Spherulitic Growth Rates and Coalescence Phenomena in Polypropylene/Polyethylene-Based Ionomer Blends

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ABSTRACT: The isothermal radial growth rates of spherulites of polypropylene in blends with an essentially noncrystallizable ionomer have been determined by photomicroscopy. Blends containing 5 and 10 wt % ionomer, crystallized from the melt, have a grainy appearance due to ionomer entrapment and show an increased nucleation density as compared to pure polypropylene. At large supercooling, these blends also show depressed radial growth rates, which are attributed to a significant dissipation of energy by the crystallizing front to affect the rejection of the ionomer domains. Upon repeated crystallization of a given sample, an increase in the radial growth rate with melt time is observed initially giving rise to a maximum, with general behavior that is dependent upon the blend composition and the crystallization temperature. Beyond this maximum the spherulitic growth rate decreases upon further crystallization. The observed effects on the spherulitic radial growth rates with respect to repeated crystallization are attributed to the coalescence of the ionomer dispersed phase. This is consistent with a concomitant increase in the average domain size.

Introduction

The blending of polymers to produce alloys with properties selected for given applications is an area of polymer science that is presently receiving great attention.[1-3] Blending is not only economically viable but is also a versatile way of making new materials having a wide range of properties.

For polymer blends in which one of the components is crystallizable, the presence of the second component can strongly affect the crystallization process. Both the crystallization kinetics and the final crystal morphology can be very different from that of the pure crystallizing component. As reviewed recently by Martuscelli,[4] such changes have been found not only in blends of compatible polymers but also in blends of immiscible or partially miscible polymers.

In a recent study, Willis et al.[5] demonstrated the ability of a polyethylene-based ionomer to enhance the compatibility of polyolefin/polyamide blends. The morphology of the ternary polyolefin/ionomer/polyamide blends was significantly dependent upon ionomer concentration. In fact, for fixed processing conditions, the size of the dispersed phase was reduced by as much as four times due to the addition of as little as 0.5% ionomer by weight. From the physicochemical studies of the binary blend of the ionomer with polyamide,[6] specific interactions in the form of hydrogen bonding between the blend components were demonstrated. Such interactions were absent in the polypropylene or polyethylene/ionomer blends. Moreover, the ionomer severely impedes the crystallization of the polyamide but enhances the nucleation of the polyolefins, particularly in the case of polypropylene.

The present investigation concerns the effect of a polyethylene-based ionomer on the radial growth rates of spherulites of polypropylene. In the last few years many studies[7-14] have been done on the effect of elastomers on the crystallization kinetics of polypropylene. However, to the knowledge of the authors, there are no reports of studies of the effect of an essentially noncrystallizable ionomer on the radial growth rates of spherulites of a crystallizable polymer.

The main goal of this work is to study the effect of composition, crystallization temperature, and melt residence time on the spherulitic growth rates of polypropylene in binary polypropylene/ionomer blends. A study of the crystallization of blends can ultimately yield information concerning the interactions at the interface between the polymers in the blend. The effect of crystallization on the rate of coalescence of dispersed ionomer phase is also considered. Thus, the results presented in this paper will contribute to the understanding of the effectiveness of the ionomer at enhancing the compatibility of polyolefin/polyamide blends.

Experimental Section

Materials. The polymers used were polypropylene (Pro-Fax 6501) originally obtained in powder form from Himont and Surlyn 9020 from Du Pont. The polypropylene (PP) resin with 0.1% of Irganox 1076 antioxidant was subsequently compounded with a Werner and Pfleiderer (ZSK30) twin-screw extruder and converted to a pellet form. The ionomeric resin (Du Pont, Surlyn 9020) is a random terpolymer consisting of approximately 80% of polyethylene, 10% of methacrylic acid, approximately 70% neutralized with zinc, and 10% of isobutyl acrylate. Some properties of these resins are given in Table I. Prior to blending, the resins were dried under vacuum at 95 °C for 24 h.

Preparation of the Polypropylene/Ionomer Blends. Blends having 5%, 10%, 20%, and 50% by weight of ionomer were prepared according to the following procedure: The resins were melt blended in a Brabender chamber, initially set at 250 °C, using roller blades that are recommended for high shear applications. The resins were allowed to mix at 50 rpm under a constant nitrogen flow for 5 min. The melt was then rapidly transferred to a mold and placed in a hydraulic press under 2.5 MPa of pressure until the sample cooled to room temperature. The resultant molded samples were cut into specimens having dimensions of roughly 1 × 0.5 × 0.5 cm. Thin films (5–10 μm)

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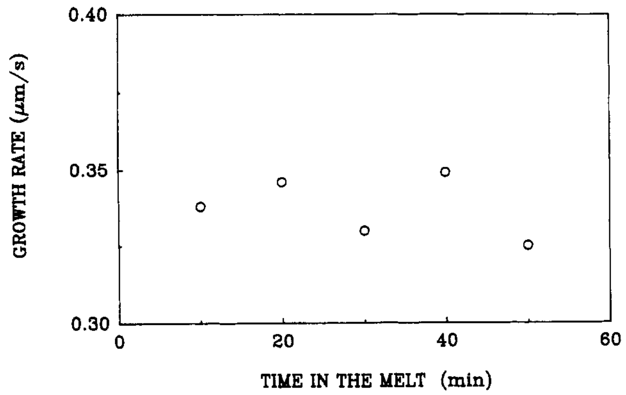

Figure 1. Reproducibility of the radial growth rates for polypropylene at 124 °C.

Table I
General Properties of Polypropylene and Surlyn

resin	melt index, g/10 min	density, g/mL	torque (250 °C), N/m	melting point, °C
PP	4.0	0.905	8.6	165
Surlyn	1.0	0.965	14.3	62

were then cut from these specimens using a Reichert Jung Supercut 2050 microtome.

Isothermal Crystallization Procedure. A Leitz Wetzlar optical polarizing microscope fitted with a Mettler FP52 hot stage was used to observe isothermal crystallization at 100× magnification. The hot stage could be held at a constant temperature to ±0.3 °C by a Mettler FP5 temperature control unit.

For the microscope study, microtomed films were placed on a microscope slide glass and melted on a hot plate while applying pressure on the cover glass. The thickness of the melted film was fixed by a 12-μm aluminum spacer between the cover glass and the microscope slide. Film thickness of the order of 12–15 μm were obtained and used in the microscope study.

The following procedure was used to view isothermal crystallization: The samples were melted on the hot stage at 200 °C for 10 min to remove crystallinity. Different distributions of spherulites were observed in successive crystallizations, indicating that the melt residence time as well as melt temperature was sufficient to remove residual crystallinity. The hot stage was then set to an intermediate temperature of 135 °C, and the sample was allowed to come to temperature equilibrium, which took approximately 2 min. When temperature equilibrium was achieved, the hot-stage control was set to the desired crystallization temperature, and equilibrium was achieved rapidly (<30 s). Photomicrographs were taken of the growing spherulites at appropriate time intervals, depending on the rate of crystallization.

Radial Growth Rate Measurements. The isothermal radial growth rates, $G = dr/dt$ (r = radius of the spherulites, t = time), were determined by measuring the sizes of the spherulites as seen in the photomicrographs as a function of time. The radii of these spherulites were measured with a semiautomatic digitizer, described elsewhere.[15]

The radius of each spherulite was taken as the average of 15–20 individual radii. From the average radii, plotted as a function of time, the radial growth rate of the spherulite was determined as the slope of the resulting straight line. For each composition and crystallization temperature, the average radial growth rate was determined from at least four radial growth rate measurements. The experimental error in these growth rates was determined to be less than 5%.

Results and Discussion

Crystallization of Polypropylene. When polypropylene is crystallized from the melt in the temperature range of 118–126 °C, the predominant spherulitic appearance observed microscopically is type I, as classified by Padden and Keith.[16] The various results presented in this investigation will mainly concern this morphology.

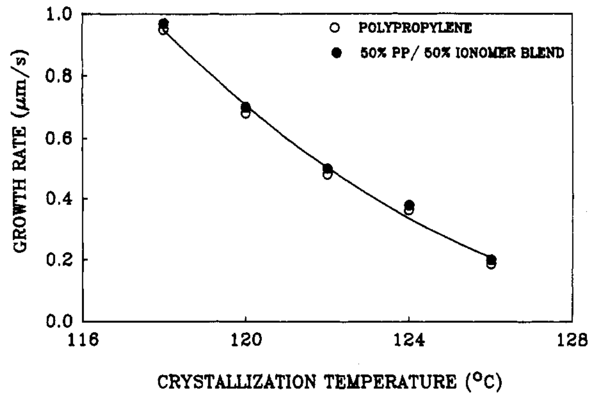

Figure 2. Radial growth rate dependence of polypropylene and the 50% PP/50% ionomer blend on crystallization temperature, for a melt time of 10 min.

A second type of spherulitic appearance (type III), introduced later in the paper, is shown to behave somewhat differently from the first.

In the region of 15–60 μm, the radii of the polypropylene spherulites crystallized from the melt increase linearly with time. To verify the reproducibility of the radial growth rates, a sample of polypropylene was repeatedly melted, for 10 min, and crystallized. As shown in Figure 1, at 124 °C the radial growth rates fluctuate about 0.33_5 μm/s and are within approximately ±0.02 μm/s of each other.

The dependence of the radial growth rate of polypropylene spherulites on the crystallization temperature shown in Figure 2 is in accordance with that predicted by the Fischer–Turnbull equation[17]

$$G = G_0 \exp\{-\Delta E_D^*/kT\} \exp\{-\Delta\Phi^*/kT\} \qquad (1)$$

where, the term $\exp\{-\Delta E_D^*/kT\}$ is referred to as the transport term and $\exp\{-\Delta\Phi^*/kT\}$, as the nucleation term, G is the growth rate of polymers, G_0 is the preexponential term, ΔE_D^* is the free energy of activation for movement across the embryo–melt interface, $\Delta\Phi^*$ is the minimum free energy required for the formation of a nucleus of critical size, k is the Boltzmann constant, and T is the crystallization temperature. For crystallization above the optimum crystallization temperature, the growth rate is controlled by the nucleation process so that the activation free energy is negative and the expected inverse dependence of the radial growth rate on the temperature is observed.

Crystallization of Polypropylene/Ionomer Blends. The effect of composition on the radial growth rates of the polypropylene spherulites obtained for the blends that have been held in the melt at 200 °C for 10 min is shown in Figure 3. A small depression of the growth rate is seen at low ionomer content and low temperatures. At higher temperatures, consequently much slower crystallization, the growth rate is essentially independent of the ionomer concentration.

As shown in Figure 2, the radial growth rates obtained for the polypropylene (PP) spherulites in the 50% PP/50% ionomer blend are identical, within experimental error, to those obtained for pure polypropylene. This general pattern has also been observed by Martuscelli et al.[14,18] for the spherulitic growth of polypropylene with ethylene/propylene/diene terpolymer (EPDM). However, the growth rates of isotactic polypropylene in blends with other types of rubbers showed a significant dependence on composition and crystallization temperature,[18] which was attributed to partial miscibility.

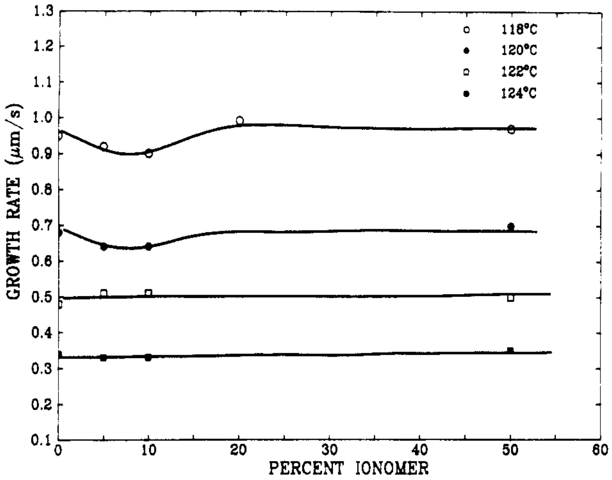

Figure 3. Composition and crystallization temperature dependence of the radial growth rates in polypropylene/ionomer blends.

It has been demonstrated that the presence of foreign inclusions in the melt, as in the case of immiscible blends, can disturb the crystallizing front.[4,14,18] If there are interfacial interactions between the blend components, the growing crystal front must do work against the dispersed phase in the melt. In the case of a one-phase melt, some energy is required to effect the rejection of the second component from the crystallizing polymer. In the case of a two-phase melt, where the second component has taken the form of droplike domains, energy must also be dissipated for the rejection, engulfment, and/or deformation of the second component.

These energy dissipations constitute energy barriers which influence the growth rate of the spherulites in the melt. Bartczak, Galeski, and Martuscelli[19] modified the classical Fischer–Turnbull equation to account for the energy dissipations which result during the crystallization of a polymer in the presence of noncrystallizable, spherical domains. The modified equation is

$$G = G_0 \exp\{-\Delta E_D^*/kT\} \exp\{-\Delta\Phi^*/kT\} \times \exp\{-(E_1 + E_2 + E_3 + E_4 + E_5)/kT\} \quad (2)$$

where E_1 is the energy dissipated by the crystal to effect the rejection of the second component into interlamellar regions, E_2 is the energy dissipated by the spherulite front to effect the rejection of droplike domains in the melt, E_3 is the kinetic energy required to overcome the inertia of the drops, E_4 is the energy required to form new interfaces between the spherulite and drop when engulfment occurs, and E_5 is the energy dissipated when the engulfed drops are deformed by the crystallizing front. The equations that describe the growth rate, taking into account these energy dissipations, derived by Bartczak et al.,[19] are summarized in Table II.

The crystallization of polymer blends whose components have phase separated in the melt is influenced both by the size of the dispersed phase and the interfacial energies. The driving force for the rejection, engulfment, and/or deformation processes lies in the difference of the interfacial free energy between the crystallizing front and inclusions, γ_{ps}, and the interfacial free energy between the melt and inclusions, γ_{pl}:[20-22]

$$\Delta F = \gamma_{ps} - \gamma_{pl} \quad (3)$$

For $\Delta F < 0$, the dispersed domains in the melt are more likely to be engulfed than rejected by the growing front. However, when $\Delta F > 0$, the situation is more complicated. At slow rates of crystallization, the domains are pushed along by the growing front, while at higher rates they are simply engulfed. At some intermediate rate, the domains may be pushed for short distances before being engulfed by the crystallizing front. Engulfment occurs when the viscous hindrance caused by the motion of the domains overwhelms the forces of repulsion. This implies a critical rate at which the pushing of the domains no longer occurs and engulfment takes precedence. Using these arguments, for a given ΔF, there must be a critical domain size such that, at a constant growth rate, domains of this size or larger are simply engulfed and no longer pushed by the growing front. Engulfment occurs above this critical size because the hydrodynamic force is proportional to the domain size while the repulsive forces are determined by factors such as the shape of the interface behind the particle.[19] The critical size itself is dependent on the system, i.e., on the interfacial energies, viscosities, and heat conductivities.

Table II
Growth Rate Expressions for Spherulites in an Incompatible Polymer–Polymer System

description	expression[a]
rejection of the dispersed phase	$G \cong \dfrac{G_1}{1 + E_1/RT_c} \cong \dfrac{G_1}{1 + \dfrac{3\mu_m c \eta_m G_1 R'}{2\rho_m r^2 RT_c}}$
engulfment of the dispersed phase	$G = G_1 \exp\{E_3/RT_c\}$ $= G_1 \exp\{-(3c\mu_m \Delta F/(\rho_m r RT_c)\}$
deformation of the dispersed phase	$G = G_1 \exp\{E_4/RT_c\}$ $= G_1 \exp\{-U(k)(3c\mu_m \gamma_{ps}/(\rho_m r RT_c)\}$

[a] G_1 is the undisturbed growth rate; μ_m is the molecular weight ofthe repetitive unit; c is the volume concentration of the second component in the blend; η_m is the viscosity of the matrix; R' is the temporary radius of the spherulite; ρ_m is the density of the matrix; r is the radius of the ionomer domains; $U(k)$ is a deformation function; R is the gas constant; and T_c is the crystallization temperature.

In this study, only marginal differences in the radial growth rates of polypropylene spherulites resulted from the addition of ionomer. This is as expected for immiscible blends with minimal interfacial interactions. Indeed, the freeze-fractured surface of a compression-molded sample of 80% PP/20% ionomer blend (Figure 4), as observed by scanning electron microscopy,[6] shows the ionomeric phase as spherical domains embedded in the polypropylene matrix with very little adhesion between the two phases. On this basis, it is unlikely that there is significant adhesion between the phases in the melt, indicating that ΔF is approximately equal to zero or positive. Thus, the relative extent of rejection and engulfment of the ionomer domains will be determined by the rate of crystallization and the size of the dispersed phase.

At low ionomer concentrations and low crystallization temperatures, significant energy dissipation must be involved in rejection of the domains as the spherulite grows. This energy loss retards the radial growth of the spherulites, as seen in Figure 3. Therefore, the radial growth rate is depressed as compared to that of pure polypropylene.

The binary blends also consistently show a greater primary nucleation density than pure polypropylene at all compositions and crystallization temperatures (Figure 5). The ionomer is acting as a nucleation site for the poly-

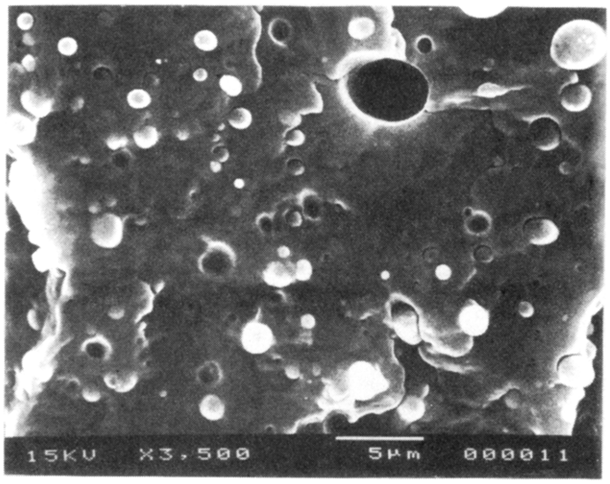

Figure 4. SEM photomicrograph of the freeze-fractured surface of the compression-molded sample of the 80% PP/20% ionomer blend[6] as obtained from the Brabender mixing chamber. The ionomeric phase is seen as the spherical entities.

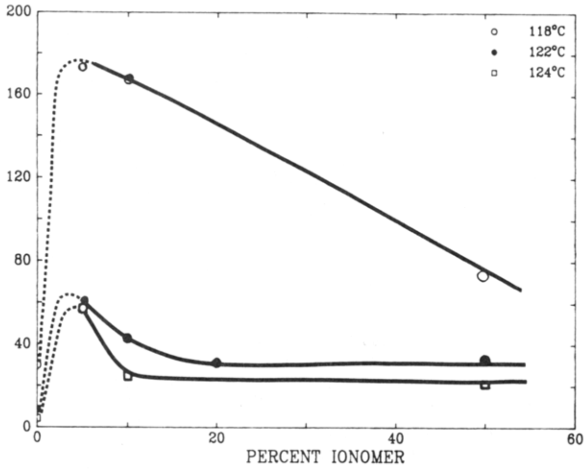

Figure 5. Nucleation density, after 10 min melt time, as a function of the percent ionomer in the blend, at different crystallization temperatures.

propylene spherulites, as suggested previously by Willis et al.[6] based on DSC observations. This effect is most pronounced for the 95% PP/5% ionomer blend, possibly reflecting the smaller ionomer domain size and concomitantly larger surface area available for nucleation. A similar synergistic effect upon nucleation was observed by Martuscelli et al.[18] for iPP/PIB blends. The effect, as well as the observed reduction in the growth rate, was attributed to the preferential dissolution of imperfect crystals (molecular fractionation). It is possible that these processes are also responsible for the observations shown in Figure 5 for the polypropylene/ionomer blends.

Effect of Coalescence on the Growth Rate. The overall morphology of the blends containing 5% ionomer, as viewed without cross polarizers at a temperature of 124 °C, is illustrated in Figure 6. It shows the presence of the ionomer phase as approximately spherical domains embedded in the polypropylene spherulites. Initially, a linear increase in the average domain size with melting time is observed, for those domains of sufficient size to be detected microscopically, with a change in slope at approximately 45 min as seen in Figure 7. By comparison, for the 50% PP/50% ionomer blend, the domains are much larger and a simple linear increase in the average size with melting time is observed, as seen in Figure 8. It should be noted that, in the 50% PP/50% ionomer blend, the measured diameters have extended beyond the thickness of the film. Thus, the domains are no longer spherical as in the 95% PP/5% ionomer blend but have taken the form of disks. If volumes, rather than diameters, are plotted as a function of melt time, calculated for spheres in Figure 7 and disks in Figure 8, then identical trends are observed. The important point is that the size increases with melt time, regardless of the shape of the dispersed phase. Furthermore, the rate of increase

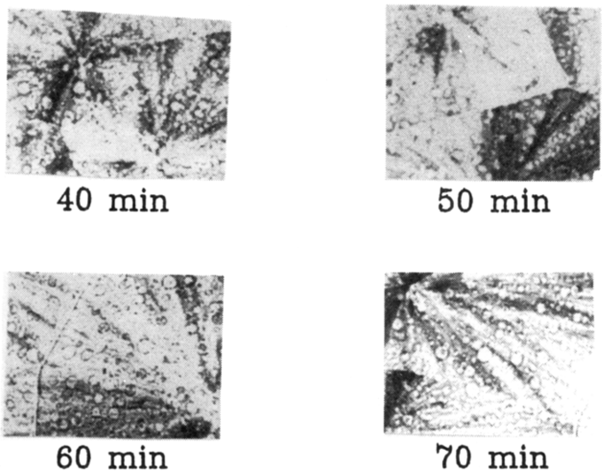
40 min
50 min
60 min
70 min

Figure 6. Photomicrographs illustrating the coalescence of the ionomer domains as a result of repeated melting (10-min period) and crystallization for the 95% PP/5% ionomer blend, at a crystallization temperature of 124 °C.

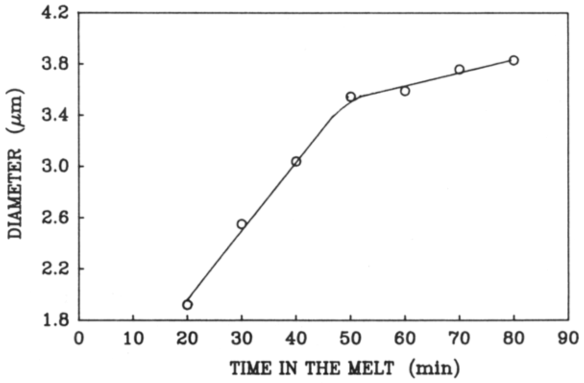

Figure 7. Increase in the size of the ionomer domains with repeated melting (10-min period) and crystallization, for the 95% PP/5% ionomer blend, at a crystallization temperature of 124 °C. The time indicates the cumulative melt time.

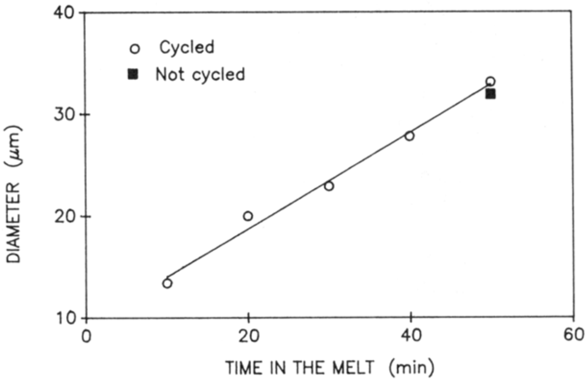

Figure 8. Increase in the size of the ionomer domains with repeated melting (10-min period) and crystallization, for the 50% PP/50% ionomer blend, at a crystallization temperature of 124 °C.

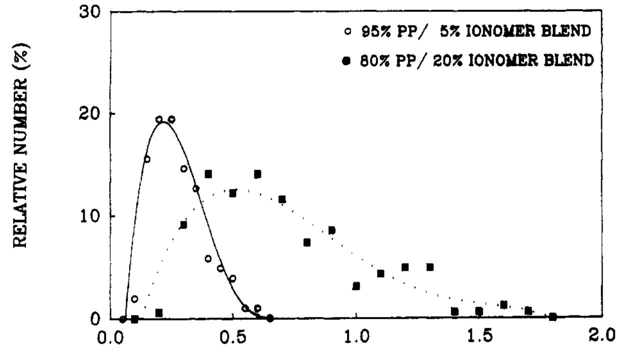

Figure 9. Ionomer domain size distribution in the 95% PP/5%ionomer blend and 80% PP/20% ionomer blend obtained from cryogenically fractured surfaces.

is much greater for this blend than for that containing 5% ionomer.

The increase in ionomer domain size could be due to either or both of two factors, namely, phase separation during the time spent in the melt and/or rejection (or pushing of the domains) during repeated crystallization. As shown in Figure 7, for the 95% PP/5% ionomer blend, the average size of the ionomer domains increases rapidly until the fourth crystallization. Upon further crystallization, the rate of increase in the average size of the domains is diminished. This suggests that, at the point where the change in slope occurs, there is a depletion in the number of domains of radius less than a critical size. Ionomer domains of radius less than the critical size are being rejected by the crystallizing front and as a consequence are coalescing. Therefore, coalescence not only is occurring while the polypropylene is in the melt phase but also is induced by crystallization. In the case of the 50% PP/50% ionomer blend, where domains are larger than the critical size, coalescence occurs predominantly in the melt. This was confirmed by separate experiments that showed increases in domain size with melt time when the crystallization steps were omitted, also shown in Figure 8 (filled square).

The initial size distribution in the ionomer phase in the blends was determined from cryogenically fractured surfaces observed using scanning electron microscopy and is shown in Figure 9.[6] The size distributions after repeated crystallizations at 124 °C as determined using photomicroscopy are shown in Figure 10. The sharp drop-off in the number of domains for the first crystallization (Figure 10) probably reflects limitations in detection at the magnification level used. It is evident that initially it is predominantly the smaller domains (less than 1 μm) that are being rejected by the crystallizing front and coalescing into the larger ones. In the case of the 50% PP/50% ionomer blend (Figure 8), the size of the domains is well above that critical size. Even though some ionomer may be present within interlamellar regions, which may give rise to some rejection, domain size increase is occurring predominantly as a result of coalescence during the time that the polypropylene is in the melt.

As mentioned before, it is predicted that the radial growth rates of spherulites in phase-separated polymer blends can be influenced by the size of the dispersed particles. Estimates were made of the effect of domain size on energy terms E_1, E_3, and E_4, using the equations of Bartczak and co-workers[19] shown in Table II, for the PP/ionomer blends. The results, assuming $\Delta F = 1$ erg/cm^2 and $\gamma_{ps} = 1$ erg/cm^2, for the 95% PP/5% ionomer blend at a spherulitic radial size of 30 μm and a growth rate of 0.92 μm/s, are shown in Figure 11 for the crystallization temperature of 118 °C. It should be noted that the interfacial free energies were chosen in accordance with results previously reported for polypropylene/polyethylene[23] at 140 °C. The viscosity of the blend at the crystallization temperature was estimated from measured viscosities at higher temperatures (~200 °C)[24] and low shear rate (17 s^{-1}) assuming Newtonian flow and using the concept of activation energy from the Arrhenius equation. These equations predict that, at small domain size, the energy of rejection has a considerable influence on the spherulitic growth rate. The energies due to deformation and occlusion make much smaller contributions to the total energy dissipation. Increasing the interfacial free energy between the polymers in the blend has the effect of increasing the energy of deformation and engulfment. However, for reasonable changes (ΔF and γ_{ps} from 0.1 to 10 erg/cm^2), these energies remain much smaller than the energy of rejection. As the ionomer domain size increases, the total of these energies decreases in magnitude until, for domain size greater than 4 μm, they are essentially negligible.

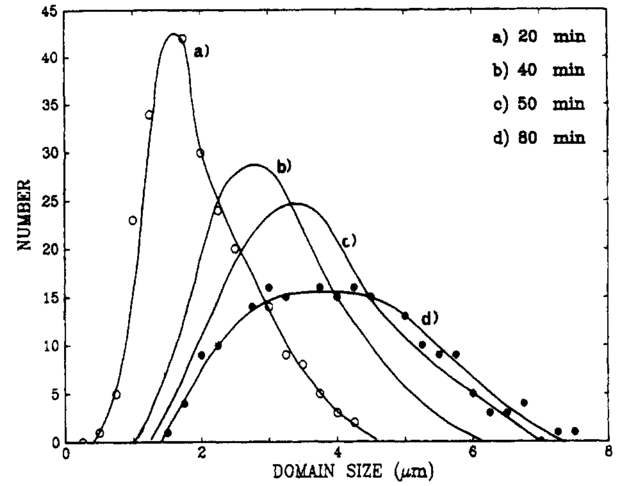

Figure 10. Ionomer domain size distribution in the 95% PP/5% ionomer blend at total melt times of (a) 20 min, (b) 40 min, (c) 50 min, and (d) 80 min and a crystallization temperature of 124 °C. The melt times correspond to repeated melting and crystallization at 10-min intervals.

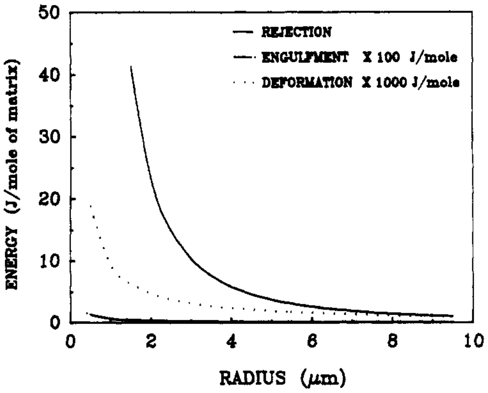

Figure 11. Estimated energies of rejection, engulfment, and deformation for the 95% PP/5% ionomer blend as a function of ionomer domain size at a crystallization temperature of 118 °C.

The inclusion of these energy terms in eq 2 allows the prediction of the growth rate at a certain ionomer domain size. As shown in Figure 12 for the crystallization temperature of 118 °C, an increase in the radial growth rate of the spherulites is predicted, with an increase in domain

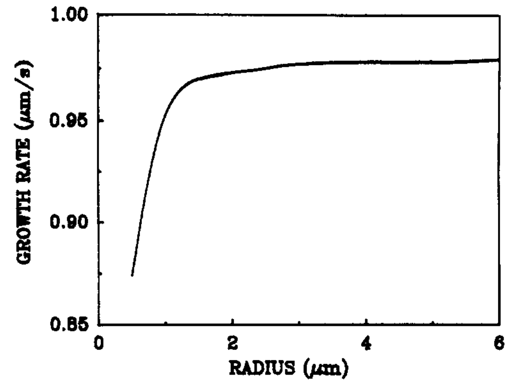

Figure 12. Theoretical growth rate dependence on the ionomer domain size as estimated for the 95% PP/5% ionomer blend at a crystallization temperature of 118 °C.

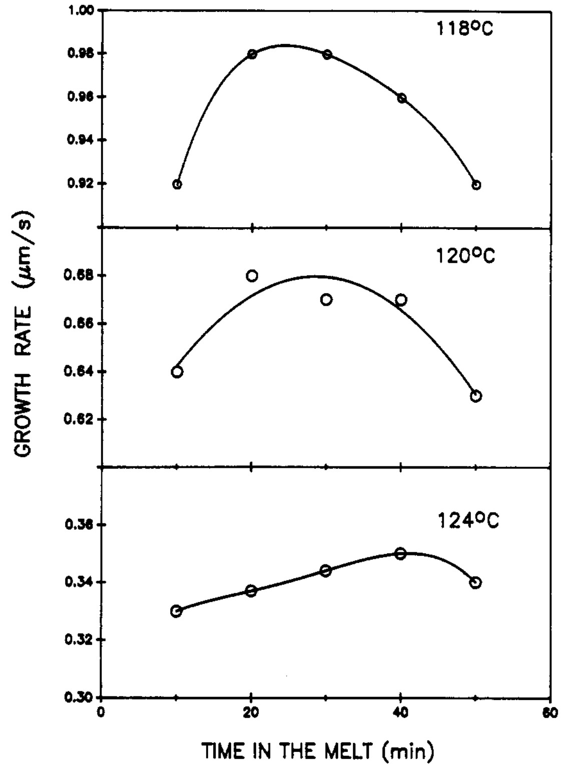

Figure 13. Growth rate dependence of the 95% PP/5% ionomer blend with repeated melting (10-min period) and crystallization at various crystallization temperatures.

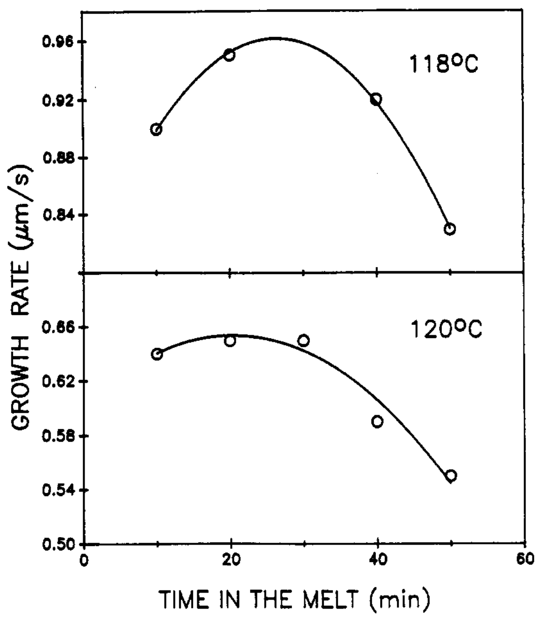

Figure 14. Growth rate dependence of the 90% PP/10% ionomer blend with repeated melting (10-min period) and crystallization at various crystallization temperatures.

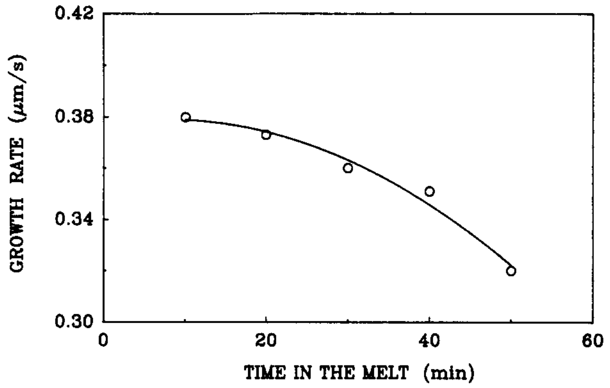

Figure 15. Growth rate dependence of the 50% PP/50% ionomer blend with repeated melting (10-min period) and crystallization at a crystallization temperature of 124 °C.

size leading toward the growth rate of the pure polymer at the same temperature. Above a certain domain size (4 µm), where the energy of rejection is essentially negligible, the growth rate of the crystallizing polymer is no longer affected by the presence of the second component.

The effect of domain size on the growth rate of the polypropylene spherulites can be observed experimentally when blends containing 5% and 10% ionomer are repeatedly melted for 10 min and crystallized. As shown in Figures 13 and 14, an initial increase in the radial growth rate is observed, followed by a decrease when the sample has been crystallized several times. This gives rise to a maximum growth rate which is dependent upon the blend composition and the crystallization temperature. It is interesting to note that if the maximum radial growth rates, rather than the values for 10 min, are plotted in Figure 3, the growth rates are essentially independent of ionomer concentration at all temperatures. When the 50% PP/50% ionomer blend is repeatedly crystallized, only a decrease in the radial growth rate is observed, as shown in Figure 15.

The initial increase in the growth rate (Figures 13 and 14) is mainly due to the rejection of the smaller ionomer domains (less than the critical size) into interspherulitic regions. Since the size of the domains in the 95% PP/5% ionomer blend is initially much smaller than that of the 90% PP/10% ionomer blend as demonstrated in Figure 9, the growing front requires more energy to effect their rejection. Consequently, the initial growth rate is reduced by a greater extent than in the 90% PP/10% ionomer blend.

Through coalescence during crystallization and melting, the domains increase in size such that a significant fraction is above that critical size. During subsequent crystallization, the growing front dissipates less energy in rejecting these domains, due to their larger size, and a radial growth rate increase is observed leading to the maximum. As mentioned previously, the maximum growth rate corresponds closely to the radial growth rate obtained for pure polypropylene at the same temperature. Furthermore, at a temperature of 124 °C, the maximum growth rate for the 95% PP/5% ionomer blend occurs at relatively the same time as the change in slope observed for the domain size increase with melting time (Figure 7).

This strongly supports the idea that rejection of the ionomer domains affects the coalescence mechanism, which in turn directly affects the radial growth rate of the polypropylene spherulites.

The speed of the crystallizing front, at any constant small domain size, also influences the perturbation observed in the growth rate of the spherulites. At high crystallization temperatures, where the growth rate is relatively slow, less energy is dissipated to effect the rejection of the ionomer domains. As a result, the initial growth rate is not decreased, with respect to pure polypropylene, to the extent that it is for a sample that is crystallized at lower temperatures.

Although the increases in the radial growth rates with melt time, observed at short times for the samples containing 5% and 10% ionomer, are in accordance with the equations derived by Bartczak, the maximum in the growth rates and subsequent decreases are not consistent with the theoretical predictions. Two explanations can be offered: (1) Viscosity increases with melt time. Since the transport term in the classical Fischer–Turnbull equation can be described in terms of the WLF equation, increases in viscosity after several crystallizations would be expected to decrease the radial growth rate. However, an increase in viscosity after coalescence of ionomeric domains seems rather unlikely. Furthermore, the direct verification of such an effect is very difficult, since it requires a measurement of the viscosity of the matrix polymer in the blend, and this is not a trivial task. (2) Limited miscibility of low molecular weight fractions of ionomer in the polypropylene would seem to offer a better explanation. Increasing quantities of this fraction of ionomer during repeated melting would result in a diminished radial growth rate. Once the effects of rejection/engulfment/deformation become negligible and the growth rate has reached its maximum, this ionomer, present within the polypropylene, would be responsible for the observed hindrance to crystallization. Therefore, throughout the crystallization study, there is competition between the influences of phase size and the influence of limited solubility on the growth rate. The process is not of a sequential nature but a direct competition until such time as the domains are large enough that they no longer play a role in the crystallization process (Figure 15).

Crystallization Behavior of the Type III Spherulite. The complex crystalline structure of polypropylene manifests itself not only at the crystal lattice level but also at the level of the polarizing microscope where a variety of spherulite types have been classified by their appearance in crossed polarized fields.[16]

In the temperature range of 118–126 °C, a second spherulitic morphology, appearing highly luminous amidst darker spherulites, was noted and can be seen in Figure 16. The grainy structure observed in this photograph is due to the ionomer trapped within the polypropylene spherulites. This spherulitic appearance was classified as type III by Padden and Keith.[16] It was later shown[25–26] that this spherulitic morphology crystallizes with the hexagonal, β, crystal structure while the predominant form (type I, in this study) crystallizes with the monoclinic, α, structure. It has also been found[16,25,27] that once type III spherulites nucleate, their rate of radial growth is 20–70% faster than that of type I.

During this study, the type III spherulites were found to behave similarly to the predominant spherulitic form with respect to physical interactions with the ionomer domains. In Figure 17, a plot of the growth rate as a function of time in the melt shows a very rapid initial radial growth rate increase, followed by a decrease toward longer total melt times. However, when this plot is compared to that of type I at the same composition and temperature (Figure 13), the depression of the growth rate at a short melting time is found to be much larger. The radial growth rate of the type III spherulites is 30% greater than that of the type I spherulite at the same crystallization temperature (120 °C) and is consistent with observations previously reported by Norton and Keller.[27] Therefore, the more significant depression of the initial growth rate is due to the larger quantity of energy required to effect the rejection of the ionomer domains.

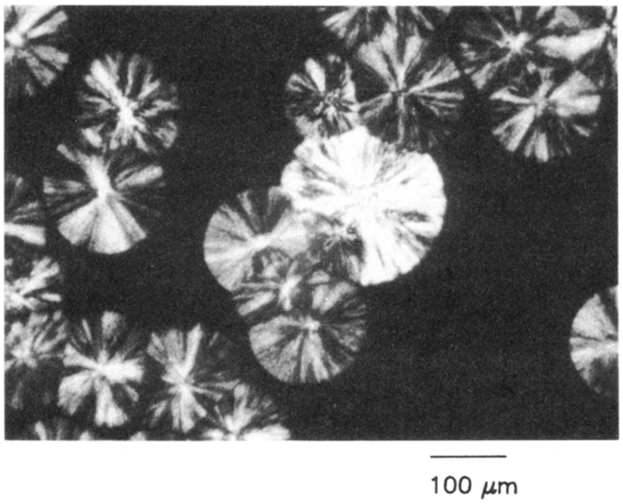

Figure 16. Type III spherulitic morphology (bright) amidst the much darker type I as observed for the 90% PP/10% ionomer blend at a crystallization temperature of 120 °C.

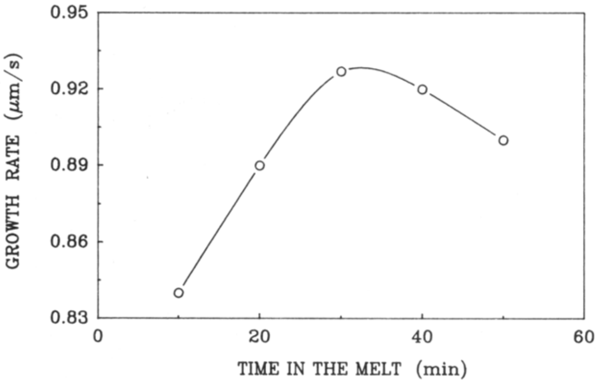

Figure 17. Growth rate dependence of the type III spherulite with repeated melting (10-min period) and crystallization in the 90% PP/10% ionomer blend at a crystallization temperature of 120 °C.

Conclusion

The spherulitic growth of polypropylene in binary polypropylene/ionomer blends is disturbed to a certain extent by the presence of the ionomer component in the melt. In fact, for the blend that contains 5% ionomer, a small depression of the radial growth rate is observed at a temperature where the crystallization proceeds rapidly. This depression is due to energy dissipated by the growing polypropylene spherulitic front in rejecting the ionomer domains. The dispersed ionomer is also found to act as a nucleation site for the polypropylene spherulites. The nucleation effect is more pronounced at lower ionomer contents possibly due to the smaller ionomer domains being more efficient nucleation sites due to the greater surface area available for nucleation.

Coalescence of the ionomer domains occurs during the time spent in the viscous melt. However, the coarsening of the dispersed ionomer appears to be accelerated when the sample is repeatedly melted and crystallized. This suggests that a crystallization-induced type of coalescence is also occurring. A combination of these two effects results in a linear increase of the domain size with time as a sample is repeatedly melted for 10 min and crystallized. This coalescence phenomenon as well as the "speed" of the crystallizing front is shown to have an effect on the radial growth rate of the polypropylene spherulites. A radial growth rate depression occurs as the spherulite is rejecting the second component, the effectiveness of which is dependent on the crystallization temperature. Maximum growth rates are observed at the point where the rejection of the dispersed domains is at a minimum or the size of the dispersed phase is well above that critical size required for rejection. Once the domain size is greater than the critical size, coalescence occurs predominantly in the melt. After this point, the radial growth rate decreases as the ionomer domain size is increased. This radial growth rate decrease beyond that maximum cannot be explained using the equations for rejection, engulfment, and deformation.

Future work will involve studies of the influence of the chemical characteristics of the ionomer (such as functionalities, neutralization, etc.) on the crystallization and coalescence phenomena of polypropylene/polyethylene-based ionomer blends. By modifying the chemical structure of the ionomer, the interfacial free energy between the matrix polymer and the dispersed phase will be changed, which would yield more information about the importance of interfacial energies on the crystallization kinetics of an immiscible blend.

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Notes

Variable-Temperature FT-IR Studies of Organic Carbonate Solutions

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Introduction

Although the intermolecular structure of amorphous Bisphenol A polycarbonate (BPAPC) is ill-defined, a number of smaller, well-characterized BPA-based carbonate systems have been examined extensively.[1] These past efforts have been oriented toward understanding how variations in fundamental conformation and structural packing at the molecular level are manifested in the macroscopic properties of these materials. Such intra- and intermolecular interactions in BPAPC analogues have been studied by a variety of techniques (principally, NMR, X-ray spectroscopy, and quantum mechanical calculations). To date, no experimental work has been reported on BPAPC using low-temperature solution IR methods.

This paper summarizes our observations of both monomeric and polycarbonate solutions using variable-temperature infrared spectral analysis (VT-IR). These