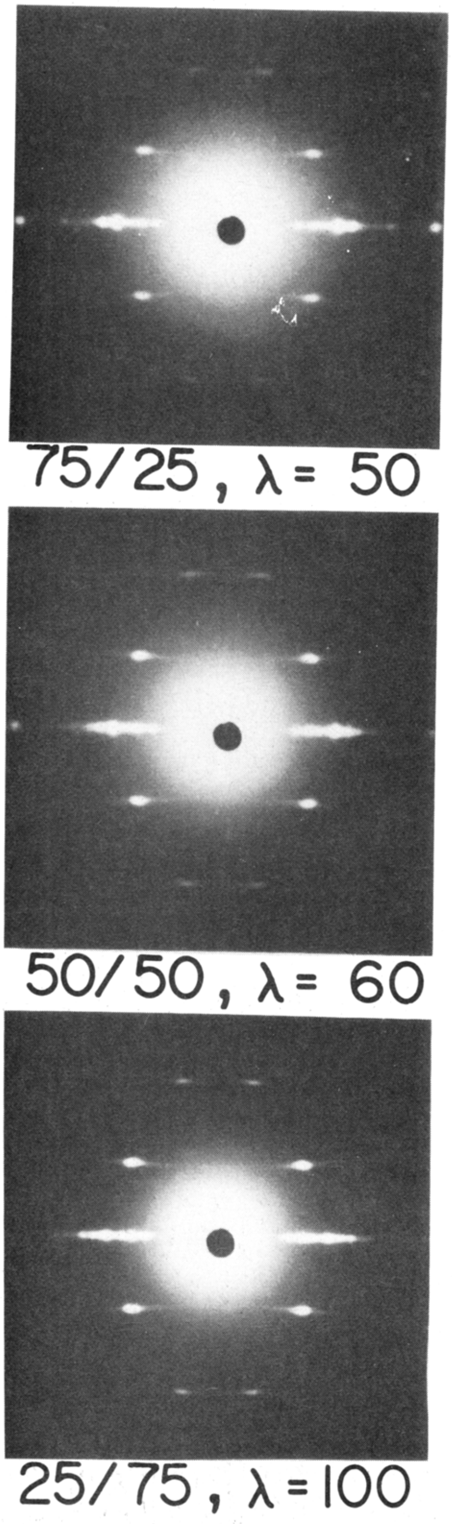

Figure 12. WAXD patterns (through view) from the blend films at the corresponding draw ratio.

the melting. However, the diagrams show that the crystal *c* axes retained a high degree of orientation with respect to the stretching direction. These results are in good agreement with that of Figure 17.

Conclusions

Polyethylene–polypropylene blend films were prepared by gelation/crystallization from semidilute solutions by using ultrahigh molecular weight polyethylene ($M_w = 6 \times 10^6$) and polypropylene ($M_w = 4.4 \times 10^6$). The PE/PP compositions chosen were 75/25, 50/50, and 25/75. The critical concentration to ensure optimum draw characteristics for each composition was determined by preparing gel films at various concentrations and studying their drawability in order to ascertain which concentration gave the best result. For all compositions a concentration of about 0.45 g/(100 mL) proved most suitable. The resultant

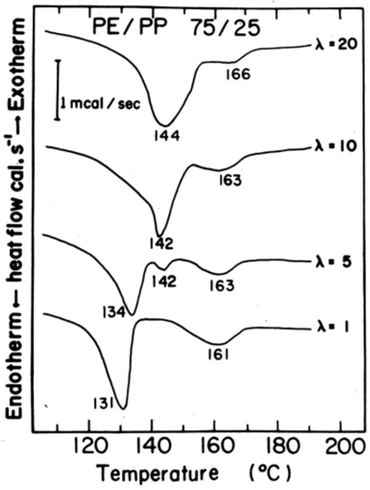

Figure 13. DSC curves of the 75/25 blend film drawn to various draw ratios λ.

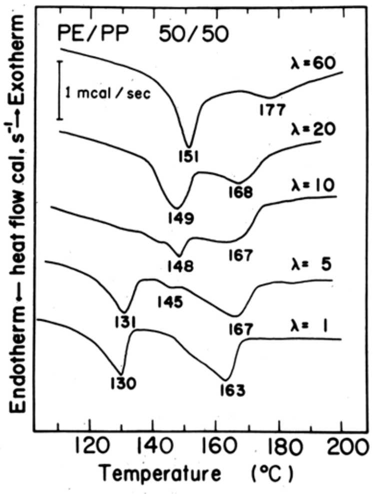

Figure 14. DSC curves of the 50/50 blend film drawn to various draw ratios λ.

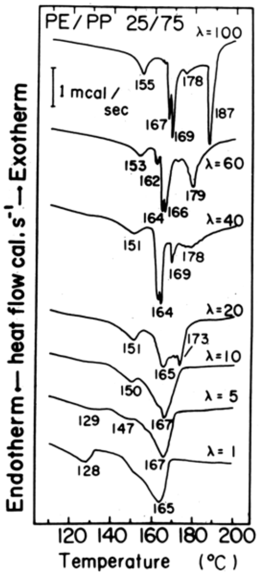

Figure 15. DSC curves of the 25/75 blend film drawn to various draw ratios λ.

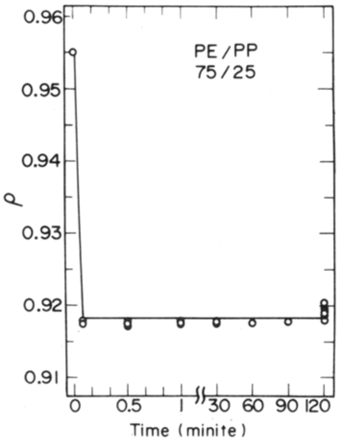

Figure 16. Change in density of undrawn films with increasing annealing time in PEG bath at 140 °C.

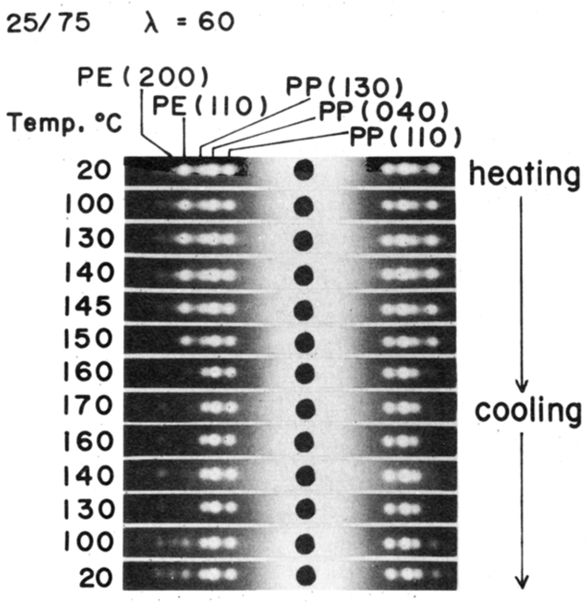

Figure 17. Change in WAXD patterns (through view) in the horizontal direction from the 25/75 blend films (λ = 60) at the indicated temperatures during heating and cooling processes.

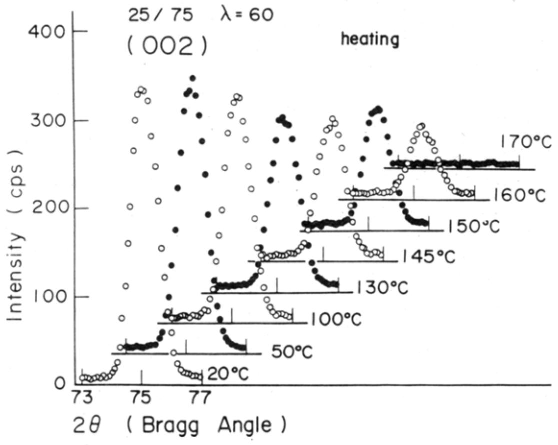

Figure 18. Change in intensity distribution for the (002) crystal plane measured for the 25/75 blend film (λ = 60) during heating.

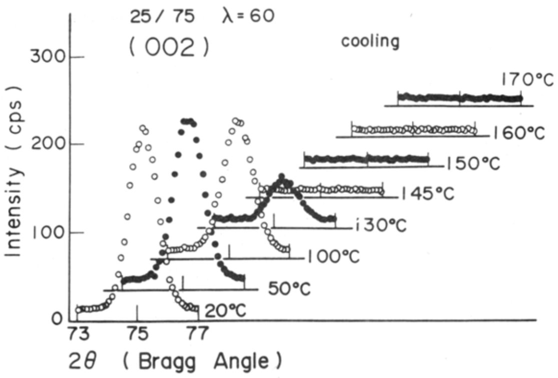

Figure 19. Change in intensity distribution for the (002) crystal plane measured for the 25/75 blend film (λ = 60) during cooling.

blend films after evaporating the solvent could be readily elongated to a high draw ratio in a PEG bath at 140 °C. The morphological properties of the blend films were dependent upon the compositions. The texture is generally fibrillar with no indication of separate polyethylene and polypropylene domains. This indicates intimate mixing of the two components despite their known incompatibility in solution. This effect is thought to be due to the existence of a suitable level of entanglement between polyethylene and polypropylene chains, which hampers the growth of separate phases of the two polymers in the gelation/crystallization process. Blends of the maximum draw ratios of the 75/25 and 50/50 films exhibit separate endotherms corresponding to the individual homopolymers. The melting point of the polyethylene component became higher than the equilibrium melting point because of superheating effects which have previously been observed for highly oriented polyethylene films.[15] The melting point of polypropylene increased with increasing draw ratio and approached the theoretical value.[5] The 25/75 blend film with λ = 60 could be kept at 160 °C, which is higher than the normal melting point of polyethylene. At 160 °C, the WAXD pattern showed no diffraction spots from polyethylene crystals. This indicates that the extended polyethylene crystals surrounded by the polypropylene matrix melted without undergoing transformation from the orthorhombic to the hexagonal phase.

Registry No. PE, 9002-88-4; isotactic PP, 25085-53-4.

References and Notes

(1) Matsuo, M.; Sawatari, C. *Macromolecules* **1986**, *19*, 2036.
(2) Sawatari, C.; Matsuo, M. *Macromolecules*, in press.
(3) Sawatari, C.; Matsuo, M. *Colloid Polym. Sci.* **1985**, *263*, 783.
(4) Flory, P. J.; Vrij, A. J. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(5) Krigbaum, W. R.; Uematsu, I. *J. Polym. Sci., Part A* **1965**, *A2*, 767.
(6) Lovinger, A. J.; Williams, M. L. *J. Polym. Sci.*, **1980**, *25*, 1703.
(7) Coombers, A.; Cannon, C. G.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1957.
(8) Noel, O. F.; Carley, J. F. *Polymer* **1975**, *15*, 117.
(9) Galeski, A.; Pracella, M.; Martuscelli, E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 739.
(10) Gohil, R. M. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1713.
(11) Zwijenburg, A.; Pennings, A. J. *Colloid Polym. Sci.* **1976**, *254*, 868.
(12) Smith, P.; Lemstra, P. J. *J. Macromol. Chem.* **1979**, *180*, 2983.
(13) Smith, P.; Lemstra, P. J. *J. Mater. Sci.* **1980**, *15*, 505.
(14) Matsuo, M.; Manley, R. S. J. *Macromolecules* **1982**, *15*, 985.
(15) Matsuo, M.; Manley, R. S. J. *Macromolecules* **1983**, *16*, 1500.
(16) Matsuo, M.; Tsuji, M.; Manley, R. S. J. *Macromolecules* **1983**, *16*, 1505.
(17) Matsuo, M.; Inoue, K.; Abumiya, N. *Seni-Gakkaishi* **1984**, *40*, 275.
(18) Matsuo, M.; Sawatari, C.; Nakano, T. *Polym. J. (Tokyo)* **1986**, *18*, 759.
(19) Matsuo, M.; Sawatari, C., in preparation.
(20) Matsuo, M. *Rheology Gakkaishi* **1985**, *13*, 4.
(21) Matsuo, M.; Sawatari, C. *Macromolecules* **1983**, *16*, 1505.