Transient crystallization of an aromatic polyetherimide: effect of annealing

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A systematic study using differential scanning calorimetry has been performed on the annealing behaviour of an aromatic polyetherimide (Ultem 5001). Although crystallization from the melt did not occur, crystallinity was easily induced in the presence of methylene chloride. With annealing, a sharp melt endotherm of the solvent-treated polyetherimide was observed. The melt temperature determined after annealing for 30 min increased progressively as the annealing temperature increased, leading to an extrapolation to an apparent equilibrium melt temperature of 369°C. However, the melt temperature, as well as crystallinity, increased with the increase of the residence time at each annealing temperature. X-ray diffraction data revealed two distinct crystalline phases; a low temperature (α) phase obtained by crystallization for 30 min at 248 and 258°C, and a high temperature (β) phase obtained at 258°C for 3 h or exceeding 258°C. Values of heat of fusion per gram of crystallite were consistent with a range of 247–261 J g^{-1} for the samples of higher crystallinity.

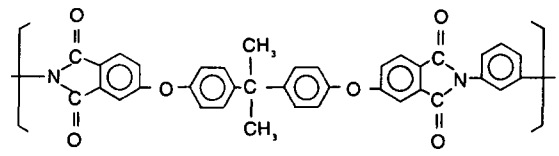
(Keywords: polyetherimide; crystallization; crystallinity; annealing; calorimetry; phase transformation)

INTRODUCTION

Solvent-induced crystallization (SINC) has been well established in polycarbonate[1–3] and poly(ethylene terephthalate)[4,5]. Wilkes and Parlapiano[1] showed that well developed spherulitic texture can be induced in polycarbonate by exposure to a non-reactive liquid or vaporous organic environment. In their studies using scanning electron microscopy, they also observed distinct plastic deformation of the induced spherulites in the polycarbonate samples which had been subjected to deformation at temperatures slightly above the glass transition temperature (T_g), 145°C.

Recently, several other SINC studies have been reported on high temperature thermoplastics including polyarylate[6], polyimidesulphone[7], polyetherimide[8], poly(aryl ether ketone ketone) (PEKK)[9], LaRC-TPI (the NASA Langley Research Center thermoplastic polyimide)[10–13] and a thermoplastic polyimide based on 4,4′-isophthaloyldiphthalic anhydride (IDPA) and 1,3-bis(4-aminophenoxy-4′-benzoyl)benzene (1,3-BABB)[14]. In the study of solvent-crystallized polyarylate[6], Berger showed a transition from shear deformation to crazing for an initially ductile amorphous material. PEKK, as pointed out by Avakian *et al.*[9], displayed two different crystal structures after either exposure to methylene chloride vapour at room temperature or low temperature annealing. These crystal structures were different from those obtained by slow cooling from the melt or by high temperature annealing. Such behaviour was not observed in poly(aryl ether ether ketone) (PEEK), which displayed only a single crystal form[9]. Crystallization which was attributed to the presence of residual solvent from processing also occurred in LARC-TPI[10–13].

Ultem aromatic polyetherimide, first reported by Serfaty[15], is an amorphous thermoplastic with the following structure for a commercially available Ultem 1000.



Our studies have been carried out on Ultem 5001 based materials, a new aromatic polyetherimide with improved solvent resistance but its chemical structure is not known from the literature. Results showed that crystallization occurred when the Ultem 5001 materials were exposed to methylene chloride[16]. Despite the original toughness, the solvent-exposed polyetherimide film specimens became brittle. Although crystallization of Ultem 5001 polyetherimide can be easily induced in the presence of methylene chloride, attempts to achieve thermal crystallization in these materials have not yet been successful. Samples appear to be amorphous once exposed to a processing temperature above the melting point, and do not appear to crystallize unless exposed to solvent.

The reluctance to melt crystallize in these high temperature polymers is partly due to the high viscosity of their melts. For example, LARC-TPI has a viscosity in the region of 10^5–10^6 Pa s at ~100°C above T_g[11], which is significantly higher than in conventional thermoplastics. As a result, crystallization from the melt is kinetically hindered and an amorphous yet crystallizable glass is formed upon cooling. However, the introduction of a good swelling agent will create sufficient mobility to allow the glass to crystallize.

The purpose of this work is to determine the effect of thermal history on the crystallization behaviour of Ultem

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5001 polyetherimide. Results of a systematic study using differential scanning calorimetry (d.s.c.) on the annealing of solvent-treated polyetherimide are presented in this paper. Degree of crystallinity as determined by wide angle X-ray diffraction, along with X-ray evidence for two different crystalline phases, are also included.

EXPERIMENTAL

Ultem 5001 polyetherimide film was obtained from the General Electric Company. Experiments of SINC were carried out in methylene chloride and in chloroform at room temperature. The solvent-treated films were then dried in vacuum for 24 h. A dried sample, weighing 4–5 mg, was prepared in an aluminum pan for each annealing treatment which was carried out via d.s.c. (Perkin-Elmer) in a nitrogen atmosphere. Annealing temperatures (T_cs) of 248, 258, 268, 278, 287 and 297°C were chosen for this study. Thermal properties were determined via d.s.c. typically at a heating rate of 20°C min^{-1}.

Wide angle X-ray diffraction data were obtained with a TEC model 210 position-sensitive detector and a Lecroy 3500 multiple-channel analyser, mounted on a Picker four-circle goniostat using monochromatic radiation at 1.5418 Å. A standard sealed copper anode X-ray tube was used at 40 kV and 20 mA. The thin film specimens from the d.s.c. pans were mounted as transmission samples onto a metal disc sample holder, using cellophane tape (Scotch Brand Tape Core Series 2-4600). The detector, as configured, had a useful range of 20° in the Bragg angle 2θ. In order to obtain complete data for each specimen, three patterns were measured for each specimen: one centred at $2\theta = 22°$, spanning $2\theta = 12–32°$; a second centred at $2\theta = 40°$, spanning $2\theta = 30–50°$; and the third centred at $2\theta = 60°$, spanning $2\theta = 50–70°$. A counting time of 2 h was routinely used for the Ultem patterns. Since the cellophane tape also scattered X-rays, blank patterns of tape alone were measured, then subtracted from the specimen patterns. The blank patterns proved to be amorphous with a single diffuse peak showing a maximum at $2\theta = 19°$. The counting time for the blank patterns was lengthened to 19 h to improve the precision of the blank subtraction process.

The X-ray diffraction patterns were transmitted from the diskette storage of the Lecroy 3500 multiple channel analyser to a VAX (TM Digital Equipment Corporation) 11/730 computer for analysis. Here the data were subjected to three operations: first, the data were corrected for background (using the cellophane tape blank patterns); second, the Lorenz-polarization correction factor f_{LP} described by Cullity[17] was applied; and third, crystalline peaks evident in the data were curve-fit by a Marquardt iterative method[18] to determine peak parameters. The second and third calculations are described more fully in the Appendix.

RESULTS AND DISCUSSION

Annealing studies

Crystallization occurred immediately after Ultem 5001 films were exposed to liquid methylene chloride. The originally translucent films became completely opaque and brittle. A typical d.s.c. thermogram, with a broad melting endotherm in the first heating scan up to 327°C, is shown in *Figure 1* (curve 1) for the methylene chloride exposed specimen; the peak of the endotherm is at 265°C. The sample was then quenched. Thereafter, a second heating scan was carried out, which displayed a T_g of 230°C without any melting endotherm (curve 2). This indicated that crystallites induced by methylene chloride exposure were completely removed by heating above the melt temperature, T_m. However, the first heating scan in *Figure 1* shows no glass transition but a baseline shift after the endothermic peak. This can be partly due to an abnormally small increment between the T_g and the T_m such that a very diffuse glass transition is masked by the melting of paracrystalline structure. Such a small temperature increment can also retard the nucleation, since sufficient supercooling required for crystallization will bring temperatures close to the glassy regions.

Our first attempt to separate the melting transition from the glass transition was carried out by annealing solvent-treated specimens at the peak of the T_m for 10 min (curve 1 in *Figure 2*). The rationale is that annealing at the peak temperature, as is well known for crystalline polymers, will first melt most of the less than perfect crystallites. However, some of the highest melting crystals remain to promote further growth upon annealing, eventually forming larger or more perfect crystallites. Consequently, the resultant microstructure after annealing will display a shift of the peak to a higher temperature. Curve 2 of *Figure 2* shows a sharper melting peak, at 280°C, which was obtained in the subsequent heating scan of the annealed sample. As expected, the T_m was higher than the original broad endotherm, 265°C, for the unannealed Ultem 5001 specimens. Again, the endothermic peak disappeared on the reheating scan (curve 3 in *Figure 2*) once the sample was heated above the T_m.

Attempts to further enhance crystal growth were carried out by annealing solvent-treated polyetherimide specimens at the various temperatures (*Table 1*). Each annealing treatment at the respective temperature required a separate film specimen. Furthermore, the procedure was carried out in a stepwise fashion; the sample at 278°C was first annealed at 248°C, followed

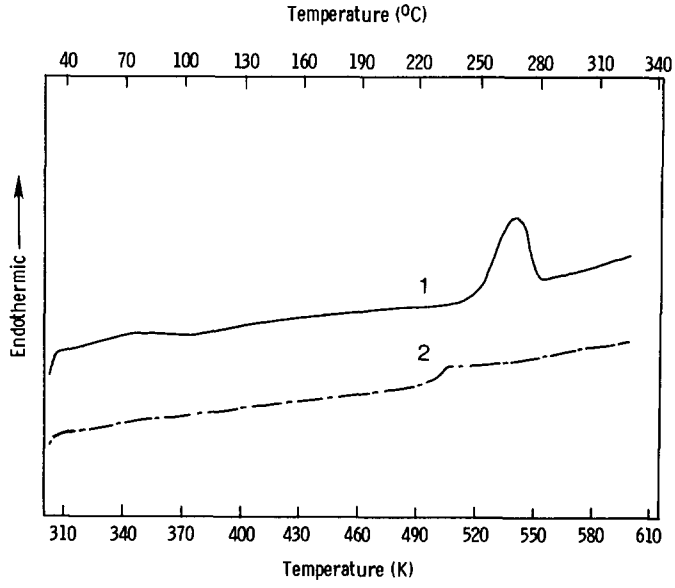

Figure 1 D.s.c. thermograms for a typical methylene chloride treated Ultem 5001 specimen: (1) first heating scan; (2) second heating scan

by 258°C and 268°C, and finally at 278°C for 30 min at each temperature. This was required since the seed crystallites would otherwise disappear had the specimens been heated directly to the final high T_c.

Figure 3 gives the d.s.c. results, in which the T_m of every melting endotherm is higher than the respective T_c. The T_m determined after annealing for 30 min increased progressively as the T_c increased. However, the T_g was constant, 230°C, for all the annealed specimens. *Table 1* summarizes the T_m as well as the enthalpy of fusion.

The enthalpy of fusion per gram of sample is dependent on the degree of crystallization and the degree of perfection of the existing crystal content. It was determined by the area under the endothermic peak, which decreased moderately as the T_c increased. Such a decrease in enthalpy of fusion can be attributed to the reduction in the recrystallization rate associated with the decrease in the degree of supercooling as the T_c approaches the true T_m. However, the reduced enthalpy of fusion (per gram of polymer) does not necessarily suggest a reduction in the enthalpy of fusion per gram of crystallite with an increase in T_c. This point will be discussed more fully in conjunction with the X-ray diffraction data.

The reduction in apparent enthalpy of fusion is especially pronounced for the specimens annealed at temperatures exceeding 287°C for 30 min, for which only very small endotherms were noticed in the d.s.c. thermograms. This is shown in curves 5, 6 and 7 in *Figure 3*. Such annealing treatments of the initially solvent-crystallized samples actually proceeded at temperatures above the temperature range which was associated with the melting endotherm of curve 1 in *Figure 1*.

Extended annealing was then carried out at 287, 297

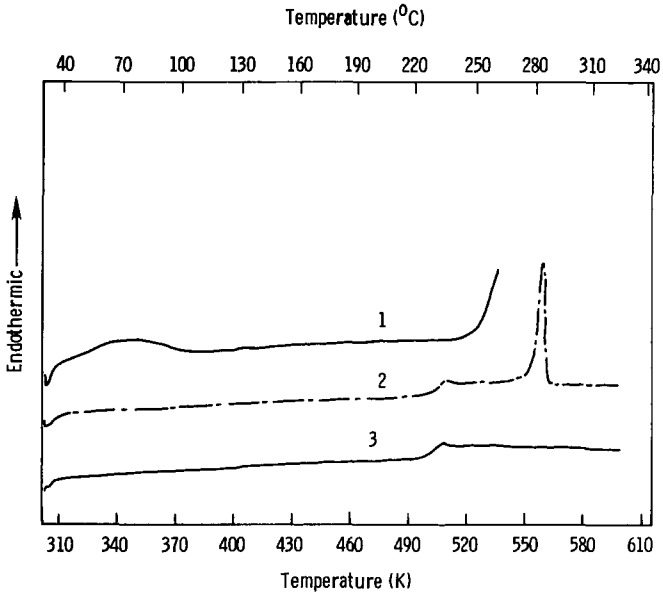

Figure 2 D.s.c. thermograms of an annealed Ultem 5001 specimen after solvent exposure: (1) first heating scan to set the anneal temperature; (2) a reheating scan right after annealing; (3) second reheating scan after annealing

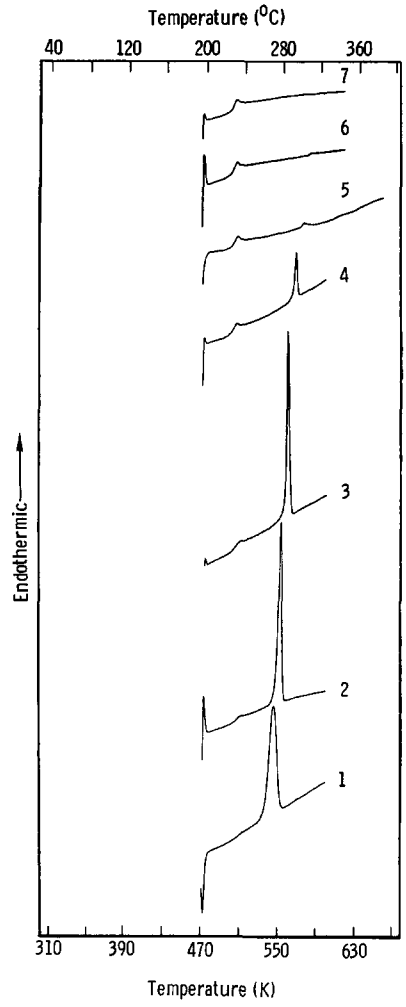

Figure 3 D.s.c. scans of solvent treated Ultem 5001 specimens annealed at various temperatures for 30 min: (1) 248°C (521 K); (2) 258°C (531 K); (3) 268°C (541 K); (4) 278°C (551 K); (5) 287°C (560 K); (6) 297°C (570 K); (7) 307°C (580 K)

Table 1 Melt temperature and enthalpy of fusion for annealed Ultem 5001

T_c		Annealed for 30 min		Annealed for 3 h		Annealed for 19 h	
(°C)	(K)	T_m (°C)	Enthalpy ($J g^{-1}$)	T_m (°C)	Enthalpy ($J g^{-1}$)	T_m (°C)	Enthalpy ($J g^{-1}$)
248	521	271	20.5	–	–	–	–
258	531	278	17.4	–	–	–	–
268	541	286	13.3	–	–	–	–
278	551	295	4.0	–	–	–	–
287	560	303	0.6	305/317	3.8	310/320	12.6
297	570	310	0.3	315/321	2.0	319/326	11.5
307	580	–	–	324	0.2	330	5.8

and 307°C for time intervals of 3 and 19 h, respectively, to increase crystal growth under conditions in which supercooling was relatively small. As described earlier, individual solvent-contacted samples were used for each annealing treatment, and all the samples were brought up to their final T_cs in a stepwise fashion with 30 min intermediate annealing times. *Figure 4* shows the d.s.c. thermogram obtained for the annealing treatment at 287°C. Instead of a single melting peak, there is now either a peak with a doublet or a peak with a shoulder. Temperatures of the melting peaks or the shoulder and melting peak were higher than the respective T_c, and increased as the residence time at each T_c increased (*Table 1*). A significant increase in enthalpy of fusion (per gram of sample) also occurred as annealing time increased.

With annealing at 307°C, little crystallization occurs at 3 h, as shown in *Figure 5*. However, when annealing was extended to 19 h, crystallization was obtained but to a small extent. This can be due to either small supercooling (resulting in unfavourable crystallization kinetics) or insufficient crystal sites for further growth. Thus, an extended holding time would be needed for those samples annealed at these higher temperatures.

An estimate of the equilibrium T_m was determined using the Hoffman-Weeks approach[19]. In this method, crystallization experiments are carried out at several temperatures, and values of the experimentally determined T_m are plotted against the respective T_c. The extrapolation of T_m *versus* T_c to intersect with the line of $T_m = T_c$ leads to the determination of an equilibrium T_m for the theoretical perfect polymer crystal. *Figure 6* shows an apparent equilibrium T_m of 369°C, based on samples annealed for 30 min. Limited data obtained for the extended annealing experiments are also included in *Figure 6* for comparison.

Experiments on the exposure to another chlorine-containing solvent, chloroform, were also examined

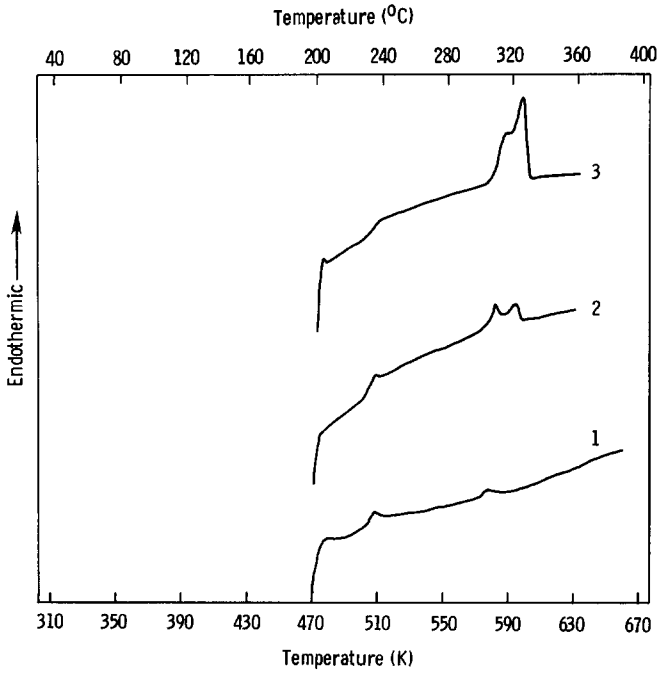

Figure 4 D.s.c. thermograms of methylene chloride treated specimens annealed at 287°C (560 K) and as a function of time: (1) 30 min; (2) 3 h; (3) 19 h

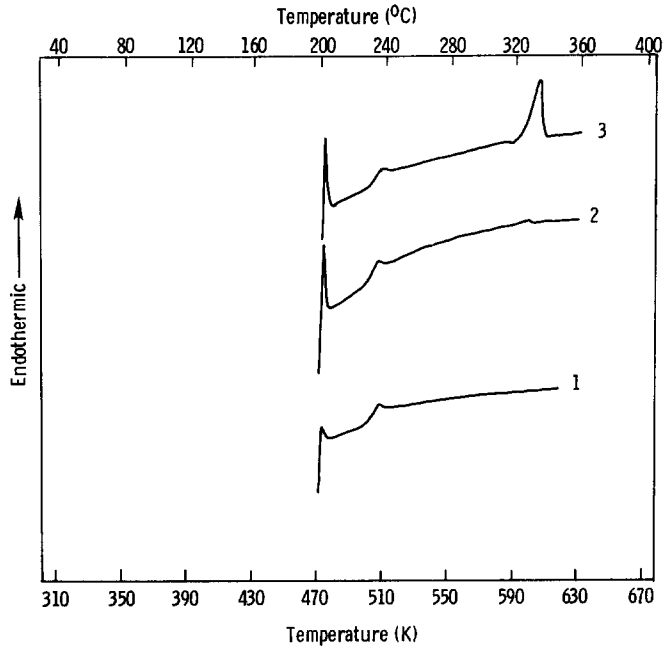

Figure 5 D.s.c. thermograms of methylene chloride treated specimens annealed at 307°C (580 K) and as a function of time: (1) 30 min; (2) 3 h; (3) 19 h

briefly. While instantaneous crystallization was observed with methylene chloride, Ultem 5001 film first swelled and then dissolved completely in chloroform. As chloroform was removed, the dried polyetherimide film became opaque. *Figure 7* shows a broad endotherm for the chloroform-treated specimen (curve 1). However, a distinct melting peak at 283°C was observed after annealing at the peak temperature (curve 4). Thus, although different crystallization behaviour was seen in these two chlorine-containing solvents, similar T_gs and melting endotherms were obtained.

X-ray measurements

To clarify observed d.s.c. results, X-ray diffraction patterns were run at room temperature (25°C) on specimens removed from the d.s.c. pans. In these data, three different types of diffraction patterns appeared, typified by those of *Figure 8*. The first type of pattern (*Figure 8a*) is totally amorphous, showing a broad halo peaking near $2\theta = 17°$; the second shows three crystalline peaks superimposed on the amorphous halo (*Figure 8b*), and the third shows as many as five crystalline peaks, differing in position from those of the second type, also superimposed on the amorphous halo (*Figure 8c*). The amorphous peak was always present, but the presence or absence, intensities and positions of the crystalline peaks varied with annealing conditions. *Table 2* shows all of the crystalline peak 2θ values and the corresponding Bragg d spacings classified into two sets: three peaks at $d = 5.94$, 5.23 and 3.65 Å attributed to a low temperature (α) phase, and five peaks at $d = 6.19$, 5.51, 4.75, 4.26 and 3.81 Å attributed to a high temperature (β) phase. The α phase appears only in two patterns: for samples annealed at 248 or 258°C for 30 min; the small number of lines observed is attributed to either crystallite imperfection, small crystallite size, or both. Any crystallinity resulting from annealing at temperatures higher than 258°C always manifested itself as the β phase. Moreover, even at a T_c of 258°C, the α phase, which

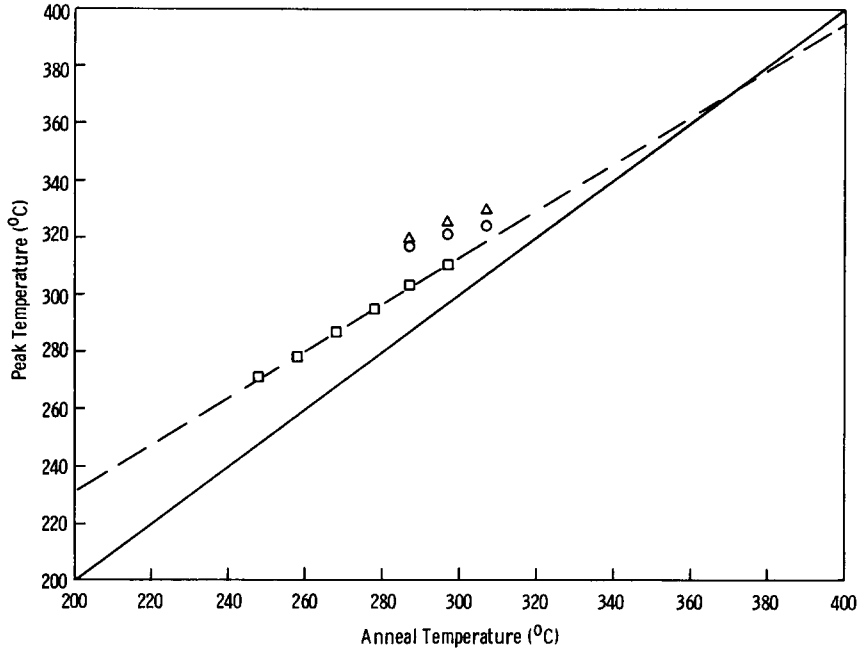

Figure 6 Plot of melt temperature *versus* anneal temperature for methylene chloride treated specimens annealed as a function of time: (□) 30 min; (○) 3 h; (△) 19 h; (--) linear regression of the data obtained by annealing for 30 min; (———) $T_c = T_m$

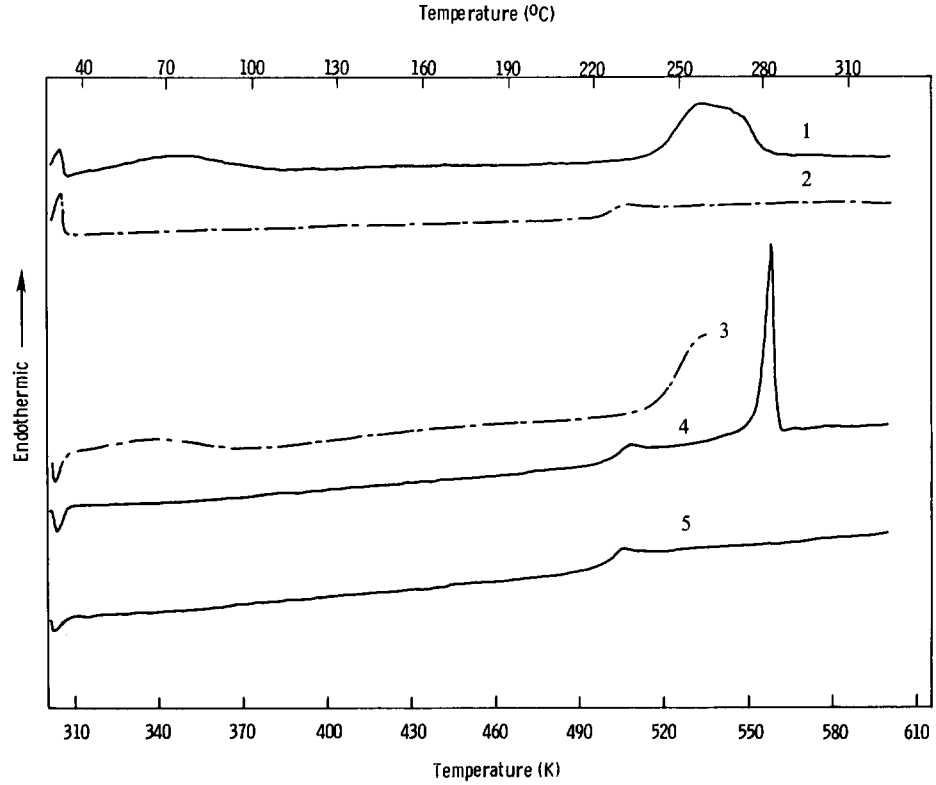

Figure 7 D.s.c. thermograms for typical chloroform treated Ultem 5001 film specimens: (1) first heating scan; (2) second heating scan; (3) first heating scan of another solvent treated specimen to set the anneal temperature; (4) a reheating scan right after annealing; (5) second reheating scan after annealing

appears after 30 min of annealing, transforms to the β phase after 3 h of annealing, indicating that the α phase is metastable relative to the β phase even at that temperature.

The apparent X-ray crystallinity (X_c) was calculated from the relative intensities of crystalline and amorphous diffraction curves, based on methods originated by Matthews *et al.*[20] and by Hermans and Weidinger[21]. Since a detailed unit cell structure has not been determined for the Ultem 5001 polyetherimide, it was not possible to apply the more rigorous methods, such as those of Ruland[22] and of Kavesh and Schultz[23,24], for determination of crystallinity.

As implemented here, after background and Lorenz-

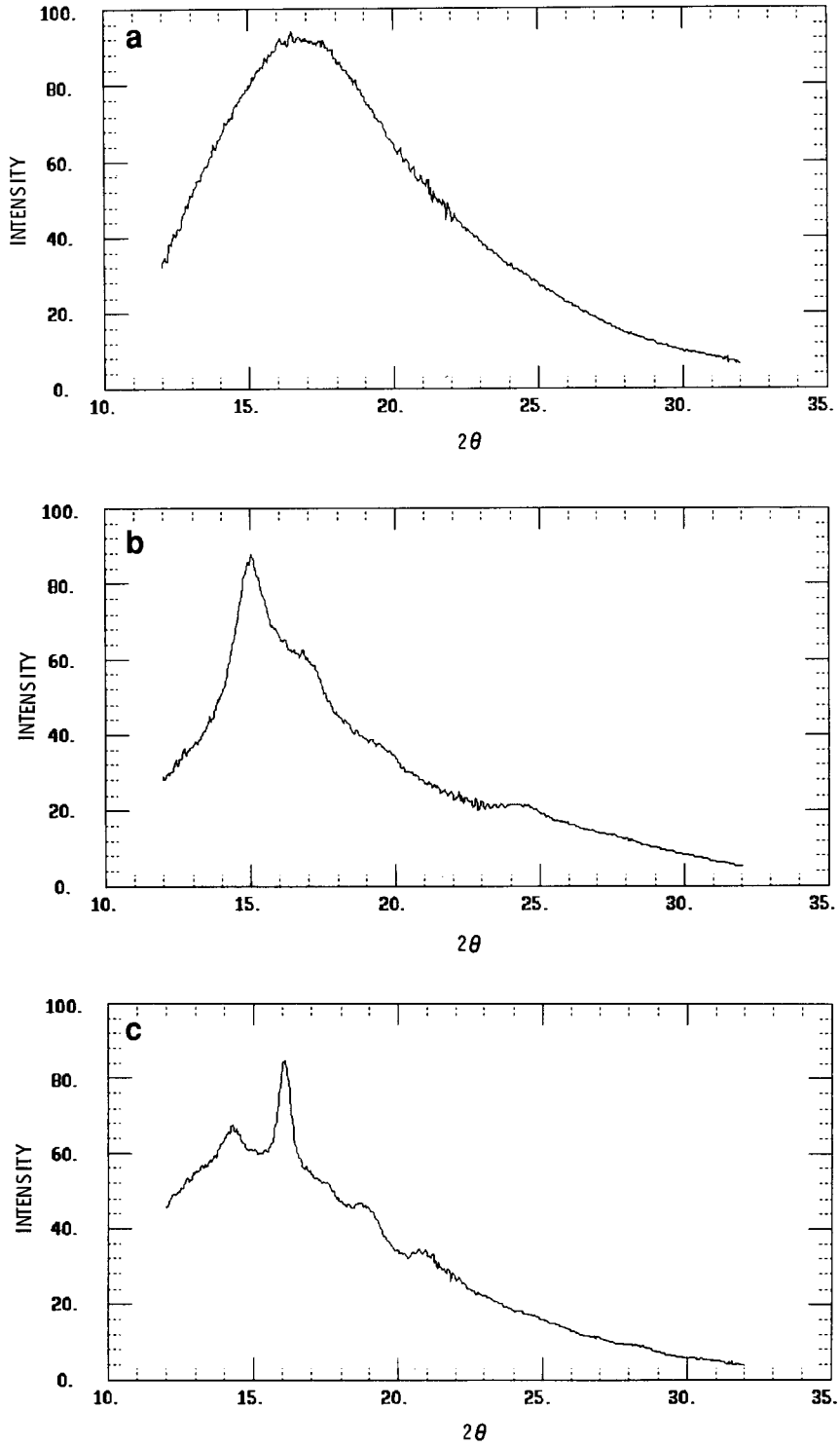

Figure 8 WAXS patterns of methylene chloride treated specimens annealed at various conditions: (a) 297°C (570 K) for 30 min; (b) 248°C (521 K) for 30 min; (c) 287°C (560 K) for 19 h

polarization corrections are applied to the data between $2\theta = 12°$ and 32°, any observed crystalline peaks are resolved mathematically from the total scattering envelope. From the peak fit parameters, the individual crystalline peak areas are summed to yield a total crystalline area A_c; X_c is then calculated as the ratio of A_c to the total area A_t:

$$X_c = A_c/A_t \quad (1)$$

Crystallinity values determined from the X-ray diffraction patterns are included in *Table 3*, along with values of heat of fusion per gram of crystallite, $\Delta H/X_c$. The crystallinity values are quite low, ranging from 0 to 0.083. The two highest crystallinities are observed at 0.083 and 0.070 for the α-phase samples obtained by crystallization for 30 min at 248 and 258°C, respectively; the samples showing β phase crystallinity have, at best, X_c values up to 0.053 obtained for 30 min at 268°C. Since the X_c values have a precision of no better than, and

Table 2 Crystalline peaks for Ultem 5001 for various annealing conditions

Temperature (°C)	Temperature (K)	Time (h)	$2\theta^a$ (deg)	d (Å)	Phase	d (ave) (Å)
258	531	0.5	14.90_8	5.94_2	α	5.94
248	521	0.5	14.92_5	5.93_5	α	
258	531	0.5	16.93_4	5.23_6	α	5.23
248	521	0.5	16.96_6	5.22_6	α	
248	521	0.5	24.36_2	3.65_3	α	3.65
258	531	0.5	24.43_6	3.64_3	α	
287	560	19.0	14.22_2	6.22_8	β	6.19
287	560	3.0	14.22_9	6.22_4	β	
278	551	0.5	14.34_0	6.17_6	β	
268	541	0.5	14.37_9	6.16_0	β	
258	531	3.0	14.40_3	6.14_9	β	
307	580	19.0	15.93_8	5.56_1	β	5.51
297	570	3.0	15.98_2	5.54_5	β	
287	560	19.0	15.99_9	5.54_0	β	
297	570	19.0	15.99_7	5.54_0	β	
287	560	3.0	16.00_2	5.53_9	β	
258	531	3.0	16.29_2	5.44_0	β	
268	541	0.5	16.32_3	5.43_0	β	
258	531	3.0	18.26_6	4.85_7	β	4.75
268	541	0.5	18.66_2	4.75_4	β	
307	580	19.0	18.81_3	4.71_7	β	
297	570	19.0	18.82_2	4.71_5	β	
287	560	19.0	18.94_6	4.68_4	β	
307	580	19.0	20.75_9	4.27_9	β	4.26
287	560	19.0	20.87_1	4.25_6	β	
297	570	19.0	20.90_6	4.24_9	β	
258	531	3.0	23.28_3	3.82_0	β	3.81
268	541	0.5	23.39_5	3.80_2	β	
278	551	0.5	23.45_2	3.79_3	β	

[a]Peak positions have been corrected for non-linearity of the detector

Table 3 Crystallinity and crystalline heat of fusion of Ultem 5001 samples

Annealing conditions				Heat of fusion	
Temperature (°C)	Temperature (K)	Time (h)	Crystallinity, X_c, by X-ray	ΔH (J g^{-1})	$\Delta H/X_c$ (J g^{-1})
248	521	0.5	0.083	20.5	247
258	531	0.5	0.070	17.4	249
268	541	0.5	0.053	13.3	251
278	551	0.5	0.023	4.0	174
287	560	0.5	0.000	0.6	0
297	570	0.5	0.000	0.3	0
287	560	3.0	0.022	3.8	173
287	560	19.0	0.048	12.6	263
297	570	3.0	0.010	2.0	200
297	570	19.0	0.044	11.5	261
307	580	3.0	0.000	0.2	0
307	580	19.0	0.030	5.8	193

possibly less than, two significant digits, it is anticipated that considerable error would propagate into the $\Delta H/X_c$ values, particularly at the lower X_c values. Nonetheless, it appears that the $\Delta H/X_c$ values are quite consistent for the samples exceeding $X_c = 0.030$; those five samples show $\Delta H/X_c$ values of 247, 249, 251, 261 and 263 J g^{-1}. Note that two members of this group are α phase samples, while three are β phase samples. Evidently the two crystalline phases have the same or quite similar heats of fusion.

CONCLUSIONS

Although thermal crystallization has not been achieved in Ultem 5001 polyetherimide, a rapid nucleation for crystal growth can be easily induced by methylene chloride exposure. As a result, an initially ductile amorphous polyetherimide is observed to embrittle. D.s.c. data display that the T_m increases progressively with an increase in T_c. This suggests that crystallization at higher temperatures can be achieved through careful stepwise treatments. The extrapolation leads to an apparent equilibrium T_m of 369°C, based on measurements of samples annealed for 30 min. Two distinct crystalline phases, a low temperature (α) and a high temperature (β) phase, were observed by X-ray diffraction. Crystallinity values were quite low, suggesting the profound effects of polymer viscosity as well as the small increment between T_g and T_m in hindering crystallization. By combining d.s.c. and X-ray results, values of the heat of fusion per gram of crystallite are consistent with a range of 247–261 J g^{-1} for samples of higher crystallinity. The limited experiments in chloroform indicate that the crystallization behaviour can differ in other solvents. Therefore, it would be of interest to explore the effect of solvent or vapour type on the crystallization of Ultem 5001 polyetherimide, and thermal stability of the induced crystals.

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APPENDIX

X-ray intensity calculations

The data were corrected on a VAX (TM Digital Equipment Corporation) 11/730 computer for background (using the cellophane tape blank patterns) and the Lorenz-polarization correction factor f_{LP} was applied. This factor, which corrects for certain X-ray instrumental effects, including the polarization effects of both the monochromator diffraction and the sample diffraction, is given[17] by:

$$f_{LP} = (1 + \cos^2 2\theta/\cos^2 2\theta_m)/(\sin^2 \theta \cos \theta) \quad \text{(A1)}$$

where 2θ is the sample Bragg angle, the independent variable; and $2\theta_m$ is the Bragg angle of the monochromator reflection, the graphite (0 0 2) reflection in this case. [Note that the equation (A1) used here differs from the common form given by Cullity[17] in that $(1/\cos^2 2\theta_m)$, representing the polarization ratio of the incident beam, replaces the $\cos^2 2\theta_m$ of Cullity. This results from the geometry of the Picker monochromator, in which the monochromator diffraction plane is perpendicular to the sample diffraction plane, rather than parallel, as assumed by Cullity. Thus the incident beam has the inverse of the polarization presumed by Cullity.]

The X-ray data analysis programs also include a procedure for peak curve fitting. In this method, the intensity curve for a selected range of data, which includes a peak maximum, is fit to a combination of a straight line baseline and either a Gauss or Cauchy peak function, given by:

$$I_{calc}(2\theta) = A_1 + A_2 \cdot 2\theta + P(2\theta, A_3, A_4, A_5) \quad \text{(A2)}$$

where the peak function P can be identified as either the Gauss function:

$$P(2\theta, A_3, A_4, A_5) = G(2\theta, A_3, A_4, A_5) = A_3 \exp\{-[4 \ln 2 \cdot (2\theta - A_4)/A_5]^2\} \quad \text{(A3)}$$

or as the Cauchy function:

$$P(2\theta, A_3, A_4, A_5) = C(2\theta, A_3, A_4, A_5) = A_3/\{1 + [2(2\theta - A_4)/A_5]^2\} \quad \text{(A4)}$$

In either instance, 2θ is the independent variable, while A_1–A_5 are adjustable parameters: A_1 is the constant (intercept) part of the baseline straight line; A_2 is the slope of the baseline straight line; A_3 is the maximum intensity of the peak (Gauss or Cauchy) curve; A_4 is the peak position of the peak curve; and A_5 is the full width at half maximum (FWHM) of the peak curve.

The Marquardt Method, as described by Press *et al.*[18], is used as an iterative procedure for fitting the experimental data $I_{expt}(2\theta)$ to the calculated function $I_{calc}(2\theta)$. The calculation converges to yield a solution set A_1–A_5 for the Gauss and for the Cauchy function; the correct solution is taken as the one of the two with the lower value of χ^2, a weighted least squares parameter.