

Transparency of Recycled Polypropylene Film

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SYNOPSIS

Turbidity of quenched polypropylene films was measured as a function of the film thickness and number of times film was recycled. Turbidity τ is defined by $\tau = (1/d) \ln(I_0/I_t)$, where I_0 and I_t are the intensity of the incident and transmitted lights, respectively, and d is the thickness of the sample. We assume here that most of the attenuation of light is due to scattering from superstructure in the film, such as spherulites, since no characteristic absorption bands are present in the wavelength region studied in this work. Turbidity varied sigmoidally with film thickness. It remained constant when the film thickness was lower than ca. 400 μm and then increased with film thickness and reached a plateau around 800 μm . When the film preparation was repeated, turbidity increased exponentially with the number of recycles. The spherulite size, however, was an invariant against the number of recycles and was dependent upon film thickness. The variation of turbidity with film thickness and the number of recycles is discussed.

INTRODUCTION

Isotactic polypropylene (PP) is one of the most familiar polymers used in industry and in daily life. Turbidity or haze of semicrystalline polymers restricts industrial application because of low transparency, although these polymers usually have superior mechanical properties to amorphous polymers. Therefore, it is of importance to explore methods to reduce turbidity of crystalline polymers.

There are several ways to increase transparency, e.g., (i) to increase the fraction of amorphous phase, (ii) to reduce the size of spherulites, and (iii) to destroy spherulite texture by stretching or by some other method. In order to increase transparency, crystalline polymers are usually thermally quenched or crystallized by adding nucleating agents. Thermal quenching, however, reduces dimensional stability of polymers. Nucleating agents bring a contamination problem when the polymer is used as a container or as wrapping film for food, drugs, and so on. For these purposes, therefore, it is necessary to increase

transparency without thermal quenching or nucleating agents.

As is well known, PP has three kinds of crystallographic states, i.e., monoclinic, hexagonal, and trigonal structures.¹ In addition, the so-called smectic phase is known as a paracrystalline state. This smectic phase is found when molten PP is quenched. However, it is not stable and is transformed to the monoclinic phase by annealing at a temperature higher than 40°C² or 80°C.³ Norton et al.⁴ classified the spherulite structures of PP into five categories according to the nature of the spherulites. Since these spherulites affect the optical properties of PP, it is important to control these crystal and paracrystal structures and their superstructure such as spherulites in order to increase the optical properties of PP.

Idemitsu Petrochemical Co., Ltd.^{5,6} developed a novel method which is a thermal quenching of molten polypropylene by flowing fluid followed by annealing at a given temperature so as to reduce dimensional instability against heat. The films prepared by this method have spherulitic and/or sheaflike textures of a few microns order near the film surface whereas no distinct structure is observed by an optical microscope.^{7,8} Therefore, it is consid-

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ered that the film consists of small crystallites of the monoclinic form and amorphous phase.

In a commercial production process, it is important to get rid of waste product. These are usually recycled so as to improve cost performance. However, this recycling process often brings unfavorable effects, e.g., degradation as well as an increase in turbidity.

In this paper, we investigate film thickness and the influence the number of recycles has on turbidity of polypropylene films, in terms of turbidity measurement, densitometry, and optical microscopy. A further study on film thickness dependence of PP films from the crystallographic point of view will be reported in a forthcoming paper.⁹

THEORETICAL

When light propagates through a film, it is absorbed and scattered by the medium in the film. When the film thickness is thin enough the following equation is given:

$$I_t/I_0 = \exp[-(\tau + \epsilon)d] \quad (1)$$

where I_0 , I_t , τ , ϵ , and d are the intensities of incident and transmitted light, turbidity, absorbance, and the thickness, respectively. In eq. (1), we neglect the contribution of reflection from both surfaces of the medium. In the case of $\tau \ll \epsilon$, eq. (1) can be written by

$$I_t/I_0 = \exp(-\epsilon d) \quad (2)$$

Equation (2) is so-called the Lambert-Beer law. However, in the case $\tau \gg \epsilon$, eq. (1) is written as

$$I_t/I_0 = \exp(-\tau d) \quad (3)$$

Thus the turbidity τ is defined similarly to the absorbance ϵ based on the Lambert-Beer law. Therefore, if the wavelength of the light is chosen to be away from characteristic absorption bands of polypropylene, most of contributions of attenuation of light by the film result from scattering by the film. Since the contribution of absorption, i.e., absorbance, is independent of film thickness whereas that of turbidity is not, the absorption effect shows a negligible or invariant contribution to the thickness dependence of the attenuation of light. Therefore, the turbidity τ is defined by eq. (3) in this paper.

EXPERIMENTAL

Isotactic polypropylene (PP) having number and weight average molecular weights of 5.8×10^3 and 40.7×10^4 , respectively, was supplied by Idemitsu Petrochemical Co. Ltd., Japan. The melt index was 2–3 g/10 min.

Figure 1 shows the method of the film preparation. PP films were prepared from PP pellets with a hot press. PP pellets were melted between a set of ferrotype plates for 30 min at 250°C under a pressure of 150 kg/mm², and then quenched with ice water. The film thickness was varied from 100 μ m to 1 mm by changing the thickness of spacers. These as-prepared samples were coded as P0s. First recycled samples (P1s) were prepared with the same manner as the P0 films except that small pieces (ca. 5 \times 5 mm²) of P0 films were used instead of PP pellets. Second recycled films (P2s) were prepared from small pieces of a P1 film. Five successive recycled films from P1s to P5s were thus prepared. The film thickness was kept constant at either 400 or 600 μ m during the recycling process so as to avoid effects of the film thickness dependence.

Turbidity was measured with a UV-visible light spectrometer UV-160 (Shimadzu Co., Ltd). The wavelength was 632.8 nm. Samples were dipped in a medium whose refractive index is close to PP so as to reduce reflection of the incident light on the surface of the sample. Tetrachloroethane having a refractive index of 1.4573 was chosen as the medium.

Densitometry was conducted with a density gradient column prepared with ethanol and water.

The size of spherulites was measured with a small angle light scattering apparatus which has a linear image sensor developed in this laboratory.¹⁰ The spatial resolution of the image sensor is 28 μ m.

In addition to those measurements, polarized microscopy and wide angle X-ray diffractometry were

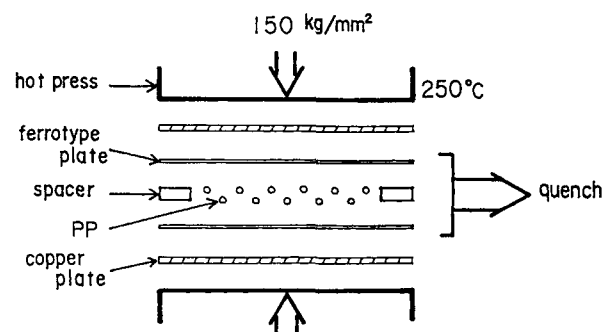


Figure 1 Schematic representation of the film preparation.

concluded in order to clarify the crystalline structure of the samples.

RESULTS AND DISCUSSION

Thickness Dependence of Turbidity

Figure 2 shows the variations of turbidity as a function of film thickness for as-prepared samples (P0s). Turbidity increases sigmoidally with increasing film thickness. It remains constant when the film thickness is less than 400 μm and then gradually increases with increasing film thickness. If the superstructure which affects optical properties of the film does not change with thickness, turbidity should remain constant since the turbidity is normalized with thickness [see eq. (3)]. Therefore, Figure 2 indicates that superstructure changes with increasing film thickness.

Figure 3 shows the thickness dependence of spherulite radius. The spherulite radius was estimated from a peak maximum in the intensity distribution curve of so-called H_v light scattering patterns by using the following equation^{11,12}:

$$(4\pi/\lambda)R \sin(\theta_{\max}/2) = 4.09 \quad (4)$$

where λ and θ_{\max} are the wavelength of the light in the medium and the scattering angle at peak maximum, respectively. The variation of spherulite radius is well correlated with that of turbidity, indicating that turbidity change with thickness is mainly due to variation of spherulite radius. Since the turbidity is related to the integrated scattered intensity over the reciprocal space, it is a function of the spherulite radius and the number of spherulites in the irradiated volume.¹¹ However, it also depends

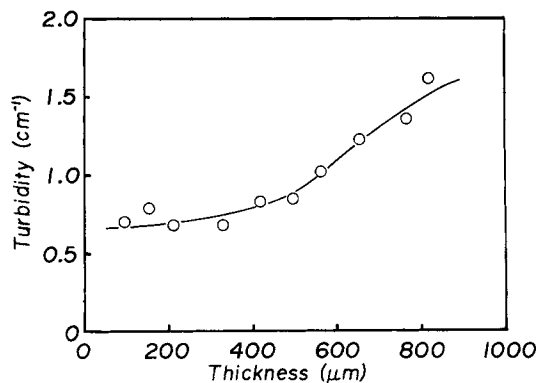


Figure 2 Variations of turbidity as a function of film thickness for as-prepared samples (P0s).

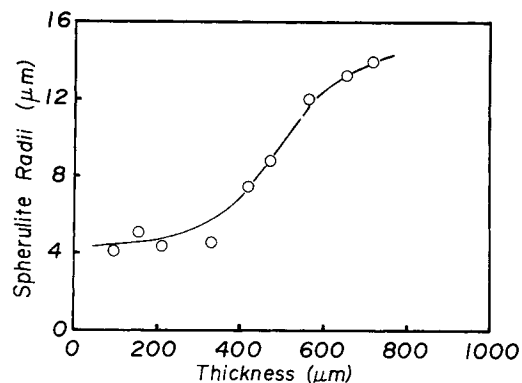


Figure 3 Thickness dependence of spherulite radius for P0.

on the difference in polarizabilities along the tangential and radial directions of the spherulite and of the medium. Therefore, it is rather difficult to relate the turbidity with the spherulite radius in an explicit form. Qualitatively speaking, it can be stated that the bigger the spherulite, the greater the turbidity since the scattered intensity from a spherulite is proportional to the square of the volume of the spherulite.

Figure 4 shows the thickness dependence of density. Although the density increases with thickness, it does not show a sigmoidal increase as observed in turbidity and spherulite radius. The increase in density indicates that the degree of crystallinity changes with thickness and/or the crystal transition from smectic to monoclinic form occurs with thickness.

Figure 5 shows wide angle X-ray diffraction intensity distributions for P0 films having various film thicknesses. Up to 584 μm of the film thickness, the smectic form is dominant as is often observed in quenched PP. For thicker films, the monoclinic structure becomes dominant, which is usually ob-

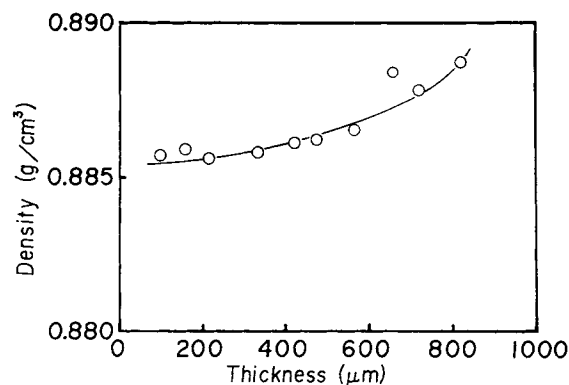


Figure 4 Thickness dependence of density.

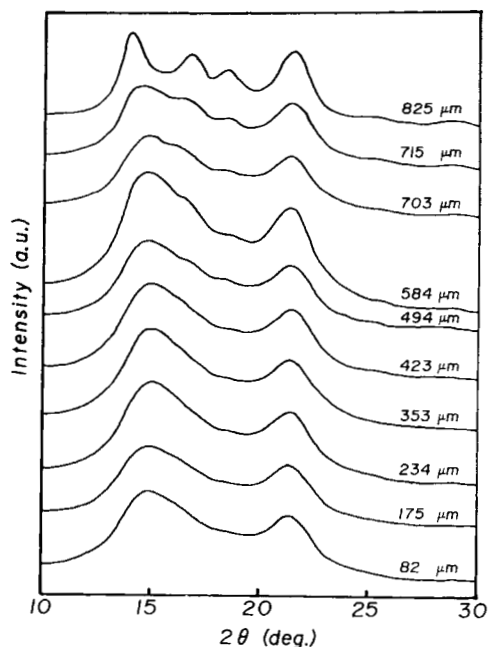


Figure 5 Wide angle diffraction intensity distributions for P0 films having various film thicknesses.

served for gradually crystallized PP. Since quenching effects become less effective with increasing thickness, crystal transition from the smectic to monoclinic structure occurs and growth of spherulites takes place.

Figure 6 shows the H_v light scattering patterns for P0 films. For thin films, e.g., 157 and 332 μm

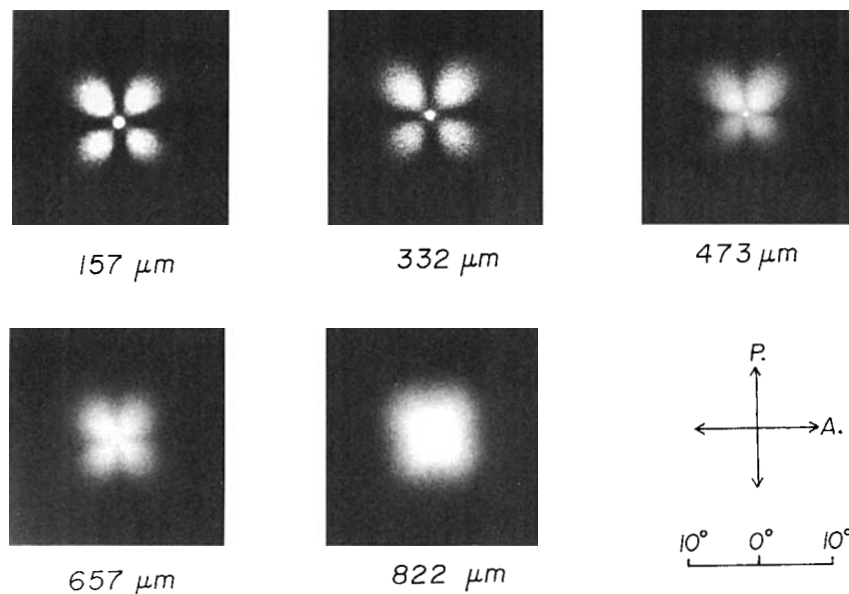


Figure 6 H_v light scattering patterns for P0 films.

thick films, clear four leaf patterns, typical of spherulites, are seen in those figures. With increasing film thickness, however, those patterns become diffuse due to multiple light scattering. This multiple light scattering also gives rise to an increase in turbidity.

It is of interest to note that the crystal transition, multiple scattering, and the steep increase in the spherulite radius occur around the same film thickness. This phenomenon may be explained as follows: Quenching is reduced for the films of thickness more than 400 μm in this particular quenching condition. This thickness is not essential since it may vary by changing the quenching condition. However, since ice-water quenching is one of the simplest and cheapest quenching methods, it is worthwhile to note this thickness as a characteristic value for PP.

Fujiyama et al.¹³ studied the structure of the skin layer in an injection molded polypropylene and found the presence of about a 600- μm -thick skin layer by polarized microscopy. The mold temperature was 40°C. They also reported that the β (hexagonal) form was found in the skin layer in addition to the α form (monoclinic) because of the presence of the (100) plane of the β form in the wide angle X-ray diffraction (WAXD) pattern. In our case, the skin layer is composed of the smectic form as discussed above. Since the smectic form has the strongest WAXD peak at the same angle to the (100) plane as the β form, the skin layer studied by Fujiyama et al. can be explained as the smectic form. Taking into account that the injection-molded PP was prepared under shear and crystallized at differ-

ent temperature, the difference in thicknesses of the skin layer between the injection-molded PP and the PP film studied here seems to be reasonable. Further discussion on the crystallographic structure of the skin layer of quenched PP films will be reported in the forthcoming paper.⁹

Effects of Recycling on Turbidity

For the recycling experiments, the film thickness was fixed to be either 400 or 600 μm since the crystal structures of the films of these thicknesses are different. The former is dominated by the smectic form and the latter by the monoclinic form (see Fig. 5, for example). This difference may affect the optical properties of PP films by recycling.

Figure 7 shows the dependence of density on times recycled. As shown in the figure, films 600 μm thick always have higher density than those 400 μm thick. With repeating recycling, the density increases for both kinds of films.

Figure 8 shows wide angle X-ray diffraction patterns for PP films having different history. As can be seen in the figure, the smectic form is dominant in P0–P2 whereas the monoclinic form becomes dominant with further increases in the number of recycles. Since the density of the monoclinic form is 0.935 g/cm³ and is greater than the smectic form (0.907 g/cm³)¹⁴, the change in the crystal form is related to the increase in mass density with multiple recycling.

Figure 9 shows *H_v* light scattering patterns for P0–P5. The film thickness was ca. 400 μm. As can be seen, the scattering patterns become more intense and diffuse by increasing the number of recycles. However, the angle at peak maximum was almost constant irrespective of number of recycles.

Figure 10 shows the spherulite size change with recycling. The number of recycles is indicated by

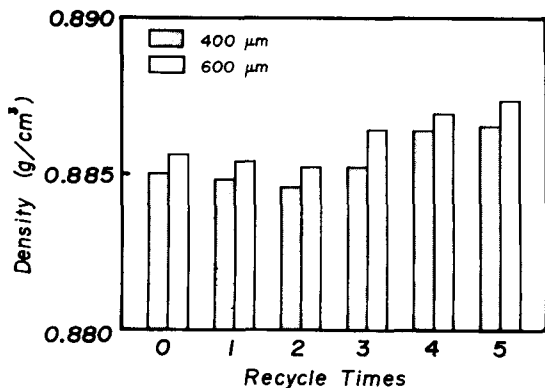


Figure 7 Dependence of density on number of recycles.

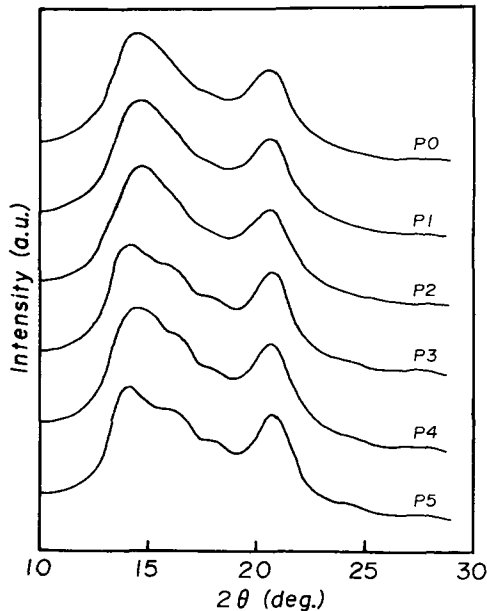


Figure 8 Wide angle X-ray diffraction patterns for PP films having different history.

different symbols. The dashed line shows the spherulite size variation of P0 film, i.e., films prepared from PP pellets. The figure shows that the spherulite size is dependent only on the film thickness but not on the number of recycles.

Figure 11(a) shows the dependence of turbidity on the number of recycles for films 400 and 600 μm thick. Turbidity increases with multiple recycles. Since the turbidity is defined by eq. (3), the increase in turbidity from 0.8 to 3.2 means a decrease in transmittance from 0.90 to 0.66. It is interesting to note that the turbidity seems to increase with the number of recycles roughly in an exponential fashion as shown in Figure 11(b).

Figure 11(b) shows the number of recycles, *t*, and the dependence of ln τ for films 400 and 600 μm thick. Since the data fall onto a straight line, for the films 400 and 600 μm thick, we obtain the following relationship:

$$\tau = \tau_0 \exp(\alpha t) \tag{5}$$

where τ₀ and α are the turbidity of P0 film and a constant, respectively. The values of τ₀ and α were estimated to be 0.738 cm⁻¹ and 0.287 for the 400 μm thick film and 0.830 cm⁻¹ and 0.259 for the 600 μm film, respectively. The thickness dependence of α was not clear in this work. Since the turbidity is a function of the concentration of dispersants, the increase in turbidity indicates an exponential increase

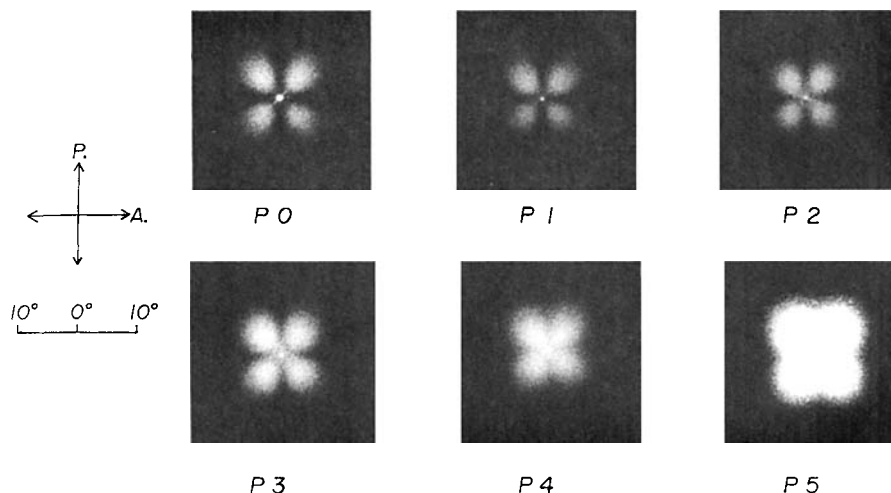


Figure 9 H_v light scattering patterns for P0 to P5. The film thickness is ca. 400 μm .

in spherulite number with the number of recycles. These facts shown in Figures 10 and 11 (a), (b) indicate that spherulites increase in number exponentially but not in size by multiple recycling.

Figure 12 shows photographs of the cross sections of P0, P2, and P5 of 400 μm thick films taken by a polarized optical microscope. White dots in the photograph show individual spherulites. As can be seen, the number of spherulites increases dramatically with multiple recycles. It is worthy to note that spherulites are located near the film surface. In the case of P2, white lines of spherulites running parallel to the film surface are seen, indicating that the spherulites are developed along the surface of P1 film. Since the P1 film was melted at 250°C for 30 min, a self-seeding of nuclei is hardly expected. Localization of spherulites along the part which was near surface before recycling indicates that oxidation and/or degradation of PP occur and the product due to these reactions is providing nuclei for spherulite formation.

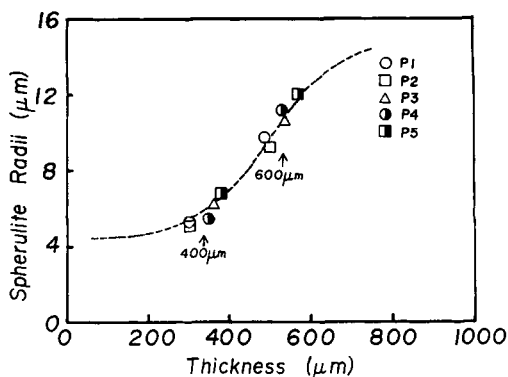


Figure 10 Spherulite size changes on recycling.

Figure 13 shows the dependence of weight average molecular weight M_w , measured with GPC, on the number of recycles. The molecular weight decreases with increasing recycles, which indicates thermal degradation occurs during the melting and hot

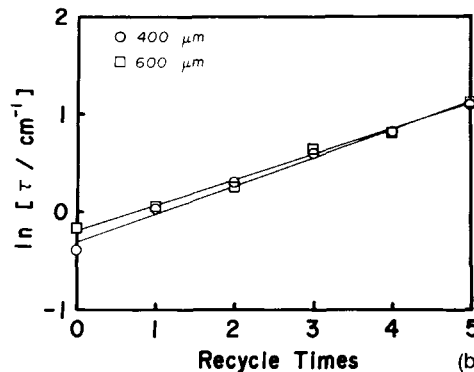
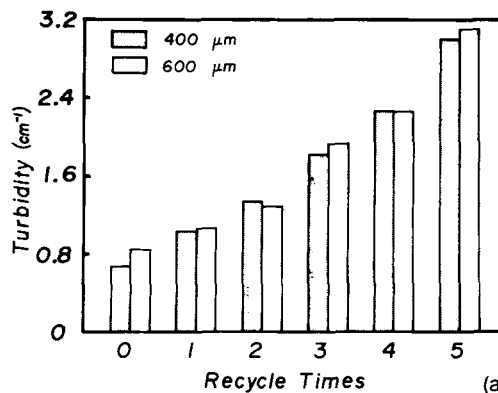


Figure 11 Dependence of turbidity on the number of recycles for films 400 and 600 μm thick: (a) linear plot; (b) semilogarithmic plot.

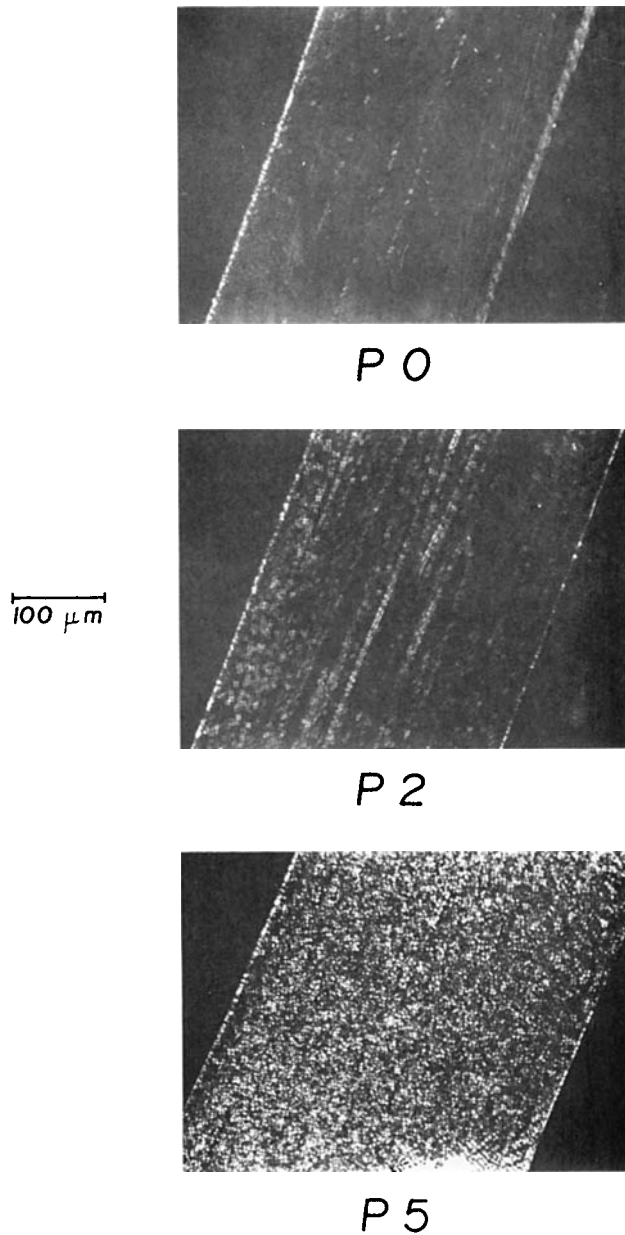


Figure 12 Photographs of cross sections of P0, P2, and P5 of 400 μm thick films taken by a polarized optical microscope.

pressing process. It is reasonable to expect that oxidation of PP takes place as well. This may induce an increase in the number of heterogeneous nuclei for crystallization.

Mechanism of Turbidity Increase by Recycling

According to the experimental results shown above, we propose a mechanism for the turbidity increase from film recycling.

From the facts disclosed in the previous section, it might be reasonable to assume that the turbidity results mainly from scattering from spherulites in the film. The scattered intensity from an assembly of spherulites is a function of the radius and the number of the spherulites, the polarizabilities along the radial and tangential directions of the spherulites, and that of the matrix.^{11,12} However, since the film preparation condition was the same for the recycling experiment and the confirmed fact that the spherulite size did not change with the recycle, we assume here that the scattered intensity is simply proportional to the number of the spherulites, N . Thus the turbidity is also proportional to N ,

$$\tau \sim N \quad (6)$$

Therefore, from eq. (5) one gets

$$N = N_0 \exp(\alpha t) \quad (7)$$

where N_0 and α are the number of the spherulites in P0 film. By taking the differential of eq. (7), one gets

$$dN/dt = \alpha N \quad (8)$$

This means that the increase in N per cycle of film preparation is proportional to N , i.e., the number of spherulites present in the system. This phenomenon can be explained as follows: Nuclei or embryo of nuclei are exclusively formed at the interface between molten PP and ferrotype plate when the film is processed. This may be due to thermal oxidation and/or degradation or contamination from the ferrotype plate. This process may be called "template nucleus formation." When PP films are melted for recycling, these nuclei keep their activity as nuclei,

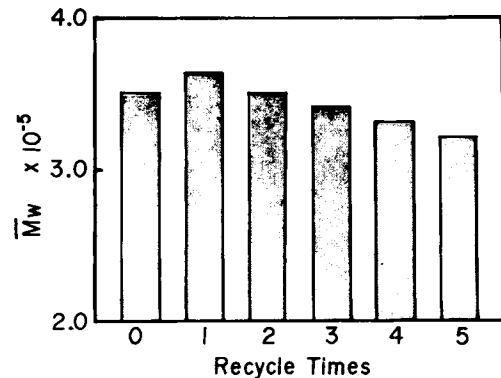


Figure 13 Dependence of weight average molecular weight M_w , measured with GPC, on the number of recycles.

even those that are melted. On cooling, spherulites are formed around them. Since several numbers of film pieces are usually stacked for pressing, the number of nuclei grows exponentially. Therefore, it might be essential to reduce the nuclei formation at the interface so as to keep high transparency of the film on recycling.

CONCLUSION

Turbidity of isotactic polypropylene films prepared by quenching of melted PP into ice water was studied as a function of the film thickness and the number of recycles. Turbidity shows a sigmoidal increase with film thickness. It remains constant for thin films (up to 400 μm) and then increases in the case of this particular quenching method. This phenomenon was in parallel with the variations of mass density and spherulite radius. It is concluded that the reduced quenching effect for thick films induces an increase of spherulites both in number of size, giving rise to the increase in light scattering.

Turbidity increases with increasing numbers of recycles. This is due to an increase in the number of spherulites but not in their size. Spherulites are located more at the area which has been near the surface of the film before melting. Thus the film surface is expected to have more nuclei than inner parts. These nuclei are formed by oxidation, degradation, and contamination during the film preparation process, i.e., template nucleus formation. Since these heterogeneous nuclei do not lose activity even if PP films are melted for recycling, it might

be essential to reduce the number of nuclei formed at the interface between PP and templates.

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