The Crystallinity of Poly(phenylene Sulfide) and Its Effect on Polymer Properties

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Synopsis

The crystallinity and crystallizability of poly(phenylene sulfide) have been examined by a number of common techniques. Several provided qualitative information, but only one, x-ray diffraction, was considered sufficiently reliable and reproducible to allow quantitative comparisons. Based on x-ray measurements, an approximate degree of crystallinity, termed crystallinity index (C_i), could be readily assigned. According to this method, virgin polymer possesses significant crystallinity $(C_i \approx 65\%)$. Curing (crosslinking) the resin below its melting point did not change the crystallinity but did affect the crystallizability. Lightly cured resin suitable for molding and film extrusion was easily quenched from the melt to give amorphous polymer. The amorphous samples crystallized rapidly when heated to temperatures >121°C (250°F). At mold temperatures below 93°C (200°F), moldings with very low surface crystallinity were produced. Annealing (204°C, 400°F) caused rapid crystallization of such moldings, and changes in crystallinity were correlated with observed changes in physical properties. The resin crystallizes so rapidly that these quenched moldings possessed a crystallinity gradient, the internal crystallinity being substantially greater. At high mold temperatures (121–204°C, 250–400°F), moldings very similar to fully annealed specimens were obtained.

INTRODUCTION

Poly(p-phenylene sulfide) (PPS) was first reported in 1897 by Grenvesse[1] who prepared the amorphous, insoluble resin by the reaction of benzene with sulfur in the presence of aluminum chloride. During the next 51 years, other workers reported the preparation of ill-defined resins of similar composition using a variety of preparative procedures.[2-4] In 1948, Macallum[5] described the synthesis of this unusual resin by the melt reaction of p-dichlorobenzene with sodium carbonate and sulfur. Lenz and co-workers[6-8] examined the Macallum polymer and polymerization process in detail and developed a more reproducible preparative procedure based on the self-condensation of an alkali halogen thiophenoxide. Recently, a commercially successful process involving the reaction of p-dichlorobenzene with sodium sulfide in a polar solvent has been developed by Edmonds and Hill[9] (Fig. 1). With the exception of the early reports, poly(phenylene sulfide) has historically been classified as a crosslinkable, thermally stable, highly crystalline polymer. In 1964, Tsunawaki and Price[10] reported x-ray data giving interplanar spacings for crystalline polymer; and in 1971, Tabor[11] and co-workers provided complete x-ray data describing the crystalline structure of the material in some
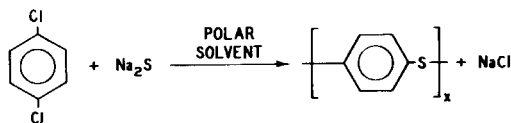
Fig. 1. Preparation of poly(phenylene sulfide).

detail. However, these data, as well as other articles describing the polymer, did not provide information concerning very important subjects such as rate of crystallization, actual per cent crystallinity, the effect of curing and molding conditions on crystallinity, the effect of crystallinity on polymer properties, etc. This paper deals with these areas of uncertainty.

EXPERIMENTAL

Poly(phenylene Sulfide). The resin used in this study was commercial material marketed under the trade name Ryton poly(phenylene sulfide) by Phillips Petroleum Company, Bartlesville, Oklahoma. Virgin resin refers to V-1 grade product, unfilled resin denotes R-6 injection molding grade, and glass-filled resin refers to R-4 grade 40% glass-filled injection molding grade.

Curing Procedure. Seven-gram samples of virgin PPS powder contained in small aluminum weighing pans were heated in air in an oven at 260°C (500°F) for the specified time. Melt flows were determined according to ASTM D-1238 using a 5-kg weight and a 316°C (600°F) barrel temperature.

Molding. Tensile specimens were molded using a New Britain reciprocating screw injection molder. Typical molding conditions were: melt temperature, 316°C (600°F); injection pressure, 15,000 psi; total hold time in mold, 45 sec; mold temperature, 38–66°C (100–150°F) unless specified otherwise.

Film Preparation. Amorphous film samples were obtained by careful slot extrusion and rapid quenching of lightly cured PPS resin.

Annealing. All annealing procedures were conducted in a forced-draft oven closely controlled at the specified temperature. Samples were quenched in ice water and times given represent total time in oven.

X-Ray Data. All x-ray diffraction patterns were obtained employing a Philips diffractometer with appropriate counting and recording equipment. Measurements were made with CuK_α radiation. The observed diffraction pattern was taken to be the sum of contributions from four components, namely, background, amorphous PPS, crystalline PPS, and glass (if present). Utilizing the assumption that crystalline PPS makes no contribution at 2θ values of 11°, 17°, 23°, 30°, and 34°, measurements at these five points were used to to estimate the contributions from background, amorphous PPS, and glass. This was done by a least-squares adjustment using empirically determined shapes for the patterns of these three components. Back calculations over the region of 17° to 23° 2θ then gave a resolution of the observed pattern into its four components. After initial experience with strip chart recording, the epperiment was automated with a minicomputer which collected the data and allowed direct reading of crystallinity indices.

Infrared Data. The infrared data presented were obtained using a Perkin-Elmer Infracord Model 137 and thin ($\approx$5 mils) PPS film.
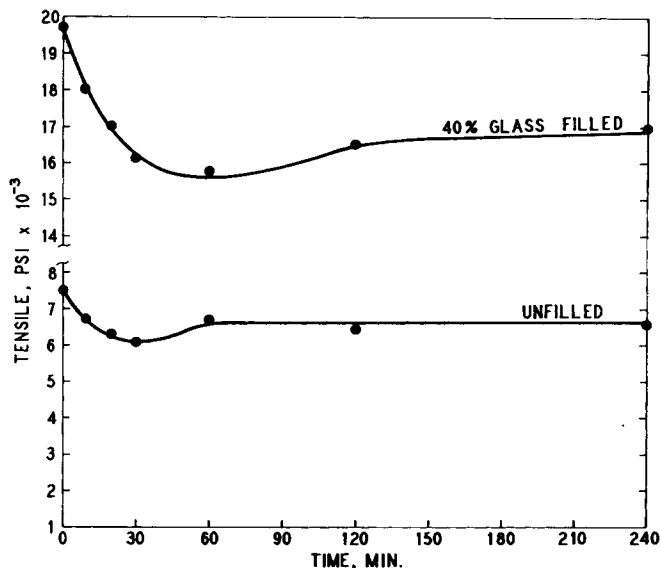
Fig. 2. Effect of annealing (204°C) on tensile strength.

EFFECT OF ANNEALING ON POLYMER PROPERTIES

Early in the investigation of PPS molding resins, prepared by lightly cross-linking virgin resin, it was observed that the physical and mechanical properties of moldings changed during initial stages of thermal aging at 121–204°C (250–400°F). For example, tensile strength decreased, flexural modulus increased, flexural strength decreased, heat distortion temperature increased, density increased and heat of fusion increased. Recent investigations have revealed that these changes occur very rapidly at temperatures above T_g. At 204°C (400°F), they occurred during the first hour for both 40% glass-filled and unfilled resins (Figs. 2 and 3, and Table I). These data strongly suggested that the observed changes were simple manifestations of crystallinity
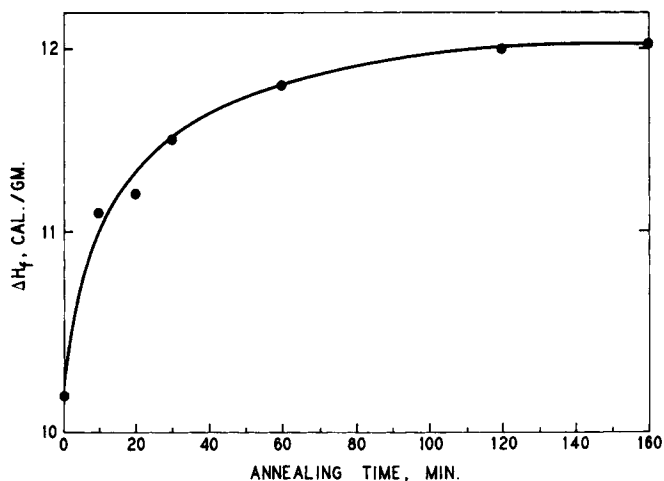

Fig. 3. Effect of annealing (204°C) on heat of fusion.

TABLE I
Effect of Annealing on Other Properties

Property	Unfilled resin		40% Glass-filled resin	
	Unannealed[a]	Annealed[b]	Unannealed[a]	Annealed[b]
Flexural strength, psi	15,000	13,000	29,000	25,000
Flexural modulus, psi $\times 10^{-6}$	—	—	1.94	2.01
Heat distortion temp., °C	100	128	>200	>200
Density, g/cc	1.32–1.36	1.36–1.40	—	—

[a] Molded at 316°C (600°F) stock temperature and 38°C (100°F) mold temperature.
[b] Annealed in oven at 204°C (400°F) for 2 hr.

changes in the polymer network and were not due to thermal degradation and/or crosslinking.

DETERMINATION OF CRYSTALLINITY

One of the first bits of definitive information concerning the crystallization of PPS was obtained from differential thermal analysis (DTA) experiments (Fig. 4).[12] When a sample of PPS that had been heated to a temperature slightly above its melting point and then rapidly cooled (i.e., quenched) was subjected to DTA, the glass transition at 85°C (185°F) was followed by a pre-melt crystallization exotherm at ≈130°C (≈266°F) and a crystalline melting point at 285°C (545°F). These data clearly indicated the amorphous nature of the quenched sample and established that the polymer network rapidly crystallized when heated much above T_g. Naturally, the thermogram of an annealed specimen, i.e., 2 hr at 204°C (400°F), did not exhibit the premelt crystallization exotherm, and T_g was barely discernible.

As is the case with many polymer systems, establishing the degree of crystallinity in PPS moldings was not an easy task. Several methods provided qualitative information regarding crystallinity but were not considered sufficient to provide quantitative information. Density measurements were not reliable since erratic results were often obtained. Heat of fusion data were consistent and reproducible but were complicated by the tendency for amorphous samples to crystallize during analysis. Likewise, infrared techniques, which will be discussed further in this paper, were judged inadequate. Therefore, attempts were made to develop a reproducible method of analysis based on x-ray diffraction measurements.

As is generally the case in polymer systems, the amorphous pattern for the resin was much broader than the crystalline pattern (Fig. 5). Based on the reasonable assumption that the amorphous pattern under the crystalline pattern can accurately be predicted by measuring intensities at 2θ values where crystalline contributions are very small or nonexistent (see experimental section), a procedure for calculating the approximate degree of crystallinity was developed. The method, similar to one previously used for cellulose[13] and poly(ethylene terephthalate),[14] involves dividing the area under the diffraction curve attributed to crystalline diffraction by the total area. According
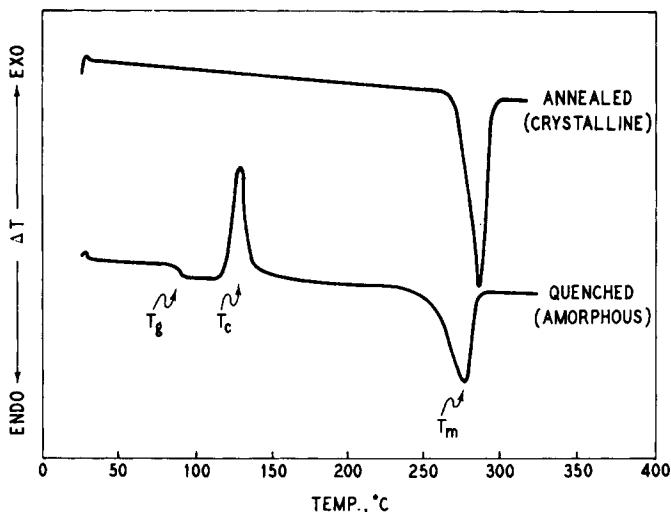
Fig. 4. DTA Thermograms.

to this procedure, only the areas between 17° and 23° 2θ were measured, and the resulting ratio of areas was termed crystallinity index C_i,

$$C_i = \frac{A_{\mathrm{cryst}}}{A_{\mathrm{cryst}} + A_{\mathrm{amorp}}} \times 100$$

where A = area under diffraction curve. Naturally, this technique measures only the surface crystallinity of the sample being examined and not the bulk crystallinity. In glass-filled samples, allowance for the glass contribution to the diffraction pattern was also made. Although the crystallinity indexes given in this paper may not correspond exactly to per cent crystallinity, they are certainly closely related to crystallinity and provide valid measurements for qualitative comparisons.

CORRELATION OF CRYSTALLINITY WITH CHANGES IN POLYMER PROPERTIES

Once a reliable and reproducible method for measuring degree of crystallinity was developed, it was of interest to determine if indeed the changes in
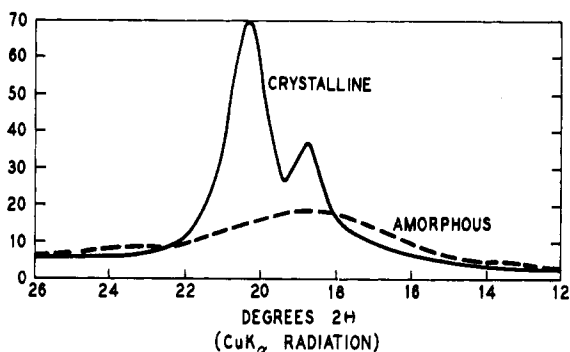

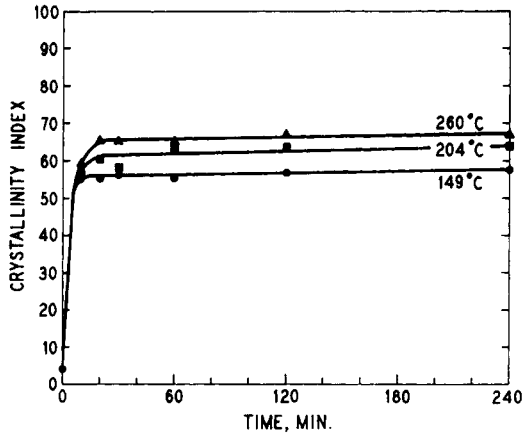
Fig. 5. X-Ray diffraction patterns of PPS.

Fig. 6. Effect of annealing temperature on crystallinity of glass-filled PPS.

properties discussed previously were caused by simple changes in crystallini-
ty. The data represented in Figure 9 show clearly that PPS specimens mold-
ed in a cold mold ($\approx$38°C, $\approx$100°F) possessed low surface crystallinity (C_i <
5%). Aging, hereafter called annealing, at 204°C (400°F) allowed rapid crys-
tallization, with the maximum surface crystallinity (C_i = 60%) being reached
during the first 30 min of heating. In fact, most of the crystallization oc-
curred during the first 10 min of annealing. Additional studies involving
glass-filled resin revealed that the annealing temperature influenced the "lev-
eling off" point in the crystallization process (Fig. 6). At 149°C (300°F), the
crystallinity plateaued at a C_i some 10% below that attained at 260°C
(500°F). This phenomenon is probably associated with greater polymer
chain mobility at the higher temperature, thus allowing the molecules to ar-
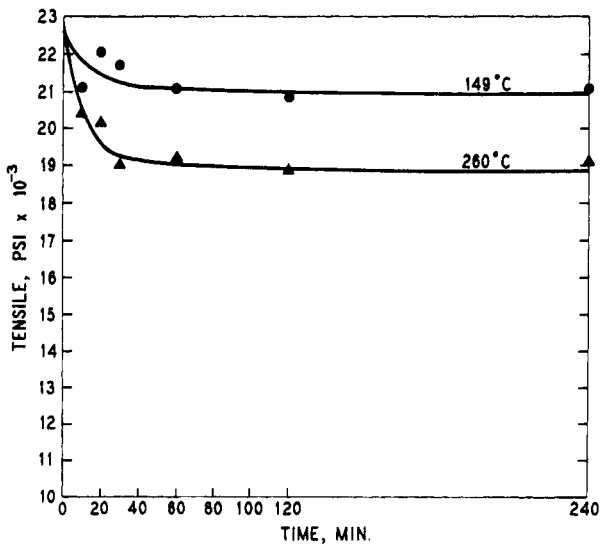range themselves so as to produce greater crystallinity. In complete agree-

Fig. 7. Effect of annealing temperature on tensile of glass-filled PPS.
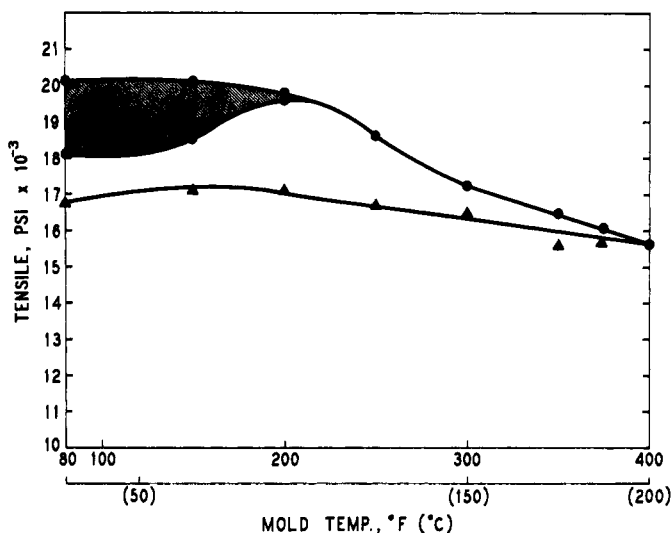
Fig. 8. Effect of mold temperature on tensile of glass-filled PPS. (●) as molded; (▲) annealed, 204°C/2 hr.

ment with this observation was the fact that decreases in tensile strengths paralleled the crystallinity values; the higher the annealing temperature, the lower the tensile strength (Fig. 7).

An increase in polymer crystallinity, such as observed in annealing PPS, is usually accompanied by an *increase* in tensile strength rather than a decrease as is observed with PPS. This departure from normal behavior is no doubt associated with the modest molecular weight and slightly crosslinked nature of the polymer. It is suggested that the crystallization of molded PPS specimens, rather than having a reinforcing effect, introduces interfacial strain in the polymer network, thus producing "weak" sections where failure under ex-
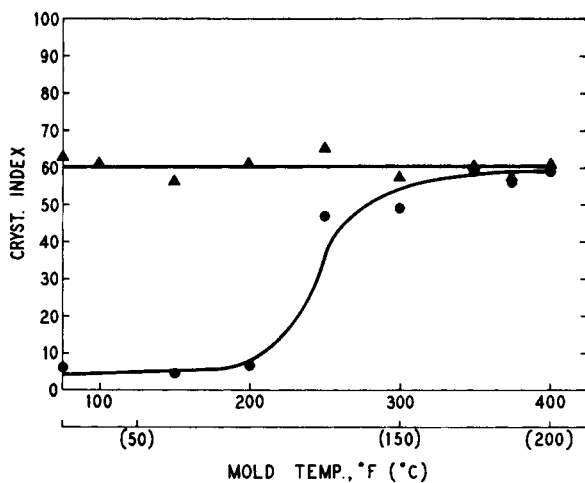

Fig. 9. Effect of mold temperature on crystallinity: (●) as molded; (▲) annealed, 204°C/2 hr.

ternal stress is initiated. Recent investigations involving higher molecular weight linear PPS resin reinforce this hypothesis since increases in tensile strength upon annealing have been observed. This phenomenon also explains the extremely erratic behavior of tensile strengths during intermediate stages of crystallization (see Fig. 7).

Once the rapidity with which thin PPS moldings crystallize was established and the changes in crystallinity were related to certain physical changes in the polymer, it was not surprising to find that degree of crystallinity and concomitant properties were dependent on mold temperature. Although values varied somewhat, tensile strength of PPS moldings generally decreased as mold temperature was increased, e.g., 38° → 204°C (100–400°F). At high mold temperature, even though "in mold" time was relatively short (e.g., 45 sec), there was little difference in annealed and unannealed specimens. At mold temperatures below 93°C (200°F), the degree of crystallinity remained low due to quenching in the amorphous stage. Between 93°C

TABLE II
Effect of Curing on Crystallinity

260°C (500°F) Cure time,[a] hr	Melt flow,[b] g/10 min	Crystallinity index	
		As Is	Melted and annealed[c]
0	≈6000	63	61
1	220	—	58
3	15	—	56
16	0	—	36
24	0	62	31

[a] Cured below melting point of 285°C (545°F).
[b] Determined at 316°C (600°F), 5 kg weight.
[c] Samples melted, quenched, and annealed at 204°C (400°F).

(200°F) and 121°C (250°F), a substantial increase in crystallinity was observed; and at mold temperatures in the 177–204°C (350–400°F) range, crystallinities approaching those of fully annealed specimens were attained. The effects of mold temperature on tensile strength and crystallinity are given in Figures 8 and 9, respectively. The shaded area in Figure 8 indicates the range of values obtained. The dramatic change in crystallinity resulting from annealing quenched (amorphous) moldings is also again apparent in Figure 9.

Determination of internal crystallinity of $\frac{1}{8}$-in.-thick PPS moldings revealed that a crystallinity gradient existed. For example, the surface crystallinity indices for quenched $\frac{1}{8}$-in.-thick PPS moldings were about 5%, whereas the indexes at the centers of the same moldings were much higher, i.e., 40–50%. These data indicated that rapid internal annealing occurred as the moldings cooled. Internal surfaces for x-ray diffraction measurements were obtained by carefully removing portions of the molding by machining. Similar results were obtained from planed surfaces, indicating that the differences in crystallinity were not a result of heat buildup and subsequent crystallization during surface removal.

EFFECT OF CROSSLINKING ON CRYSTALLINITY

When heated in air at temperature above or slightly below its melting point, PPS undergoes crosslinking and/or chain extension as evidenced by a decrease in melt flow. The effect of this phenomenon on crystallinity and crystallizability of the resin in its virgin form was also determined. When conducted below the melting point (285°C, 545°F), the heating process (i.e., curing) had little or no effect on the polymer crystallinity, as shown by the data in Table II. However, curing did affect the crystallizability of the resin. Once the material was crosslinked, melted, and then annealed, the crystallinity index did not return to the original value, even upon prolonged annealing. Crosslinking at temperatures above the melting point had the same effect, i.e., reduction in ultimate degree of crystallinity. The change in crystallizability no doubt reflects the decrease in molecule mobility as crosslinking and/or chain extension proceed.

CRYSTALLIZATION OF AMORPHOUS PPS FILM

Although detailed rate studies were not conducted, some effort was made to determine the minimum temperature at which crystallization occurred at an appreciable rate. Molding studies (Fig. 9) and the T_g value for PPS suggested that this temperature was probably greater than 93°C (200°F). In this qualitative study, it was convenient to place samples of thin ($\approx$20 mils) amorphous film in a preheated oven and follow the loss in transparency as a
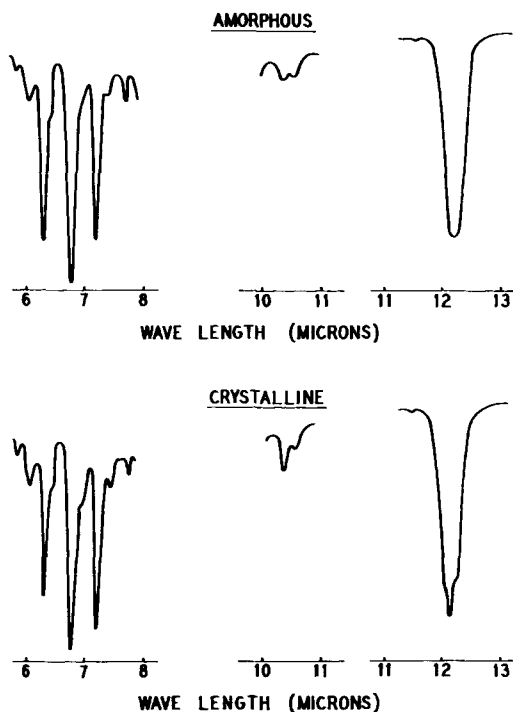

Fig. 10. Infrared spectral differences in amorphous and crystalline PPS.

function of temperature and time. Amorphous film (C_i < 5%) was amber in color and completely transparent, whereas annealed (crystallized, C_i ≈ 60%) film was gray and totally opaque. Partially crystallized film was amber in color but hazy. At 93°C (200°F), a temperature slightly above T_g, crystallization was extremely slow with no change in film appearance occurring in 2 hr. At 121°C (250°F) and above, crystallization occurred at an extremely fast rate as evidenced by the film samples becoming gray and opaque, e.g., 4 min required at 149°C (300°F), 15 sec at 260°C (500°F). At 107°C (225°F), crystallization proceeded at a moderate rate.

When thin films (ca. 5 mils) are involved, infrared spectroscopy can serve conveniently as a qualitative tool giving clear evidence concerning the crystalline or amorphous nature of the resin. Absorption in three regions (6–7.5 μ, 10–11 μ, and 12–12.5 μ) can be used to follow crystallization. Amorphous film exhibits two strong bands of equal intensity at 6.3 μ and 7.2 μ. In crystalline film, the band at 7.2 μ is considerably stronger. Amorphous film exhibits two weak bands of almost equal intensity centered at 10.45 μ. As crystallinity develops, the band at 10.35 μ becomes sharper and much stronger. This change is very consistent and easily identified. The broad absorption at 12.2 μ changes shape as crystallinity develops, becoming much sharper in highly crystalline samples. All these changes are shown in Figure 10. For thicker samples, infrared attenuated total reflection spectroscopy can be used to follow changes in surface crystallinity.

CONCLUSIONS

This investigation has shown that PPS is indeed a highly crystalline polymer. Its crystallinity can be determined qualitatively by a number of techniques and quantitatively with some degree of certainty by x-ray diffraction measurements. The polymer can easily be quenched in the amorphous state where crystallinity is very low (≈5%). However, the amorphous polymer crystallizes very rapidly at temperatures above 121°C (250°F), reaching a maximum crystallinity near 65%. This crystallization affects the properties of molded resin. Curing (crosslinking and chain extending) the resin by heating in air affects the crystallizability of the resin; the greater the cure, the lower the ultimate crystallinity.

References

1. P. Grenvesse, *Bull. Soc. Chim. France,* **17,** 599 (1897).
2. J. J. B. Deuss, *Rec. Trav. Chim. Pays-Bas Belg.,* **28,** 136 (1909).
3. T. P. Hilditch, *J. Chem. Soc.,* 2579 (1910).
4. H. B. Glass, and E. E. Reid, *J. Amer. Chem. Soc.,* **51,** 3428 (1928).
5. A. D. Macallum, *J. Org. Chem.,* **13,** 154 (1948).
6. R. W. Lenz, C. E. Handlovits, and H. A. Smith, *J. Polym. Sci.,* **58,** 351 (1962).

7. R. W. Lenz and W. K. Carrington, *J. Polym. Sci.,* **48,** 333 (1959).
8. R. W. Lenz and C. E. Handlovits, *J. Polym. Sci.,* **43,** 167 (1960).
9. J. T. Edmonds and H. W. Hill, Jr., U.S. Pat. 3,354,129 (Nov. 1967).
10. S. Tsunawaki and C. C. Price, *J. Polym. Sci.,* **2A,** 1511 (1964).
11. B. J. Tabor, E. P. Magre, and J. Boon, *Eur. Polym. J.,* **7,** 1127 (1971).
12. J. N. Short and H. W. Hill, Jr., *Chem. Tech.,* **2,** 481 (1972).
13. J. H. Wakelin, H. S. Virgin, and E. Crystal, *J. Appl. Phys.,* **30,** 1654 (1959).
14. W. O. Statton, *J. Appl. Polym. Sci.,* **7,** 803 (1963).