

Enhancement of the crystallinity of a thermoplastic polyimide

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The polyimide based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,4-diaminobutane (poly(BTDA-DAB)) does not crystallize from the melt. This paper describes attempts to enhance the crystallization of this polyimide. The spherulitic growth rate and the nucleation density of pure poly(BTDA-DAB) ($M_w = 35\,300$) are quite low, namely $G = 0.031\ \mu\text{m min}^{-1}$ and $1.7 \times 10^7\ \text{cm}^{-3}$ respectively, both at 240°C . Classical nucleating agents, such as talc and non-coated glass fibre, raise the nucleation density to $6\text{--}7 \times 10^9\ \text{cm}^{-3}$ but endcapping the polyimide chains with $-\phi\text{-SO}_3\text{Na}$ endgroups results in a nucleation density of $3.3 \times 10^{15}\ \text{cm}^{-3}$. The highest crystallization rate is obtained for a sample in which 4.7% of the chains have been endcapped with $-\phi\text{-SO}_3\text{Na}$. Upon cooling from the melt at $20^\circ\text{C min}^{-1}$, the heat of crystallization of this sample is ca. $32\ \text{J g}^{-1}$, corresponding to a crystallinity of ca. 35%. Further, this paper demonstrates the synergistic effect of the simultaneous presence of $-\phi\text{-SO}_3\text{Na}$ endgroups and 10 wt% of 4-hydroxybenzophenone as plasticizer. Further optimization is necessary to obtain a high molecular weight, semicrystalline poly(BTDA-DAB) upon injection moulding. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Early condensation polyimides such as Kapton (Du Pont), made by the condensation of pyrometallic anhydride (PMDA) and 4,4'-diaminodiphenylether (DAPE), have very high T_g and T_m and are completely insoluble and unmouldable. Soluble and mouldable polyimides result from introducing, for example, flexible ether linkages. Though most of the thermoplastic polyimides are amorphous, semicrystalline polyimides have recently been produced^{1–5}.

In a recent paper, we described the synthesis and characterization of α,ω -diaminoalkane based polyimides⁶. The polymer poly(BTDA-DAB) (Scheme 1) based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,4-diaminobutane (DAB), exhibits the optimum trade-off between properties and processability, and has been selected for further investigation⁷.

As synthesized, poly(BTDA-DAB) has a crystallinity of ca. $60 \pm 5\%$ (see Figure 1) with a T_g around 174°C and a T_m close to 300°C , but no crystallization is observed upon cooling from the melt at a rate of $20^\circ\text{C min}^{-1}$ (see Figure 2). This paper describes preliminary results on the enhancement of the crystallization of poly(BTDA-DAB) from the melt.

The crystallization rate is controlled by the nucleation density and the spherulitic growth rate, which are

enhanced by nucleating agents and plasticizers, respectively. This paper will deal both with *external* nucleating agents that are finely divided seed particles, and with *internal* nucleating agents. The latter are ionic chain ends and are generally referred to as 'chemical nucleating agents' because the ionic chain ends are grafted by a chemical reaction⁸. The nucleating activity of ionic chain ends has been demonstrated in recent papers for polyethyleneterephthalate^{9,10} and PEEK¹¹. Plasticizers investigated in this study are limited to external ones.

EXPERIMENTAL

Synthesis of poly(BTDA-DAB)

The polyimides were prepared in NMP (10 wt%) according to a slight modification of the solution-imidization procedure described by Arnold *et al.*¹². For details, the reader is referred to refs 6 and 7. Solid BTDA was added to a solution of DAB and the desired amount of endcapper in NMP. After stirring at room temperature for 16 h, xylene was added to the poly(amic acid) solution and the condensation was accomplished by azeotropic removal of reaction water (4 h, 160°C), yielding the polyimide. Before cooling the polyimide solution, an excess of benzoyl chloride was added to block non-reacted amine endgroups. Upon cooling, the polyimides crystallized from solution. The fine powder was filtered off, washed with methanol and dried overnight at 180°C under vacuum.

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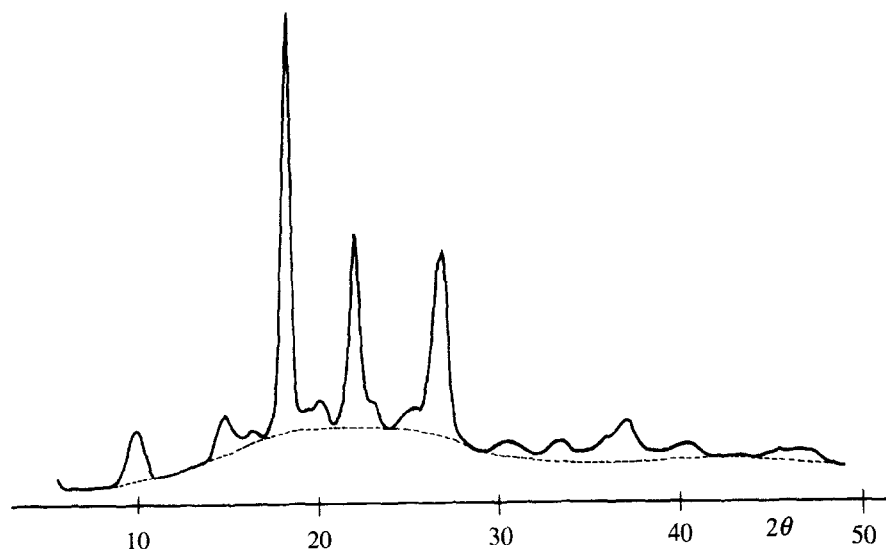


Figure 1 WAXS of as-synthesized poly(BTDA-DAB) (Table 1, entry 1). The dotted line represents a quenched, fully amorphous sample

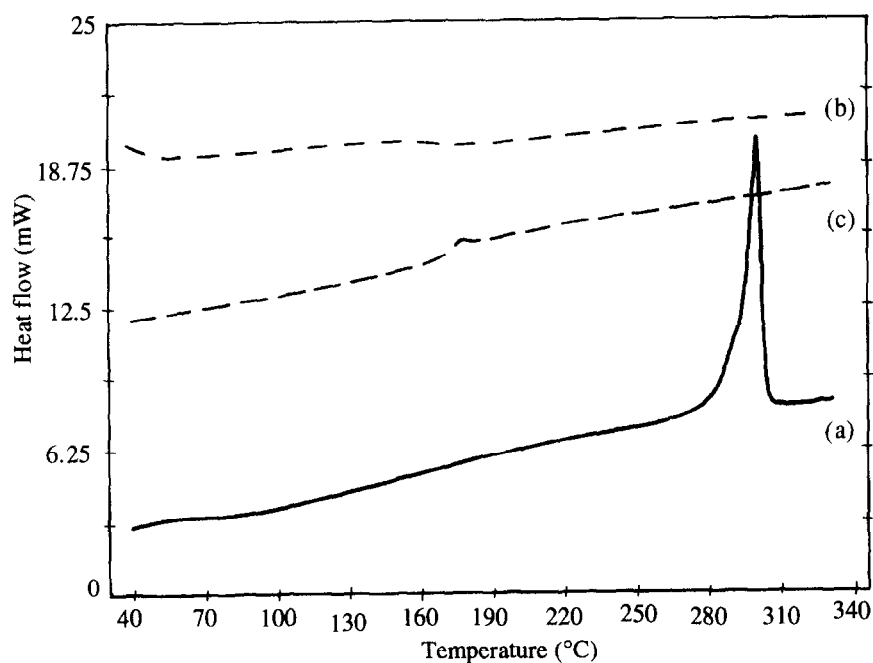
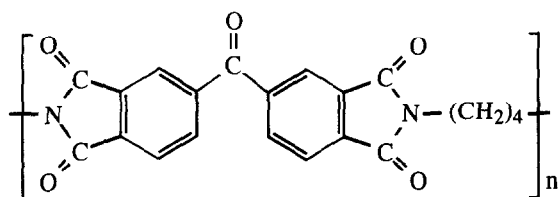


Figure 2 D.s.c. ($20^{\circ}\text{C min}^{-1}$) of as-synthesized poly(BTDA-DAB): (a) first heating; (b) cooling; (c) second heating



Scheme 1

Analyses and instrumentation

D.s.c. traces were recorded on a Perkin-Elmer DSC-7. T_g measurements were determined at a heating rate of $20^{\circ}\text{C min}^{-1}$ on a second heating. T_{cc} and ΔH_{cc} values were established at a cooling rate of $20^{\circ}\text{C min}^{-1}$. Half crystallization times $t_{0.5}$ were taken from an isotherm at 240°C .

The spherulitic growth rate and nucleation density were determined under nitrogen atmosphere with a

Jenaval polarization microscope equipped with a Linkam THMS 600 heating stage. The films were prepared by heating the polyimide powder under nitrogen at 330°C for 2 min followed by a quenching at a rate of $100^{\circ}\text{C min}^{-1}$ to the crystallization temperature. The obtained films were rather thick ($\sim 100\ \mu\text{m}$), but the low nucleation density experienced in plain poly(BTDA-DAB) allows the observation of individual spherulites.

The degree of crystallinity of as-synthesized poly(BTDA-DAB) was estimated from a powder diffractogram of the polyimide compared with the diffraction halo of a quenched, fully amorphous sample (Figure 1).

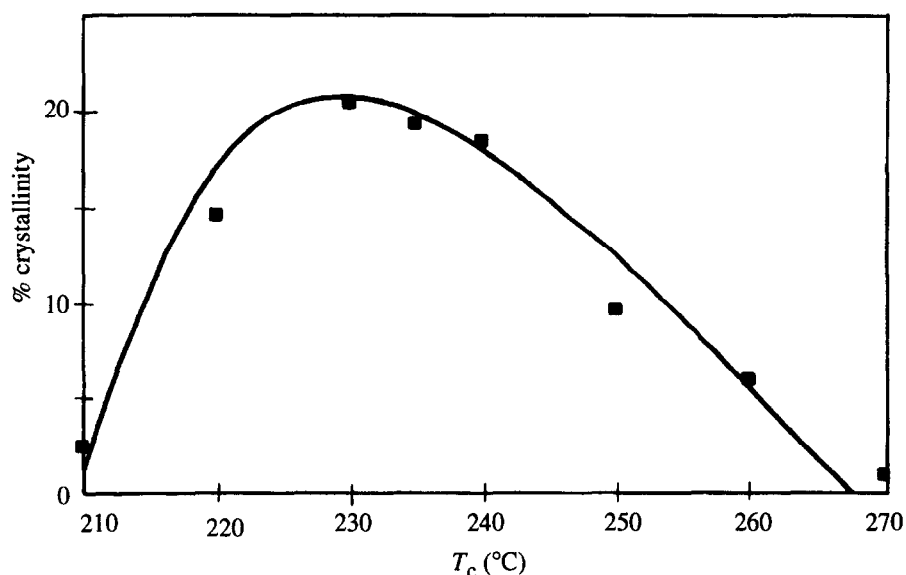
RESULTS AND DISCUSSION

Polymers

All polyimides listed in Table 1 were prepared in NMP

Table 1 Monomer composition and molecular characteristics of poly(BTDA-DAB)

Entry	Mol% diamine	Mol% dianhydride	Mol% endcapper	End group	\bar{M}_n (g mol ⁻¹)	\bar{M}_w (g mol ⁻¹)	$[\eta]$ (dl g ⁻¹)	% modified chain ends
1	49.5	50.5	–	– ϕ	11 400	35 300	0.43	–
2	48.5	49.6	1.9	– ϕ	5100	9500	0.18	–
3	49.6	50.1	0.3	– ϕ -COONa	9100	27 600	0.35	<1.0
4	49.6	50.1	0.3	– ϕ -SO ₃ Na	8400	21 600	0.33	1.3
5	48.6	51.0	0.5	– ϕ -SO ₃ Na	5400	11 100	0.21	1.7
6	48.5	50.6	0.7	– ϕ -SO ₃ Na	4500	9300	0.18	2.8
7	48.5	50.5	1.0	– ϕ -SO ₃ Na	6800	18 200	0.29	4.7
8	48.5	49.6	1.9	– ϕ -SO ₃ Na	6200	14 900	0.27	7.9
9	48.5	49.6	1.9	– ϕ -SO ₃ H	8800	23 600	0.34	17.8

**Figure 3** Crystallinity for plain poly(BTDA-DAB) (Tables 1 and 2, entry 1) after 12 h at T_c

by the two-step process described in the experimental section. For the polyimide given in entry 1, no endcapper was utilized and the dianhydride was used in a slight excess. In the case of entries 2–9, various amounts of different endcappers (e.g. aniline, 4-aminobenzenesulfonic acid or its sodium salt) were used. In all cases, the residual amine endgroup concentration is below the detection limit of 0.005 meq g⁻¹. This amine elimination limits branching and crosslinking reactions with the carbonyl groups of the polyimide chains, as described earlier^{6,7}. It is obvious that extensive branching and crosslinking will retard crystallization.

Crystallization of plain poly(BTDA-DAB)

As determined from WAXS, the polyimide powder obtained from synthesis is ca. 60% crystalline. The melting enthalpy of this sample, measured by d.s.c., is ca. 55 J g⁻¹. Comparing these results allows the calculation of a melting enthalpy of 92 J g⁻¹ for a 100% crystalline sample. This figure will be used to evaluate the crystallinity of various polyimide samples. The crystallinity attained by the plain poly(BTDA-DAB) (entry 1, Table 1) after cooling down the melt to T_c , and annealing for 12 h, is given in Figure 3. The maximum crystallinity is only ca. 20% at 230°C.

The crystalline growth of the plain poly(BTDA-DAB) is spherulitic and the nucleation instantaneous. As shown in Figure 4, the spherulitic growth rate of the plain polyimide (with $\bar{M}_w = 35\,300$) is very low. G_{\max} is equal to 0.031 $\mu\text{m min}^{-1}$ at 240°C, whereas for example, PC, PET and PE have maximum growth rates of 0.0012, 10 and 5000 $\mu\text{m min}^{-1}$, respectively. For a poly(BTDA-DAB) (entry 2) with $\bar{M}_w = 9500$, G_{\max} is equal to 0.035 $\mu\text{m min}^{-1}$. Along with polycarbonate, poly(BTDA-DAB) is one of the polymers with the lowest spherulitic growth rate. This may be due to the presence of bulky aromatic groups and cyclic imide groups that rigidify the polymer chain.

The nucleation density N for plain poly(BTDA-DAB) (entry 1, Table 1) was assessed for all T_c s (Figure 5) using the Avrami model for spherical crystals:

$$N = -\frac{\ln(1 - \lambda/\lambda_\infty)}{4/3\pi(\rho_s/\rho)(Gt)^3} \quad (1)$$

In the Avrami treatment, λ and λ_∞ represent the degree of crystallinity at time t and at the end of the primary crystallization, respectively. In this formula, ρ_s is the density of the spherulitic phase, ρ the density of the amorphous phase and G the spherulite radial growth rate. The nucleation density N of plain

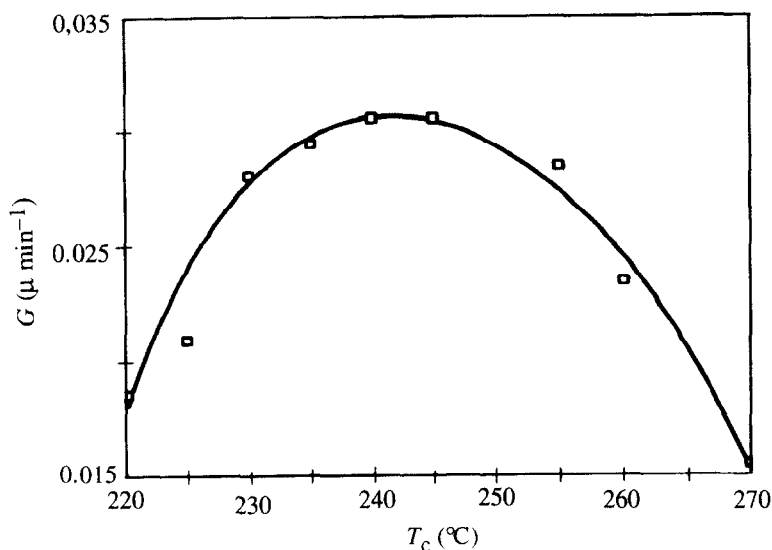


Figure 4 Spherulitic growth rate for plain poly(BTDA-DAB) (Tables 1 and 2, entry 1) versus T_c

Table 2 Crystallization data of poly(BTDA-DAB), obtained at 240 C

Entry	End group	% Modified chain ends	$t_{0.5}$ (min)	ΔH_{cc} (J g ⁻¹)	N (cm ⁻³)
1	ϕ	-	>60	0	1.7×10^7
2	ϕ	-	>60	0	1.0×10^7
3	$-\phi-COONa$	<1.0	>60	0	$<1.5 \times 10^7$
4	$-\phi-SO_3Na$	1.3	1.3	2	1.5×10^{12}
5	$-\phi-SO_3Na$	1.7	5.0	1	2.6×10^{10}
6	$-\phi-SO_3Na$	2.8	2.7	4	1.7×10^{11}
7	$-\phi-SO_3Na$	4.7	(0.1)	32	3.3×10^{15}
8	$o-SO_3Na$	7.9	(0.1)	22	3.3×10^{15}
9	$-\phi-SO_3H$	17.8	>60	0	$<1.5 \times 10^7$

poly(BTDA-DAB) was estimated for all the values of T_c (Figure 5) from samples crystallized for 720 min (12 h) at each temperature. Since we did not determine the whole crystallization kinetics, we chose as the λ_{∞} value the crystallinity degree of a sample annealed for 25 h at 240°C. The melting enthalpy of this sample was 37 J g⁻¹, which corresponds to a λ_{∞} of 40%. Its density is equal to 1.67 g cm⁻³. This figure was taken as the value of the density of the spherulitic phase ρ_s , the density ρ of amorphous plain poly(BTDA-DAB) being 1.41 g cm⁻³.

The values of N for the plain polymer calculated from equation (1) are given in Table 2, entries 1 and 2. The nucleation density is very low. Clearly, the very low rate of crystallization observed for the plain polyimide results from both a low nucleation density and a very sluggish growth rate.

Crystallization of nucleated poly(BTDA-DAB)

The addition of 3 wt% of a classical external nucleating agent such as talc raised the nucleation density N of the high molecular weight polyimide (entry 1) at 240°C from 1.7×10^7 cm⁻³ to 6.8×10^9 cm⁻³ (for the low \bar{M}_w poly(BTDA-DAB) given as entry 2, $N = 1.0 \times 10^7$ cm⁻³), whereas the addition of 5 wt% of (non-coated) glass fibre resulted in a nucleation density N equal to 6.2×10^9 cm⁻³. N was calculated on the supposition that λ_{∞} , ρ_s , ρ and G remained unchanged with respect to non-nucleated

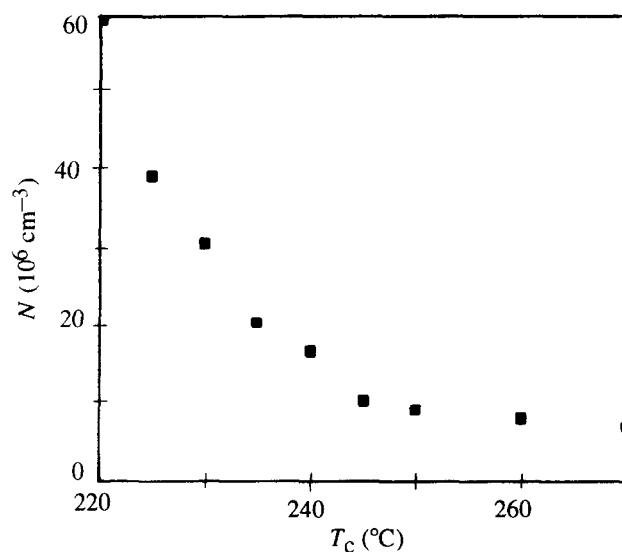
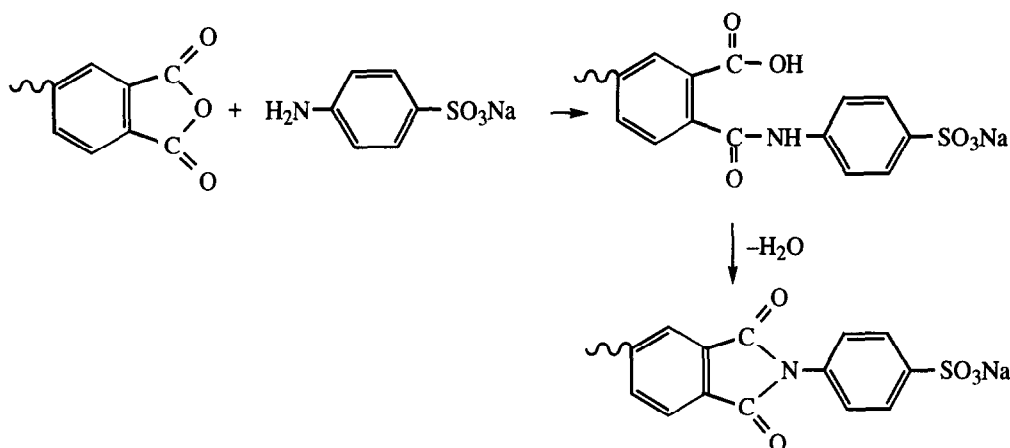


Figure 5 Nucleation density N for plain poly(BTDA-DAB) (Tables 1 and 2, entry 1) versus T_c

samples. In both cases the maximum attainable crystallinity at 240°C was ca. 34%, for which a crystallization time of 75 min was required. 1.5 wt% of sodium benzoate and sodium *o*-chlorobenzoate showed no nucleating



Scheme 2

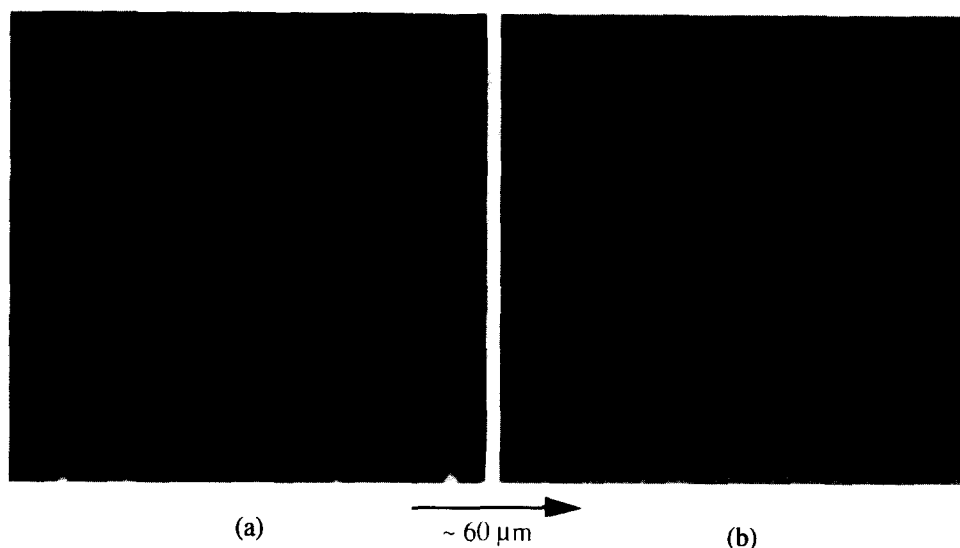


Figure 6 Optical micrographs for plain (entry 1) (a) and for $-\phi$ -SO₃Na endcapped (entry 7) (b) samples, after 2 h at 240°C

effect at all and the crystallinity after 2 h at 240°C was zero.

As quoted in the introduction, another very powerful way to increase nucleation is to graft ionic chain ends onto the polymer. It is thought that the ionic end groups associate in clusters during processing in the melt, thereby orienting the polymer chains, which facilitates crystallization. This procedure, which is known as 'chemical nucleation', can be applied to the thermoplastic polyimide studied in this paper by using a very simple chemical modification reaction that can be summarized as shown in Scheme 2.

In Table 2, some data on $-\phi$ -CO₂Na, $-\phi$ -SO₃H, $-\phi$ -SO₃Na and $-\phi$ endcapped poly(BTDA-DAB) samples are given. Crystallization data have been obtained at 240°C. For entry 3 (Table 2), [Na] and for entries 4–9, [S] was measured by X-ray fluorescence. Using \bar{M}_n , measured by g.p.c. in 0.01 M LiBr/*m*-cresol solution using universal calibration, the percentage of modified chain ends was calculated.

The crystallization rate is high enough to allow the determination of the crystallization time $t_{0.5}$ and the nucleation density N , using an expression derived from equation (1):

$$N = \frac{\ln 2}{4/3\pi(\rho_s/\rho)(Gt_{0.5})^3} \quad (2)$$

Since the high values of N did not allow a direct determination of G for the nucleated samples (entries 4–8), the G value of entry 2 ($0.35 \mu\text{m min}^{-1}$) was used for all the calculations. Values of N are not absolute figures, therefore.

Sodium sulfonate endgroups prove to be effective nucleating agents for poly(BTDA-DAB), with reduction of $t_{0.5}$ to below 0.1 min for poly(BTDA-DAB) of entries 7–8. The values given in parentheses in Table 2 mean that $t_{0.5}$ values are too small to be measured but nevertheless remain smaller than 0.1 min. High crystallization rates go with the presence of ionic chain ends. Indeed, replacement of $-\theta$ -SO₃Na ionic chain ends by neutral $-\theta$ -SO₃H acidic groups (entry 9) produces a considerable decrease of the crystallization rate. Figure 6, showing optical microscopy micrographs taken at 240°C of a plain and a $-\phi$ -SO₃Na terminated sample, is illustrative of the very substantial increase of the nucleation density resulting from the presence of ionic chain ends. Since the use of a lower molecular weight polyimide does not enhance N (compare entries 1 and 2, Tables 1 and 2), it can be concluded that the ionic chain ends are exclusively responsible for the observed higher nucleation density.

Figure 7 shows a substantial increase of the crystallization temperature on cooling, T_{cc} , as a function of the percentage of $-\phi$ -SO₃Na modified chain ends. The optimum value is around 5% modified endgroups, which

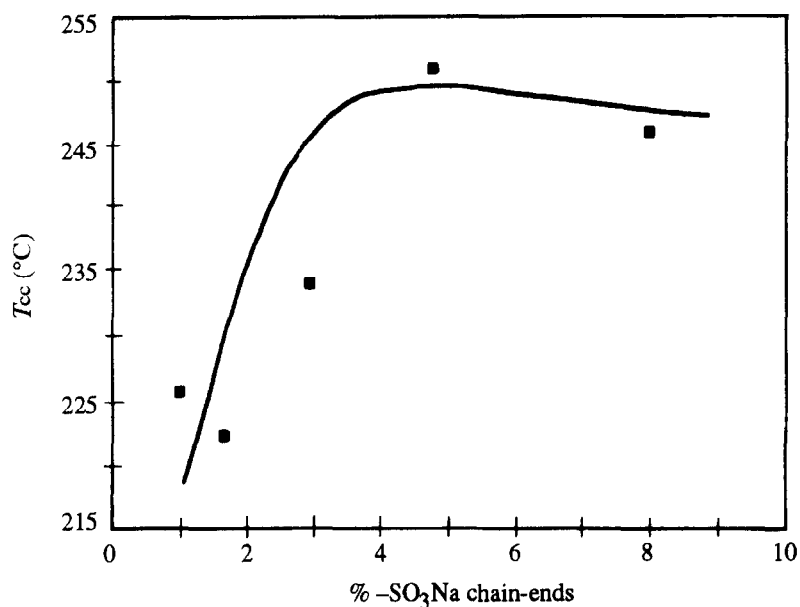


Figure 7 T_{cc} versus the percentage of chain ends containing $-\phi-SO_3Na$

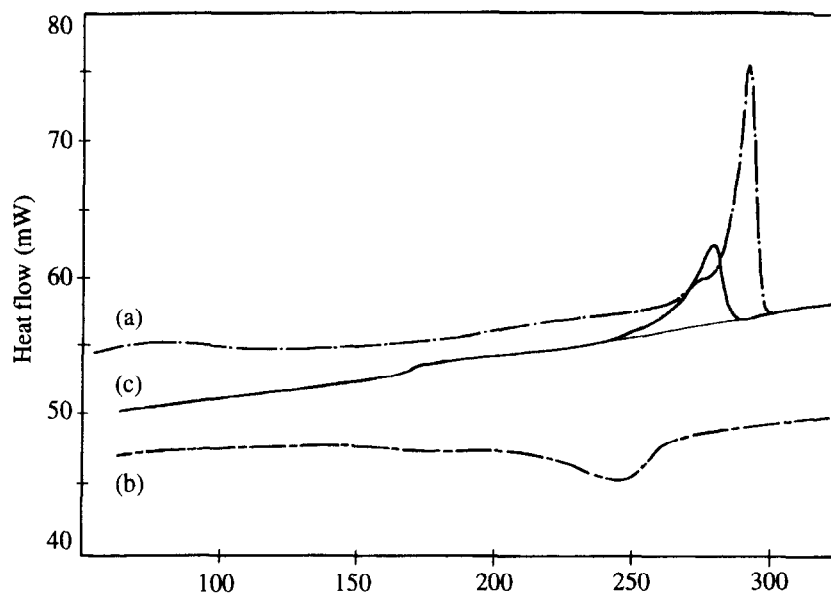


Figure 8 D.s.c. ($20^{\circ}Cmin^{-1}$) of poly(BTDA-DAB) (entry 8), containing 7.9% $-\phi-SO_3Na$ end groups: (a) first heating; (b) cooling; (c) second heating

agrees with results found for the chemically nucleated, $-\phi-SO_3Na$ terminated PEEK⁸. This behaviour is attributed to a viscosity enhancement associated with ionic chain-end association in the melt. The decrease of T_{cc} observed when the percentage of modified chain ends is over 5% shows that the increase in N caused by ionic chain ends is partially offset by a decrease in G resulting from higher viscosity of the melt. One also notices that the sample containing 5 mol% of end-capped chain ends reaches a ΔH_{cc} of $32 J g^{-1}$, which indicates a substantial crystallization ($\sim 30\%$) on cooling from the melt at a rate of $20^{\circ}C min^{-1}$.

Figure 8 shows d.s.c. traces for a $-\phi-SO_3Na$ terminated poly(BTDA-DAB) sample (entry 8 in Table 1), which should be compared to Figure 2 (entry 1 in Table 1). One observes that the chemically nucleated poly(BTDA-DAB) sample is crystallizing upon cooling at a rate of $20^{\circ}C min^{-1}$.

Crystallization of nucleated and plasticized poly(BTDA-DAB)

As shown previously¹³, the crystallization rate of a polymer which is difficult to crystallize, such as bisphenol-A polycarbonate, can be substantially enhanced by addition of limited quantities of a plasticizer. The presence of a plasticizer accelerates the spherulitic growth rate G by enlarging the crystallization window, $T_m - T_g$. However, to maintain a sufficient temperature resistance, the plasticizer concentration should be kept below a limit of around 10%. Furthermore, higher amounts of plasticizer might affect the mechanical properties negatively. Another difficulty in using plasticizers results from their volatility. In this work, we chose hydroxybenzophenone, which with a boiling point higher than $360^{\circ}C$, is not volatile.

Adding 10 wt% of 4-hydroxybenzophenone to the polyimide of entry 1 (Table 2) decreased T_g from 178 to 149°C. In this case, the spherulitic growth rate was increased from $0.031 \mu\text{m min}^{-1}$ to $0.13 \mu\text{m min}^{-1}$. However, a reduction of the molecular weight, as in the case of the polymer of entry 2 ($M_w = 9500$; $G = 0.35 \mu\text{m min}^{-1}$), produces a more important effect. Obtaining a growth rate of ca. $0.35 \mu\text{m min}^{-1}$ for a high molecular weight poly(BTDA-DAB) therefore, seems to be out of reach, although adequate mechanical properties would require a minimum M_w value of around 20 000, probably even higher.

The synergistic effect on the crystallization rate of ionic chain ends and 4-hydroxybenzophenone plasticizer was investigated for the polymer of entry 4. The addition of 10 wt% of 4-hydroxybenzophenone reduces T_g from ca. 170 to 120°C, thereby increasing the crystallization window ($T_m - T_g$) by about 50°C. This is accompanied by a reduction of $t_{0.5}$ from 1.3 to 0.9 min and a large increase of ΔH_{cc} from 2 to ca. 23 J g^{-1} .

DISCUSSION AND CONCLUSIONS

The following empirical relationship¹⁴ usually holds between T_g and T_m expressed in degrees K:

$$0.58 < T_g/T_m(\text{K}) < 0.78 \quad (3)$$

Polymers with a low $T_g/T_m(\text{K})$ value have a large crystallization window and crystallize very easily. For example, polyethylene with $T_g/T_m(\text{K}) = 0.35$ and a crystallization window of $\sim 275 \text{ K}$ has a very high crystallization rate. On the other hand, polymers like the poly(BTDA-DAB) studied here with $T_g/T_m(\text{K}) = 0.80$ are difficult to crystallize. This is the result of a narrow crystallization window ($T_m - T_g = 110 \text{ K}$) whereas, for fast crystallizing polymers such as polyethylene and polyamide 6-6, the crystallization window reaches 260 and 210 K respectively. When the $T_g/T_m(\text{K})$ ratio is higher than 0.9, the crystallization window is ca. 50 K and the polymer cannot be thermally crystallized. This is the case with poly(2,6-dimethyl 1,4-phenylene ether) (PPE).

The crystallization rate can be enhanced by raising the nucleation density and the spherulitic growth rate. The nucleation density can be increased by adding nucleating agents. In this work, we studied the effect of both classical external nucleating agents, such as talc, and attaching ionic chain ends onto the polymer. This last procedure, known as chemical nucleation, was

successfully applied to poly(BTDA-DAB). The half crystallization time $t_{0.5}$ was decreased from above 60 min to ca. 1 min or lower. Endcapping 5% of the polyimide chain ends with $-\phi-\text{SO}_3\text{Na}$ proved to be optimum.

Crystallization from the melt is further facilitated by combining the presence of $-\phi-\text{SO}_3\text{Na}$ endgroups with a plasticizer such as 4-hydroxybenzophenone. The introduction of 10% plasticizer increases the crystallization window by ca. 50 K and facilitates crystallization. However, further optimization of the crystallization rate is still necessary to obtain a high molecular weight, semicrystalline poly(BTDA-DAB) upon injection moulding.

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