Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Annealing Behavior of Isotactic Polybutene-1

K. Kishore[a]; R. Vasanthakumari[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

To cite this Article Kishore, K. and Vasanthakumari, R.(1987) 'Annealing Behavior of Isotactic Polybutene-1', Journal of Macromolecular Science, Part A, 24: 1, 33 — 47
To link to this Article: DOI: 10.1080/00222338708058507
URL: http://dx.doi.org/10.1080/00222338708058507

J. MACROMOL. SCI.—CHEM., A24(1), pp. 33-47 (1987)

ANNEALING BEHAVIOR OF ISOTACTIC POLYBUTENE-1

K. KISHORE and R. VASANTHAKUMARI

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012, India

ABSTRACT

The annealing behavior of isotactic polybutene-1 (PB-1) has been studied by differential scanning calorimetry and wide-angle x-ray diffraction. On annealing at 110°C, PB-1 yields thick crystals melting at ~140°C which are mainly of Form I. An increase in the heat of fusion (ΔH_f) and crystallinity is found for annealing times up to 12 h at 110°C; at longer times these properties decrease with increasing annealing time. The increases in ΔH_f and crystallinity are attributed to increases in the lamellar thickness in the chain direction and in crystal perfection, and subsequent decreases to degradation of the polymer.

INTRODUCTION

Polymer crystals are metastable in nature, particularly due to the high surface free energy of the fold surfaces. They have, therefore, a strong tendency to revert to states of lower free energy, leading to the strong annealing phenomenon observed for polymer crystals [1]. One of the important annealing effects is an increase in the thickness of the crystals in the direction of the chain when semicrystalline polymers are heated above a critical temperature. Thickening of crystals was observed first in solution-grown crystals of polyethylene [2, 3]. This process also occurs in bulk-melt-crystallized and highly drawn samples [4-10]. Two interpretations have been put forward: 1) thickening in the solid state by a diffusion mechanism which consists of the translation of molecular sequences through the lattice, and 2) through the partial or complete melting of the crystals, followed by recrystallization from the melt.

Isotactic polybutene-1 (PB-1) is reported to crystallize mainly in two forms, stable Form I (hexagonal structure) and metastable Form II (tetragonal structure). The tetragonal form changes to the hexagonal form [11, 12] on standing at ambient temperature. In the present work, PB-1 has been studied by differential scanning calorimetry (DSC) and wide-angle x-ray diffraction (WAXD) techniques to investigate the annealing behavior in terms of its novel polymorphic transformations.

EXPERIMENTAL

Polymer PB-1 was a sample of Shell 0400. The sample, sandwiched between two glass slides, was melted at 180°C in air and maintained at this temperature for 5 min. Afterwards, the sample temperature was suddenly brought down to 95°C, and the sample kept at this temperature for 24 h, when thin films of ~0.5 mm thickness were obtained. The samples were cooled to room temperature (28°C) and kept for 5 h. These samples were used for heating rate effect and annealing studies.

A Du Pont 990 Thermoanalyzer and DSC cell were employed. Temperature was calibrated by using an indium sample for a wide range of heating rates (0.5 to 100°C/min). The annealed samples were scanned at a heating rate of 5°C/min. WAXD scans were obtained with CuK_α radiation using a Philips PW 1050/70 vertical goniometer. IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer. ESR spectra were recorded at room temperature on a Varian E-109b ESR spectrometer. Dynamic thermogravimetry (TG) was run by using a Stanton Redcroft TG 750 thermobalance for the PB-1 sample at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of Heating Rate

The effect of the heating rate on the DSC thermograms of PB-1 is shown in Fig. 1. Two endotherms are obtained at heating rates of 5-20°C/min. The low-temperature peak corresponds to the melting of the metastable Form II,

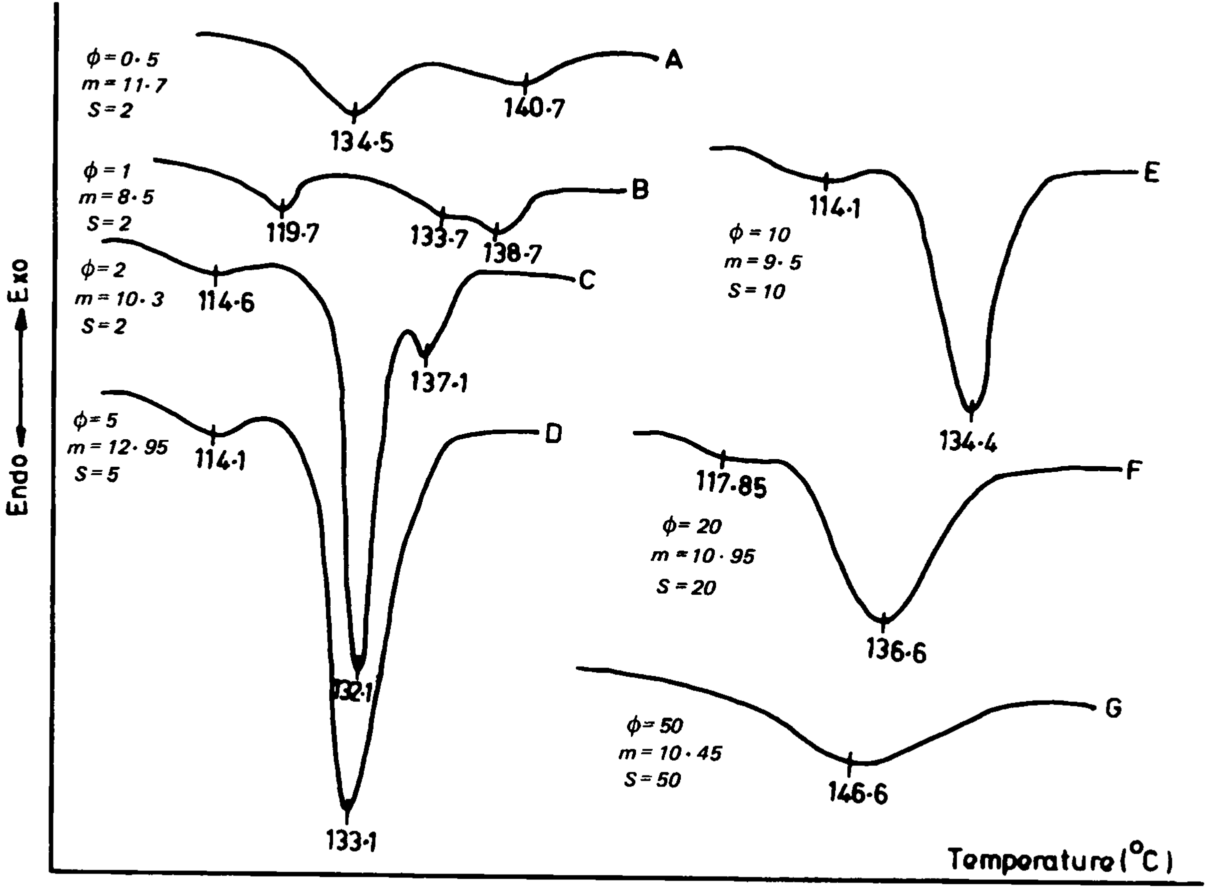

FIG. 1. DSC traces for melting of PB-1. ϕ = heating rate in °C/min, m = weight of the sample in mg, s = sensitivity of Y axis in mV/cm.

and the high-temperature peak to the melting of the stable Form I. However, at lower heating rates (1 and 2°C/min), three endothermic peaks were observed; they are due to the melting of Form II, Form I, and of thick crystals, respectively. Interestingly at the lowest heating rate (0.5°C/min), one observes two endotherms corresponding to the melting of the Form I and that of the thickened crystals. The absence of the low-temperature endotherm ocrresponding to Form II at 0.5°C/min suggests that crystals of Form II reorganize to thick crystals and Form I.

A plot of the melting temperatures versus the heating rates is given in Fig. 2. For the crystals of Forms I and II, the melting temperatures decrease initially and then increase. The increase in peak temperature as the heating rates are lowered from 2 to 0.5°C/min suggests the occurrence of crystal thickening. The appearance of the additional melting peak at low heating rates (Fig. 2c) confirms this conclusion, especially for Form I. Further, the results are concordant with observations for PB-1 single crystals [13], which have shown that the thickness of crystals of Form I increases while that of Form II does not significantly change with annealing temperature and time.

The increasing melting temperature at higher heating rates is attributed to superheating [14, 15] which occurs on account of the slow rate of melting of the polymer crystals compared to the rate of heating of the DSC pan. Because of this superheating effect, it appears that Form I predominates at higher heating rates. The melting points of Forms I and II merge into the broad peak at 50°C/min.

Melting Characteristics of PB-1 on Annealing

Typical DSC curves of the annealed PB-1 samples at 110°C taken immediately after the annealing was terminated are shown in Fig. 3. Unannealed PB-1 reveals two peaks, the lower one corresponding to the melting of Form II and the other due to the melting of Form I. As annealing progresses, an additional peak appears around 140°C, which is due to the melting of thickened crystals. Careful analysis of Fig. 3 shows that crystals of Form II are much more stable than those of Form I, even after prolonged annealing, and it is Form I which undergoes thickening, giving rise to the extra peak around 140°C. This inference is in agreement with the findings of Woodward and Morrow [13] on the annealing of PB-1 single crystals.

The annealed samples were kept at room temperature for 5 days so that Form II was converted completely into Form I, and Fig. 4 shows their DSC scans. It shows only the melting endotherms of Form I and thickened crystals.

The melting temperatures of PB-1 as a function of annealing time are presented in Figs. 5 and 6, the former immediately after annealing and the latter

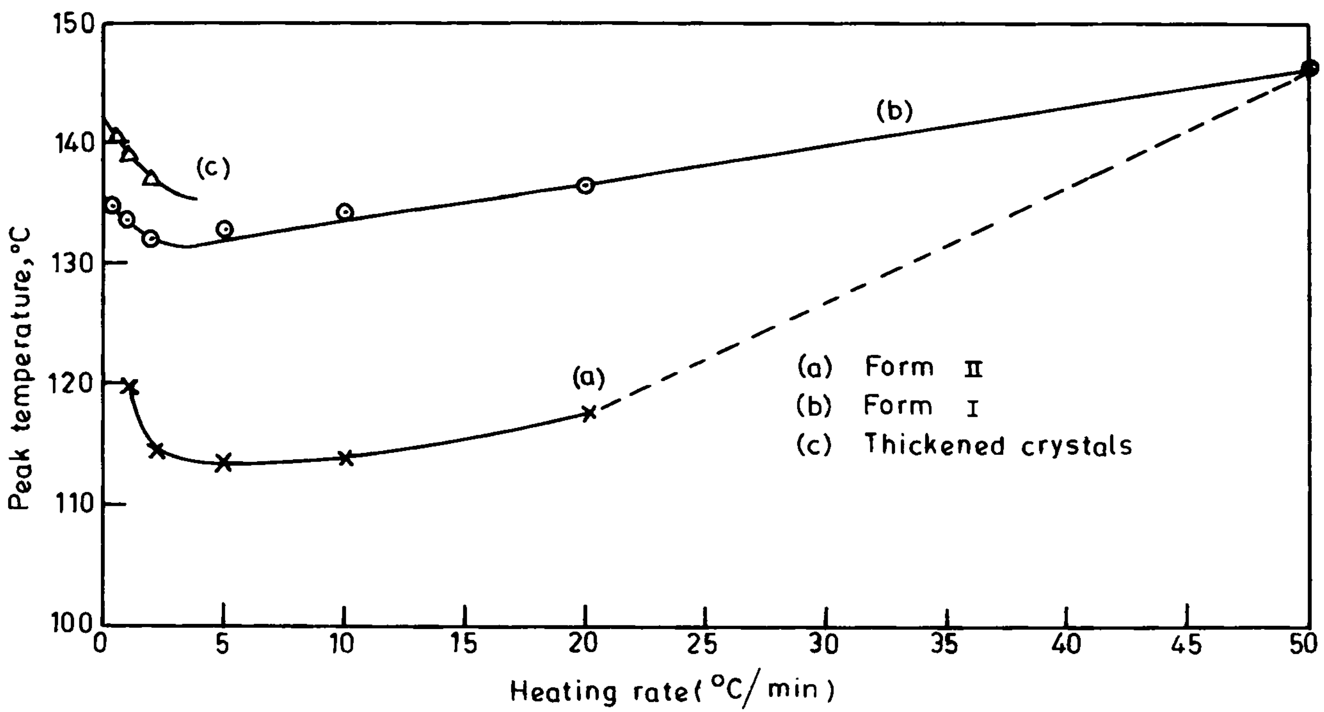

FIG. 2. Melting peak temperature of PB-1 as a function of heating rate.

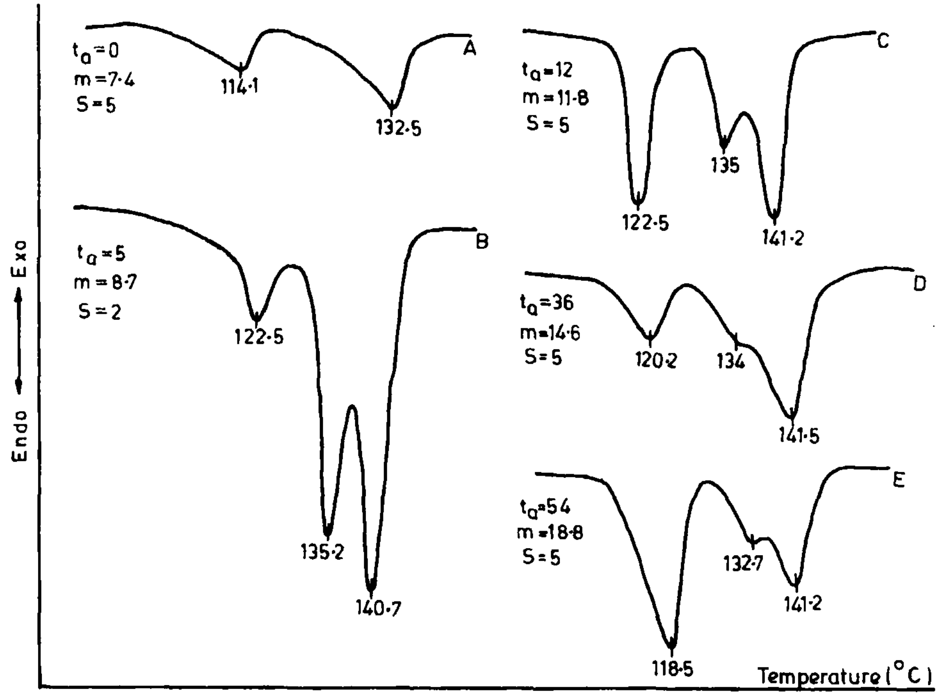

FIG. 3. DSC traces of PB-1 for different annealing times at 110°C. t_a = annealing time in h, *m* = weight of sample in mg, *s* = sensitivity of Y axis in mV/cm.

after 5 days storage. Annealing of the samples up to 12 h resulted in an increase of the melting temperature, followed by a decrease for longer annealing times. The initial rise is due to the reorganization of the lamellar structure in the amorphous and crystalline phases, leading partly to crystal perfection and to an increase in the lamellar thickness. The later decrease may be due to polymer degradation.

A dynamic TG of unannealed PB-1 (Fig. 7) clearly demonstrates that PB-1 starts decomposing at about 250°C. Measurements in air at 110°C showed no appreciable weight loss up to 100 h. However, samples turned yellow after about 50 h, which may be due to some oxidative degradation. To support this, the yellow colored samples were extracted with benzene, and the IR spectrum of the benzene extract shows a carbonyl peak around 1 700 cm^{-1} (Fig. 8),

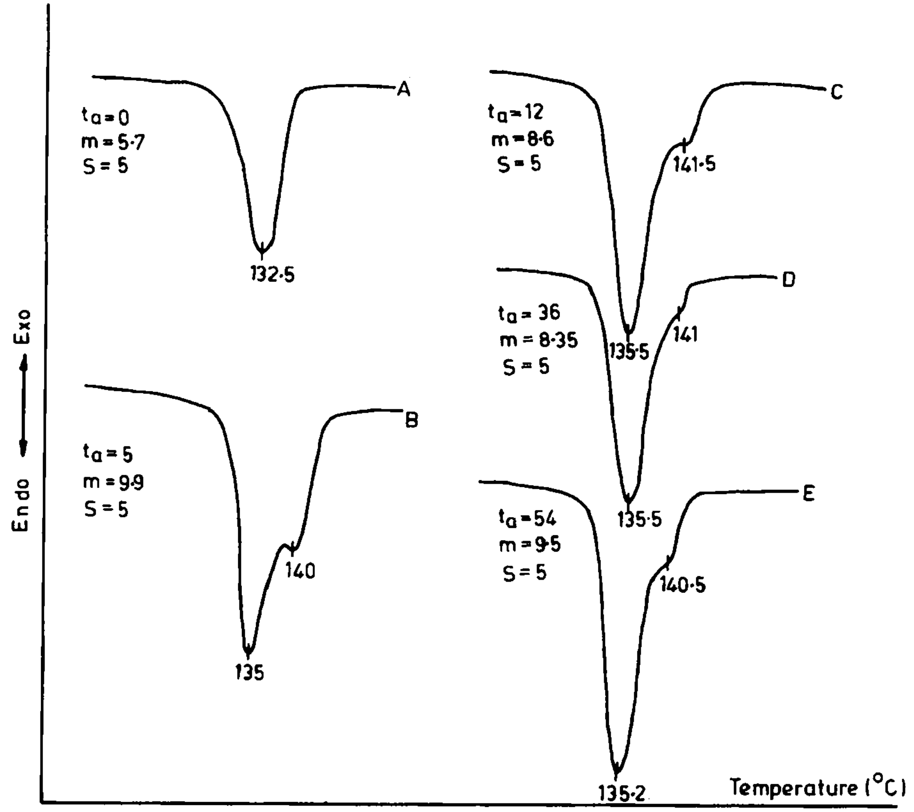

FIG. 4. DSC traces of PB-1 annealed for different times at 110°C and then kept at room temperature for 5 days. t_a = annealing time in h, m = weight of sample in mg, s = sensitivity of Y axis in mV/cm.

confirming oxidative degradation of PB-1. Further, the ESR spectrum of the sample annealed at 110°C for ~24 h shows a signal ($g = 2.003$) (Fig. 9) attributable to the free radicals produced during the degradation process. In conclusion, the decrease in the melting temperature after 12 h can be attributed to the onset of oxidative degradation.

The heat of fusion of the perfectly crystalline material is reported to be 1 500 and 1 270 cal/mol for Forms I [11] and II [13], respectively. The de-

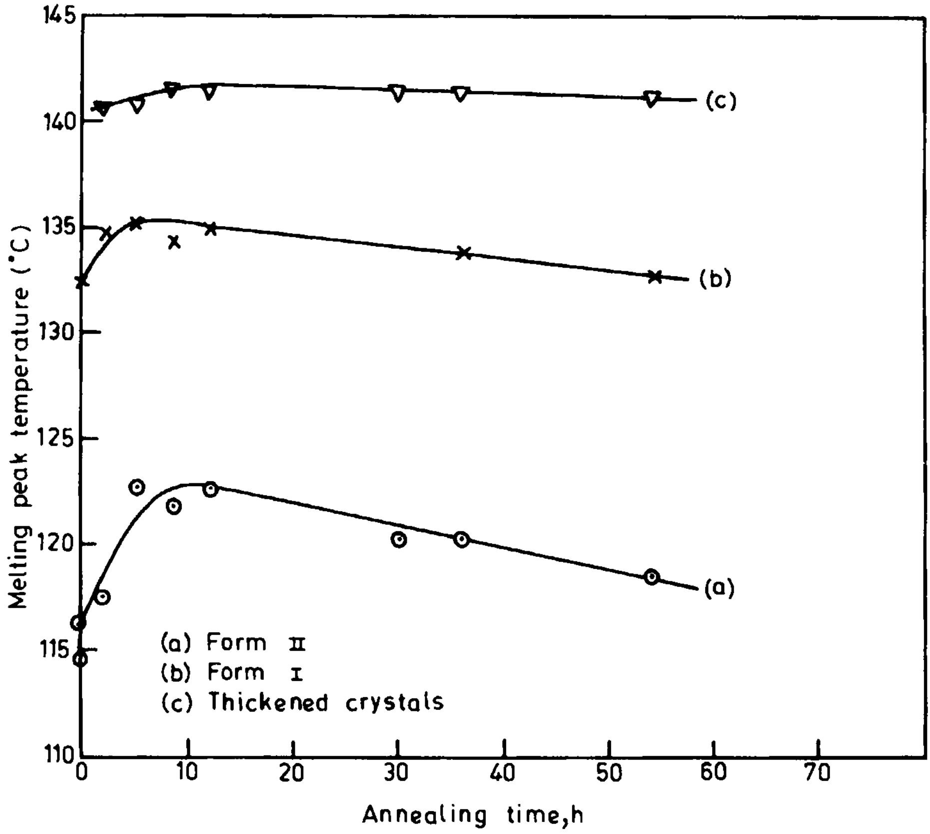

FIG. 5. Melting peak temperature of PB-1 annealed at 110°C and scanned immediately as a function of annealing time.

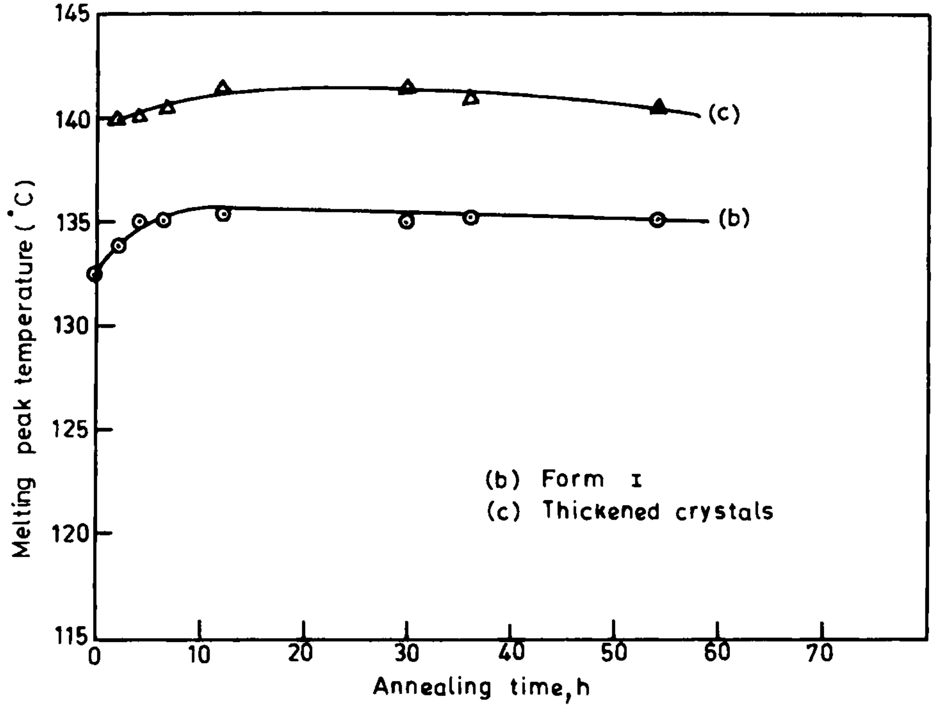

FIG. 6. Melting peak temperature as a function of annealing time. PB-1 annealed at 110°C and then kept at room temperature for 5 days.

gree of crystallinity (α) was calculated from $\alpha = \Delta H_f/\Delta H_f^*$, where ΔH_f^* is the heat of fusion of the perfectly crystalline material and ΔH_f that calculated from the observed area under the endothermic peak. Since crystals of Form II were completely transformed to Form I on storage, the upper curves in Figs. 10 and 11 represent Form I while the points in the lower curve correspond to different proportions of Forms I and II. ΔH_f increases up to 12 h of annealing time and then decreases (Fig. 10). The corresponding crystallinity increases from 70 to 90% and then decreases (Fig. 11). The increases in ΔH_f and crystallinity is attributed partly to the increasing thickness of the lamellae and partly to rising crystal perfection, whereas the later decrease in ΔH_f and crystallinity is attributed to oxidative degradation of the sample.

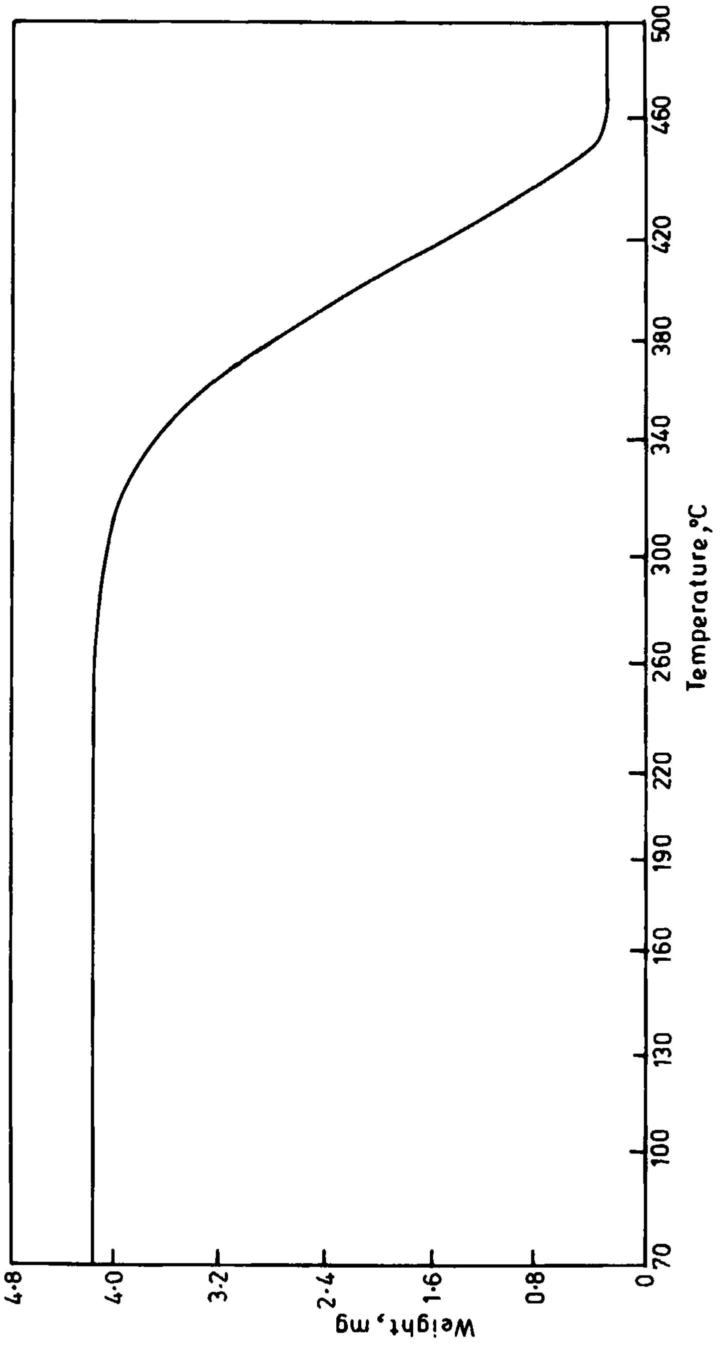

FIG. 7. Dynamic TG trace of PB-1.

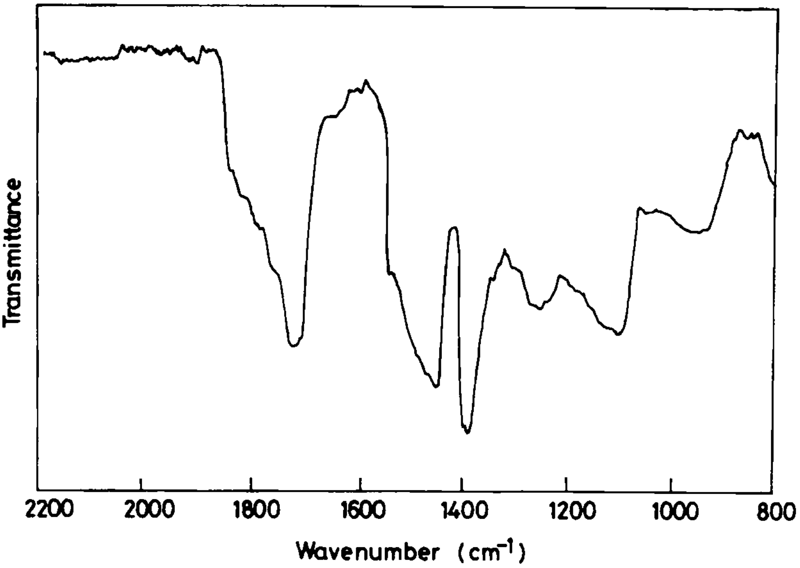

FIG. 8. IR spectrum of the benzene-soluble portion of PB-1 annealed at 110°C for 50 h.

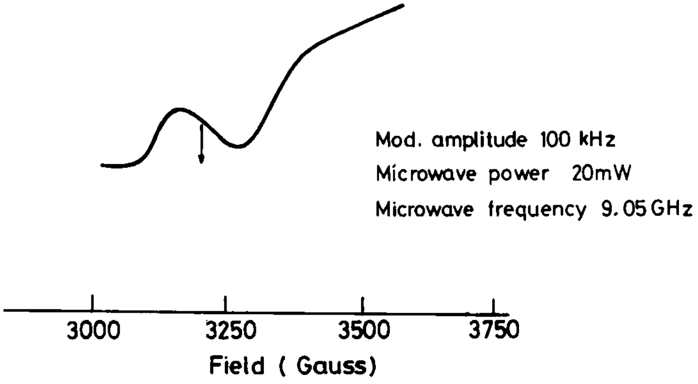

FIG. 9. ESR spectrum of PB-1 annealed at 110°C for 24 h.

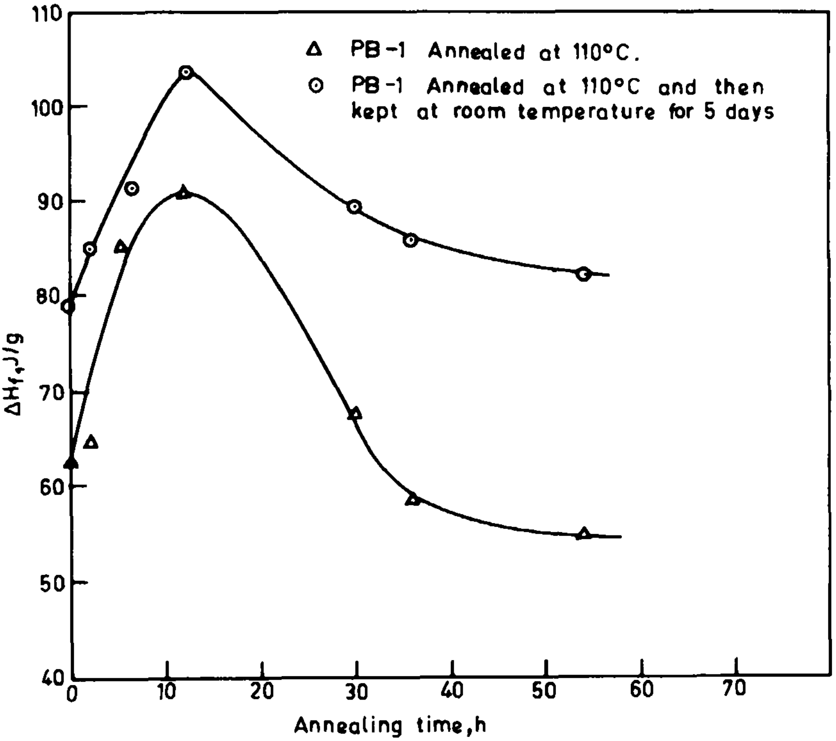

FIG. 10. Heat of fusion, ΔH_f, as a function of annealing time.

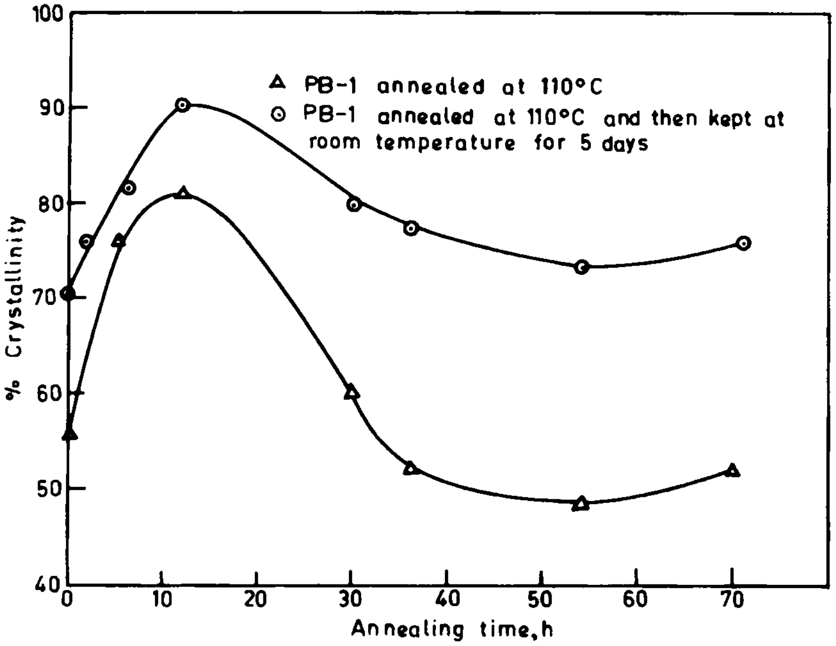

FIG. 11. Percent crystallinity as a function of annealing time.

The original polymer and the annealed samples exhibit strong wide-angle x-ray diffraction maxima at 2θ 9.7, 17, and 20.2° (Fig. 12). Annealing of the samples increases the diffraction peak height and shifts the maxima slightly to higher angles (Fig. 12). These results also support that annealing of PB-1 increases the crystal perfection of the polymer.

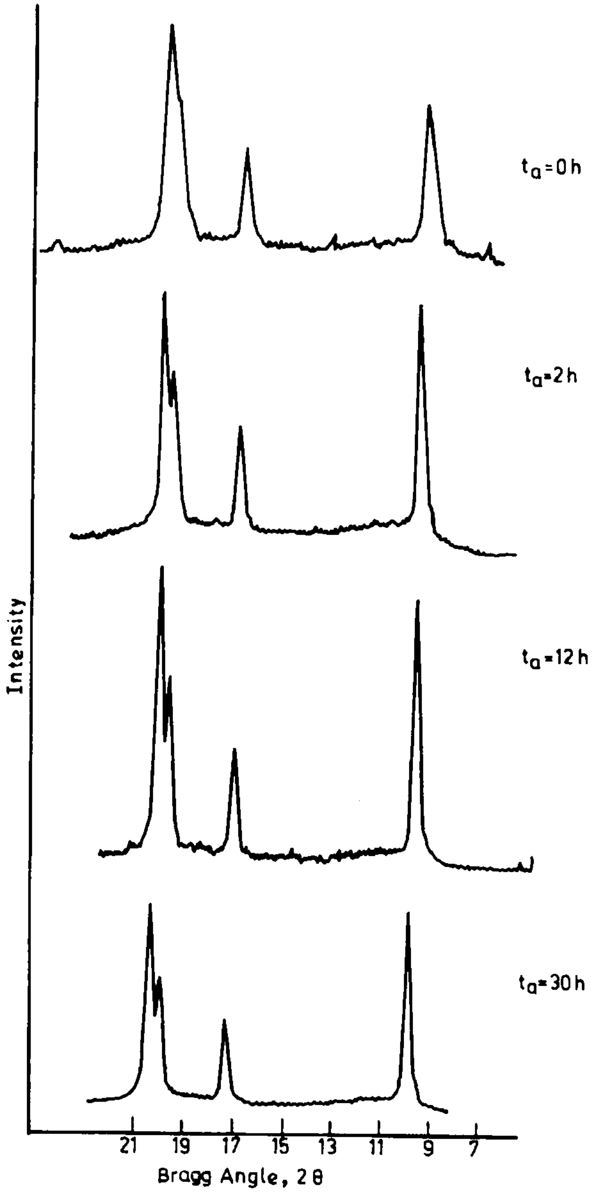

FIG. 12. WAXD scans of PB-1 at different annealing times.

ACKNOWLEDGMENT

The authors thank the Plastics Department, Shell Development Company, U.S.A., for providing the sample.

REFERENCES

[1] B. Wunderlich, *Macromolecular Physics,* Vol. 2, Academic, New York, 1976, Chap. 7.
[2] A. Keller and A. O'Connor, *Discuss. Faraday Soc., 25,* 114 (1958).
[3] W. O. Statton and P. H. Geil, *J. Appl. Polym. Sci., 3,* 357 (1960).
[4] E. W. Fischer and G. F. Schmidt, *Angew. Chem., 74,* 551 (1962).
[5] N. Morosoff, K. Sakooku, and A. Peterlin, *J. Polym. Sci., Polym. Phys. Ed., 10*(7), 1221 (1972).
[6] M. Mitomo, K. Nakazato, and I. Kuriyama, *Polymer, 19*(12), 1427 (1978).
[7] A. J. Kovacs, C. Straupe, and A. Gauthier, *J. Polym. Sci., Polym. Symp., 59,* 31 (1977).
[8] S. Gogolewski, *Colloid Polym. Sci., 257*(8), 881 (1979).
[9] S. G. Turley and H. Keskkula, *J. Appl. Polym. Sci., 9,* 2693 (1965).
[10] G. Farrow, *Polymer, 4,* 191 (1963).
[11] F. Danusso and G. Gianotti, *Makromol. Chem., 61,* 139 (1963).
[12] J. Boor and J. C. Mitchell, *J. Polym. Sci., A1,* 59 (1963).
[13] A. C. Woodward and D. R. Morrow, *J. Polym. Sci., Part A2, 6,* 1987 (1968).
[14] B. Wunderlich, *Polymer, 5,* 611 (1964).
[15] H. G. Zachmann, *Kolloid-Z. Z. Polym., 206,* 26 (1965).
[16] J. Boor Jr. and J. C. Mitchell, *J. Polym. Sci., 62,* 570 (1962).

Received June 1, 1985
Revision received January 18, 1986