Effects of Molecular Weight and Comonomer Content on the Optical Clarity of Crystallized Syndiotactic Polystyrene Sheets

YI-BIN HUANG, THOMAS E. WESSEL

Engineering Plastics Research and Development, The Dow Chemical Company, Midland, Michigan 48667, USA

Received 30 September 1998; accepted 31 January 1999

ABSTRACT: Clear and high-crystallinity sheets can be prepared consistently from syndiotactic polystyrene (sPS) simply by annealing amorphous sPS sheets at a temperature ranging from 150 to 180°C. The combination of its high clarity and high crystallinity makes sPS sheet suitable for many food/medical packaging applications. A series of sPS polymers with various molecular weight and para-methylstyrene (PMS) comonomer content were used in this study for gaining a mechanistic understanding of the cause for this unusual coexistence of high crystallinity and high clarity. Results show that high molecular weight is preferred for high sheet clarity. The effect of the comonomer content, however, is more complicated; instead of a monotone response to % PMS, the sheet clarity was found to peak at 4% PMS. A mechanism based on the regime growth theory of crystallization was used to interpret successfully the above behavior. Briefly, increasing molecular weight reduces the crystal growth rate and thus shifts the growth pattern to regime III, resulting in more clear sheet. Increasing % PMS reduces both the nucleation and crystal growth rates and thus shifts the growth pattern to either regime I (lower clarity) or III (higher clarity) as controlled by the relative magnitude of the two rate reductions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2455–2461, 1999

INTRODUCTION

Typically, when a semicrystalline polymer crystallizes via quiescent crystallization, it becomes hazy as a result of light scattering by its crystallites. Thus, it is difficult, if not impossible, to obtain both high crystallinity and high clarity from a semicrystalline polymer sheet at the same time.

Syndiotactic polystyrene (sPS), a new polymer currently under development by The Dow Chemical Co. (Dow), was found to break the above rule under certain conditions. It was discovered previously, by researchers at Idemitsu Petrochemical Co. (IPC), that clear and high-crystallinity sPS sheets could be produced by annealing 150-μm-thick amorphous sPS sheets in a narrow temperature range from 150 to 170°C.[1] The crystallinities of the amorphous sheets were lower than 14% initially; after annealing, the crystallinities increased to higher than 40%. The sheets annealed at a temperature between 150 and 170°C were visibly clear, whereas those annealed below 150°C or above 170°C were visibly hazy.

sPS was first synthesized in 1985.[2] It is completely different from conventional, atactic polystyrene in both physical properties and manufacturing method. Synthesized from styrene monomer using metallocene catalysts, sPS has the highest melting point (270°C) of any single-monomer polymerization product. Based on its crystalline nature, sPS offers much higher heat resistance and chemical resistance than the conventional styrenic polymers. And, because sPS

Correspondence to: Y.-B. Huang.

Journal of Applied Polymer Science, Vol. 73, 2455–2461 (1999)
 CCC 0021-8995/99/122455-07

features very low moisture absorption, it provides excellent dimensional stability. Other benefits include low specific gravity, exceptional electrical properties, and high modulus. sPS is expected to compete with liquid crystal polymers, polyphenylsulfide, polyamides, and polyesters in applications such as injection molded electrical and electronic parts, automotive parts, optical films, capacitor films, fibrous filter elements, and food/medical packaging sheets. For the packaging application, sheets with both high crystallinity and high clarity are often needed.

In this study, IPC's study mentioned above was expanded with a series of sPS polymers with various molecular weight and para-methylstyrene (PMS) comonomer content for the following two objectives. First, the authors wanted to see whether a wider temperature range could be obtained. A wider operating window is desired by fabricators for the ease of obtaining consistent clarity in their products. Second, the authors attempted to gain a mechanistic understanding of the cause for this unusual coexistence of high crystallinity and high clarity.

A leading mechanism for interpreting the balance of crystallinity with optical clarity is the regime growth theory introduced by Hoffman and Lauritzen,[3–6] in which three regimes were introduced. Regime I growth, occurring at high temperature, is defined to be the regime where the crystal growth rate (g) is significantly higher than the nucleation rate (i). In this growth pattern, a polymer chain has sufficiently long time to diffuse into the nucleation site and fold into lamella before it meets the next nucleation site at the growth front. Therefore, the resulting polymer structure contains thick and long lamellae and few tie molecules connecting lamellae. The observed properties of the resulting polymer are lower optical clarity, lower toughness, higher crystallinity, and higher modulus.

On the other hand, regime III growth occurs at lower temperature than the regime I growth and is defined to be the regime where the crystal growth rate is significantly lower than the nucleation rate (i.e., $g \ll i$). In this growth pattern, a large number of nucleation sites are formed at the growth front and they can easily interrupt the chain folding process of a polymer molecule. As such, the resulting polymer structure contains thinner and shorter lamellae and more tie molecules. The observed properties are higher optical clarity, higher toughness, lower modulus, and lower crystallinity. Finally, regime II growth is defined to be the regime where g and i are in the same order of magnitude, resulting in polymer structure and properties between those resulted from the above two growth regimes.

PLAN OF STUDY

To investigate whether the "clear crystallinity" observed in sPS sheets is indeed related to the regime growth theory, the authors planned to use a series of sPS polymers with various molecular weights and PMS comonomer contents. Molecular weight would affect chain mobility and, consequently, crystal growth rate. PMS comonomer introduces chain defects in sPS and thus should affect nucleation rate, crystal growth rate, and overall crystallinity.

The authors also planned to focus on high temperature, i.e., temperature higher than 150°C. This is due to a practical concern that the annealing at lower temperature needs much longer time to develop maximum crystallinity. For example, based on the authors' experience, 1 h is needed to ensure the samples annealed at or below 140°C develop maximum crystallinity. This long processing time would not be economically feasible in actual industrial fabrication processes.

EXPERIMENTAL

Materials

The resins used in this study were produced by Dow and converted to 300-μm-thick sheets using a 1-inch single screw extruder (Killion Extruders, Inc., Cedar Grove, NJ). The measured Mw (in g/mol) and NMR-determined mol % PMS of these sheet samples are listed in Table I.

Annealing

The annealing experiments were performed using an Iwamoto BIX-703 batch stretcher (Iwamoto Inc., Japan). The reason to use this Iwamoto stretcher rather than a conventional oven is twofold. First, its large heating chamber with quick hot air circulation offers a more uniform temperature environment than a conventional oven. Second, the clamps in the stretcher provide a convenient mechanism for holding the edges of the sheet during annealing. Without holding the edges, a sheet would deform during the annealing.

Table I Description of the Materials Used in This Study

Sample ID	Aimed Mw Level	Measured Mw (K)	% PMS (by NMR)
A	Low	221	—
B	Low	211	4.7
C	Low	217	10.2
D	Medium	234	—
E	Medium	268	3.5
F	Medium	289	8.8
G	Medium	279	9.8
H	High	333	—

An 11.5 × 11.5 cm sheet of sPS was gripped by the clamps in the center of the heating chamber and annealed for 10 min. The region of the sheet inside the clamped boundary is 10 × 10 cm.

Haze Measurement

A HunterLab Ultrascan spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA) was used to quantify the haze of these samples. Both diffuse transmittance and total transmittance were measured from the samples, and then, % haze was calculated using the following formula:

$$\% \text{ Haze} = \frac{\text{Diffuse Transmittance}}{\text{Total Transmittance}} \times 100$$

DSC Determination of Crystallinity

A differential scanning calorimeter (DSC) (model no. DSC 2910, TA Instruments, Inc., New Castle, DE) was used for the determination of % crystallinity of these samples. DSC scans were run on ca. 10 mg specimens from room temperature to 320°C at the heating rate of 20°C/min. An example of the result from such a scan is shown in Figure 1. The % crystallinity was calculated using the following formula:

$$\% \text{ Crystallinity} = \frac{\text{Heat of melting} - \text{Heat of cold crystallization}}{53.2 \text{ Joules/g}} \times 100$$

where, the 53.2 Joules/g is the heat of fusion of the theoretical 100% crystalline sPS.[7] In this example (Fig. 1), calculating from the heat of melting of 27.28 Joules/g and the heat of cold crystallization of 16.77 Joules/g, the % crystallinity in this sheet was determined to be 19.8%.

Atomic Force Microscopy

Atomic force microscopy (AFM) images were obtained on a Nanoscope III (S/N NS3-519) using a MultiMode Small Sample AFM (S/N 218, Digital Instruments, Inc., Santa Barbara, CA) and "G" scanner head (S/N 161G) to reveal the surface structure of sPS sheets. The microscope was operated in the Tapping Mode™ (trademark of Digital Instruments) where the lever is oscillated at resonance and the feedback control adjusts for constant tapping amplitude. This is still a contact mode of AFM; however, the normal forces and shear forces are greatly reduced over conventional static deflection contact-mode AFM. The images were recorded in constant force mode where the sample z position is adjusted during scanning to keep the r.m.s. (root mean squared) lever deflection constant. This constant force contour image represents the topography. Scanning was carried out in air using commercially available silicon cantilevers (125-μm long) and tips with nominal force constants of 48 N/m (unit #1507, L025). Estimated normal scanning forces under these conditions are in the 10^{-8} to 10^{-9} N range. Digital images are composed of 512 × 512 pixels.

Transmission Electron Microscopy

Thin sections of the sPS sheets approximately 500-Å thick were prepared on a Reichert-Jung Ultracut E ultramicrotome from the interior of the sheets and examined by transmission electron

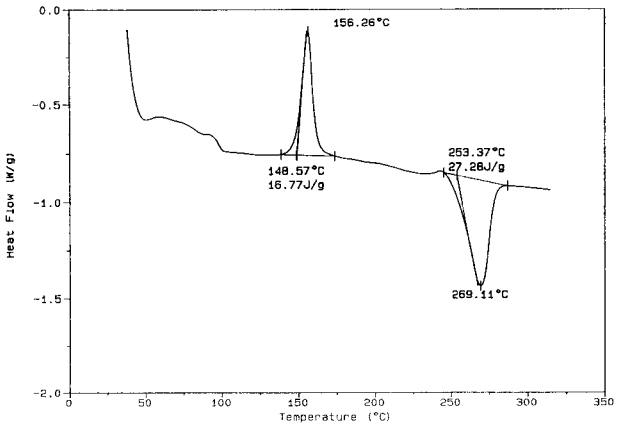

Figure 1 A typical DSC scan for SPS sheets (heating rate: 20°C/min).

Table II Summary of DSC Data for Determination of Percent Crystallinity

Sample ID	Annealing Temp. (°C)	Heat (J/g)		% Crystallinity
		Cold Crystallization	Melting	
A	No annealing	15.11	25.19	18.9
	150	0.00	28.67	53.9
	160	0.00	27.97	52.6
	170	0.00	27.15	51.0
	180	0.00	28.93	54.4
B	No annealing	17.15	21.20	7.6
	150	1.43	20.48	35.8
	160	0.00	20.15	37.9
	170	0.00	20.41	38.4
	180	0.00	20.64	38.8
C	No annealing	17.38	21.59	7.9
	150	1.51	20.04	34.8
	160	0.00	16.47	31.0
	170	0.00	20.97	39.4
	180	0.00	23.40	44.0
D	No annealing	16.77	27.28	19.8
	150	0.00	29.36	55.2
	160	0.00	27.21	51.1
	170	0.00	27.13	51.0
	180	0.00	28.06	52.7
E	No annealing	15.16	20.77	10.5
	150	1.10	21.28	37.9
	160	0.00	20.11	37.8
	170	0.00	21.04	39.5
	180	0.00	21.25	39.9
	190	0.00	24.72	46.5
F	No annealing	16.53	20.07	6.7
	150	0.50	19.05	34.9
	160	0.00	12.23	23.0
	170	0.00	20.02	37.6
	180	0.00	22.82	42.9
G	No annealing	18.39	22.74	8.2
	150	7.15	20.38	24.9
	160	0.00	17.69	33.3
	170	0.00	22.17	41.7
	180	0.00	23.20	43.6
H	No annealing	15.28	24.86	18.0
	150	0.83	25.83	47.0
	160	0.00	24.27	45.6
	170	0.00	23.68	44.5
	180	0.00	24.17	45.4

microscopy (TEM). The sections were collected on a 3-mm TEM grid, stained in RuO_4 vapors for 2 min, and examined in a Philips CM12 TEM operating at 120 KeV to reveal the lamellae structure.

RESULTS AND DISCUSSION

The results obtained from the DSC analysis are summarized in Table II. Annealed at 150°C for 10 min, samples A and D had developed maximum crystallinity; however, the other samples had not fully crystallized as indicated by their nonzero heat of cold crystallization. Annealed at or above 160°C for 10 min, on the other hand, all these sheets had developed maximum crystallinity as indicated by their zero heat of cold crystallization.

The % haze data are shown in Figures 2–4 with error bars showing the 95% confidence inter-

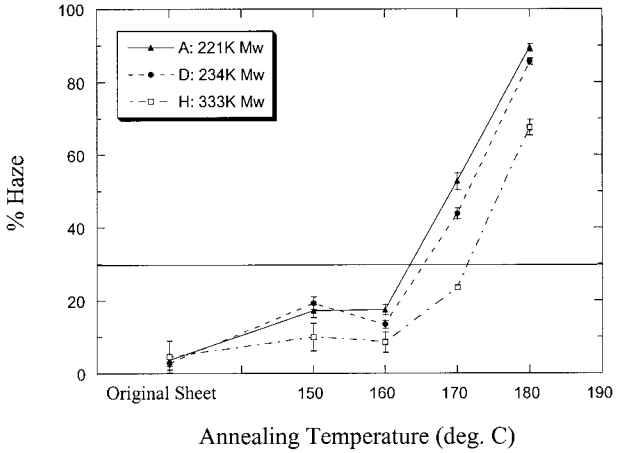

Figure 2 Effect of Mw on the % haze of sPS homopolymer sheets.

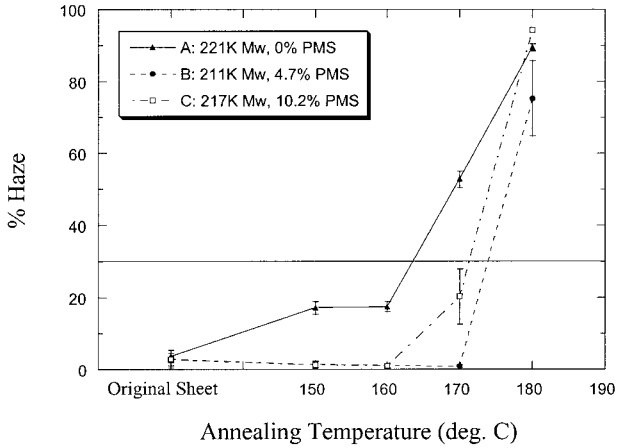

Figure 4 Effect of % PMS on the % haze of low Mw sPS sheets.

vals of the mean % haze. Figure 2 shows the effect of Mw of sPS homopolymer on the % haze of T-jump sheets obtained at various annealing temperatures. A horizontal line is drawn in Figure 2 at 30% haze for the ease of distinguishing clear sheets from hazy ones. The 30% haze was chosen as these 300-μm-thick sheets with higher than 30% haze are visibly hazy while those with lower than 30% haze are visibly clear. With this 30% haze line, one can then define a clear-to-hazy transition temperature of a sample to be the temperature at the intersection of this horizontal line with the line connecting the % haze data points of that sample. It is obvious from Figure 2 that the higher the molecular weight, the higher the clear-to-hazy transition temperature.

Figures 3 and 4 show the effect of % PMS comonomer on the haze of T-jump sheets. Surprisingly, instead of a monotone response to % PMS, the % haze data indicates existence of an optimal % PMS for the highest clear-to-hazy transition temperature. For the medium Mw series, the 3.5% PMS copolymer has the highest clear-to-hazy transition temperature (Fig. 3). For the low Mw series, the 4.7% PMS copolymer has a higher transition temperature than the 10.2% PMS copolymer and the homopolymer (Fig. 4).

To show the above optimal performance more clearly, all the transition temperature data were statistically analyzed via a response surface model[8] to yield a contour plot shown in Figure 5.

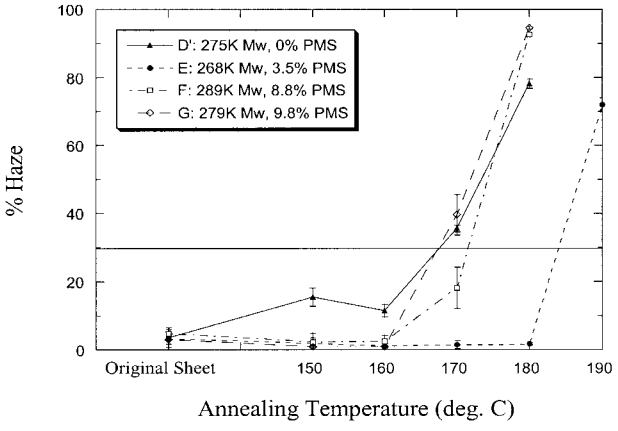

Figure 3 Effect of % PMS on the % haze of medium Mw sPS sheets. (Note: The D′ data points were obtained by interpolation from the data points of samples D and H.)

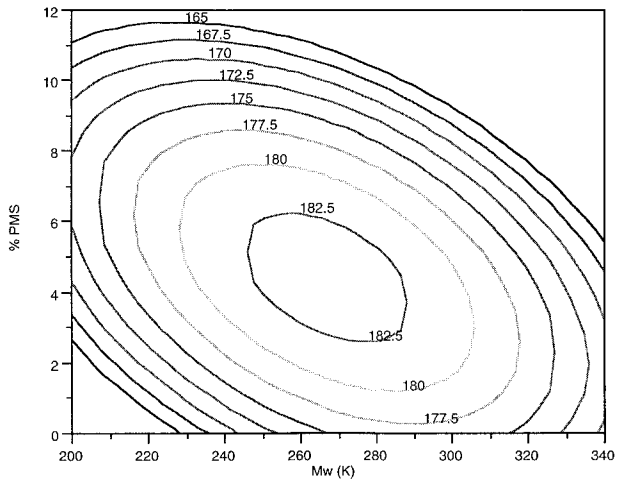

Figure 5 Contour plot showing the combined effect of Mw and % PMS on the clear-to-hazy transition temperature of sPS sheets.

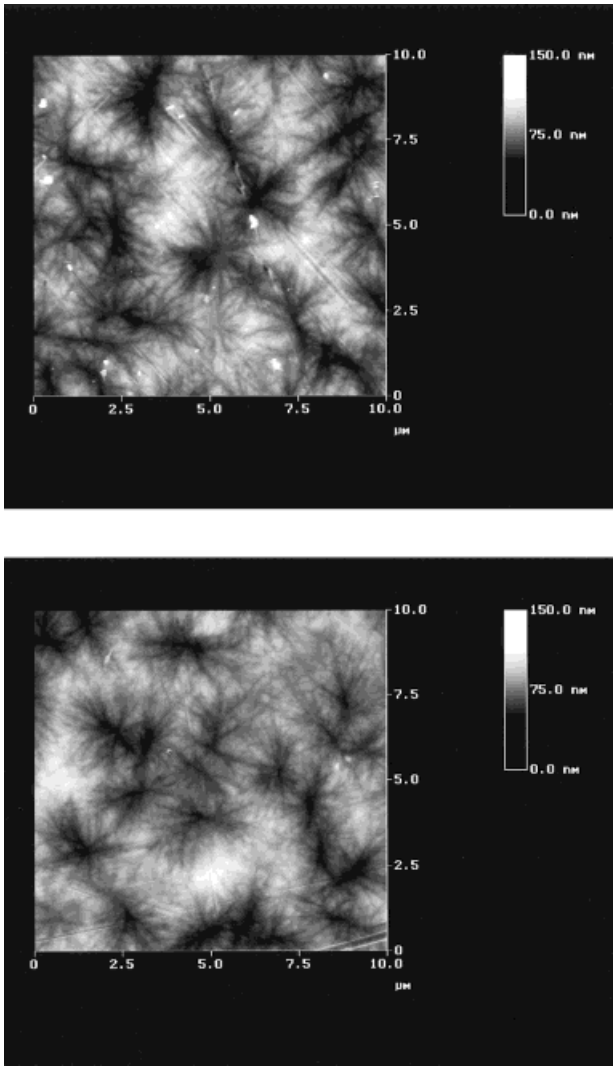

Figure 6 AFM pictures showing spherulite-like structures on the surfaces of both a clear (top, sample A annealed at 150°C) and a hazy (bottom, sample A annealed at 180°C) sPS sheet.

One can see from Figure 5 that the maximum clear-to-hazy transition temperature, higher than 182.5°C, exists around 270 K Mw and 4% PMS. In other words, one can anneal a 270 K Mw, 4% PMS-containing sPS sheet at a temperature as high as 182.5°C and still obtain a clear sheet. This high temperature exceeds the previously discovered 150 to 170°C temperature range for producing clear sPS sheets.[1] It should be noted, however, that the contours above 290 K Mw might not be reliable because there was only one sample having Mw higher than 290 K. In addition, because all the sheets annealed at 160°C (as well as at higher temperature) had developed maximum crystallinity as shown above and all the clear-to-hazy transitions occurred above 160°C, the difference in the clarity of these annealed sheets was not related to crystallinity.

To investigate the difference in crystallite structure between the clear and the hazy sheets, AFM and TEM were used. The AFM images taken from the surface of the sheets are shown in Figure 6. A 10 μm $\times$ 10 μm area of the sheet surface was imaged with the depth expressed in the gray scale on the right of the picture. There is no apparent difference in the pattern revealed between the top picture (taken from a clear sheet) and the bottom picture (taken from a hazy sheet). In other words, both pictures show very similar spherulite-like structures on the surfaces of both the clear and the hazy sheets. TEM pictures taken from the specimens sectioned from the interior of the annealed sheets are shown in Figure 7. Lamella, very short and thin, are barely discernible in Figure 7(a) taken from a clear sheet. On the other hand, significantly longer and thicker lamellae can be easily discerned from Figure 7(b) taken from a hazy sheet. Also in Figure 7(b), one can find some bundles of lamellae, which might be parts of spherulites and can certainly scatter more light than can the thin, short, and not-bundled lamellae of a clear sheet.

The interpretation of the above data based on the regime growth theory is summarized below. As shown in the introduction, regime III growth ($g \ll i$) results in higher clarity. Regime I growth ($g \gg i$), on the other hand, yields lower clarity. For sPS sheet, at a given temperature, increasing Mw increases viscosity and thus slows down diffusion. Therefore, the crystal growth rate (g) is reduced, so the growth pattern shifts to regime III ($g \ll i$), resulting in thinner lamella and more clear sheet. On the other hand, increasing % PMS comonomer, which forms defects in the sPS polymer chain, reduces both the crystal growth rate and the nucleation rate as the increase in the number of defects reduces the opportunity for aligning defect-free chain segments together. Shifting direction to either regime I or III depends on the relative magnitude of decrease in g (Δg) vs that in i (Δi). Our % haze data shown above simply indicates there is a maximum (Δg–Δi) at 4% PMS for the largest shift to regime III and, consequently, the highest sheet clarity.

CONCLUSIONS

Effect of the molecular weight of sPS homopolymer on the optical clarity of annealed sPS sheets

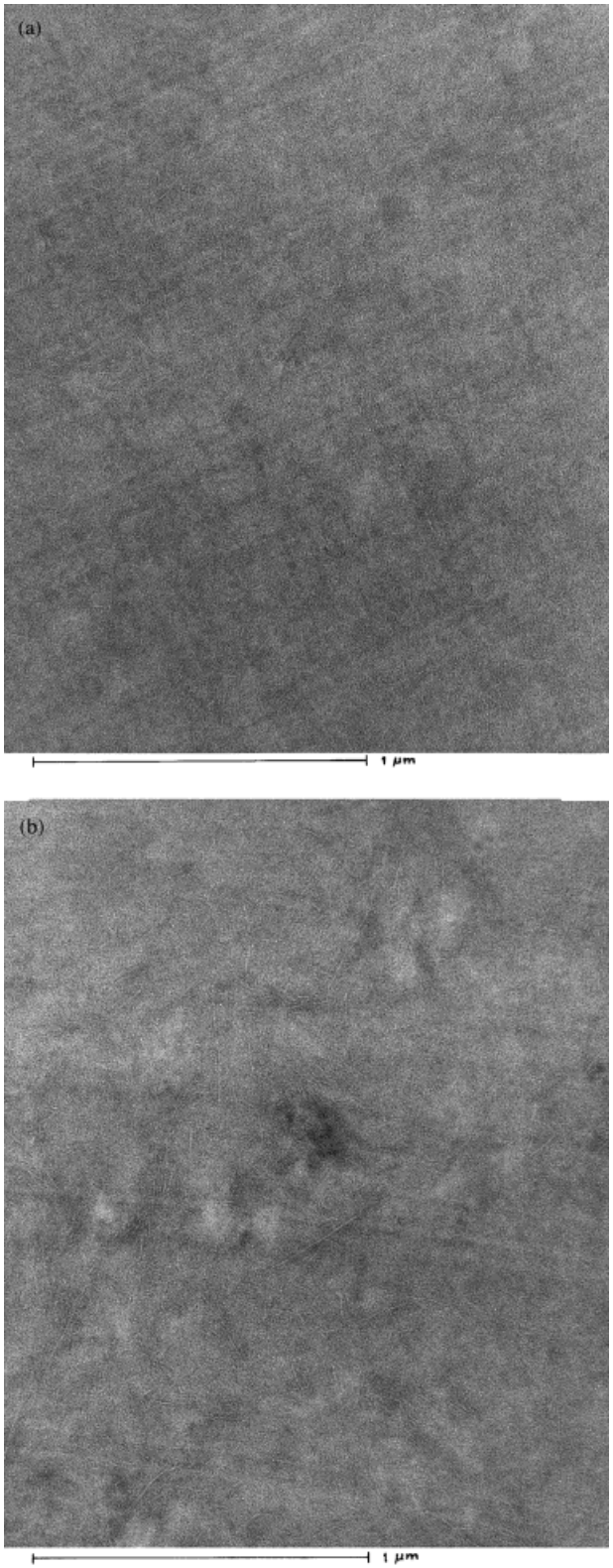

Figure 7 (a) A typical TEM picture taken from the interior of a clear sPS sheet (sample A, annealed at 150°C). (b) A typical TEM picture taken from the interior of a hazy sPS sheet (sample A, annealed at 180°C).

was studied. Higher molecular weight sPS was found to yield more clear sheets than the lower molecular weight sPS when annealed at the same temperature. In addition, the higher the molecular weight, the higher the clear-to-hazy transition temperature.

Effect of % PMS comonomer was also studied. Interestingly, instead of a monotone response to % PMS, the sheet clarity was found to maximize at 4% PMS. The widest operating temperature window for producing clear sPS sheets was found by using a medium molecular weight, 4% PMS copolymer.

Regime growth theory of polymer crystallization was successfully used to interpret the above findings. Increasing Mw slows down diffusion, reduces the crystal growth rate (g), and shifts the growth pattern to regime III ($g << i$), resulting in more clear sheet. Increasing % PMS increases polymer chain defects and thus reduces both the crystal growth rate (g) and the nucleation rate (i). Shifting direction to either regime I or III depends on the relative magnitude of decrease in g (Δg) vs that in i (Δi). The % haze data obtained in this study indicates a maximum (Δg–Δi) at 4% PMS for the largest shift to regime III and, consequently, the highest sheet clarity.

The authors acknowledge Steve Chum of Dow's Polyolefins Research for his valuable insight, suggestion, and discussion regarding this study; Greg Meyers of Dow's Analytical Sciences Laboratory for the AFM analysis; Bob Cieslinski of Dow's Analytical Sciences Laboratory for the TEM analysis; and Tom Burns, Mike Malanga, and Zhan Sun of Dow's Engineering Plastics Research for their constructive comments.

REFERENCES

1. Uchida, T.; Takebe, T.; Funaki, K.; Yamasaki, K. European Pat. Application 531705, 1993.
2. Ishihara, N.; Seimiya, T.; Kurmoto, M.; Uoi, M. Macromolecules 1986, 19, 2464.
3. Lauritzen, J. I.; Hoffman, J. D. J Appl Phys 1973, 44, 4340.
4. Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I. Treatise on Solid State Chemistry; Plenum: New York, 1976; Vol. 3; p. 497.
5. Hoffman, J. D. Polymer 1983, 24, 3.
6. Philips, P. J. Rep Prog Phys 1990, 53, 549.
7. Pasztor, A. J.; Landes, B. G.; Karjala, P. J. Thermochimica Acta 1991, 177, 187.
8. JMP Statistics and Graphics Guide, version 3.1, 131; SAS Institute: Cary, NC, 1995.