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# Synthesis and properties of $\alpha,\omega$ -diaminoalkane based polyimides

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Twenty semicrystalline polyimides based on well-known aromatic dianhydrides and aliphatic  $\alpha,\omega$ -diamines have been synthesized and characterized. Poly(BTDA-DAB) synthesized in a two-step process from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,4-diaminobutane (DAB) exhibits a rather exclusive balance between thermal/mechanical properties and processability. In the series of  $\alpha,\omega$ -diamines and BTDA the glass transition temperature ( $T_g$ ) increases linearly with the decrease in  $\text{CH}_2$  units, while the melting temperature ( $T_m$ ) shows the well-known odd-even effect. For the as-synthesized poly(BTDA-DAB)  $T_g$  and  $T_m$  are 175 and 277°C, respectively. After melt processing a sharp decrease in crystallinity is observed with X-ray and d.s.c., however annealing of injection moulded test bars results in a higher crystallinity. The semicrystalline poly(BTDA-DAB) exhibits interesting mechanical properties, e.g. a  $G'$  modulus of 1.7 kN mm<sup>-2</sup> and an Izod impact of 3.4 kJ m<sup>-2</sup>.

(Keywords: semi-aliphatic polyimides; poly(BTDA-DAB); semicrystalline polyimides)

## INTRODUCTION

Polyimides are high-performance polymers which exhibit excellent mechanical and thermal properties. They are generally synthesized in a two-step process; in the first step dianhydrides and diamines yield a poly(amic acid). The latter is ring-closed in the second step by a condensation furnishing the polyimide. All commercially available polyimides are characterized by an all-aromatic structure, which gives these materials their excellent thermal stability, high glass transition temperatures ( $T_g$ s) and melting points, and accordingly excellent properties at high temperatures<sup>1,2</sup>. In general, these all-aromatic polyimides cannot be processed by conventional techniques such as injection moulding or extrusion, unless the number-average degree of polymerization ( $\bar{P}_n$ ) is kept very low (e.g. Mitsui Toatsu's 'New TPI' has an estimated  $\bar{P}_n$  of 15–20). Therefore, most polyimides are only available as films or fibres. In these cases the polyimides are formed after processing of the precursor poly(amic acid) solutions.

Several possibilities have been elaborated to come to a balance between properties and processability by lowering the  $T_g$  and melting temperature ( $T_m$ ) of the polyimides, and a number of approaches are available. In one of the approaches a selected number of flexible bonds can be introduced into either the aromatic diamine or the aromatic dianhydride, meanwhile keeping the 'all-aromatic' character of the backbone almost unaffected. A good example is General Electric's poly(ether imide), Ultem, representing the first melt-processable high performance plastic with imide functionalities in the main chain. Ultem is an amorphous polymer with a  $T_g$  of 217°C. Its structure is given in Figure 1.

In another approach of lowering  $T_g$  (and if appropriate  $T_m$ ) of polyimides, the introduction of flexible, aliphatic segments into the main chain has been studied. Several examples have been presented<sup>3–9</sup>, however the scope and limitations of these partially aliphatic polyimides have not been investigated with respect to their use as thermoplastic engineering materials. As one of the few exceptions might serve the paper of Delano and Kiskiras<sup>10</sup>, in which the properties of mouldings of a polyimide partially based on 1,6-hexanediamine and 1,3-bis(aminophenyl)cyclohexane are reported. More recently a number of main chain polyimides have been reported in which both flexible bonds and aliphatic chain segments have been introduced into the backbone. Representative examples are partially aliphatic poly(ester imides)<sup>11–13</sup> or partially aliphatic poly(imide carbonates)<sup>14</sup>.

In this paper the synthesis and a number of selected material properties of polyimides are described for which melt processability has been achieved by the introduction of flexible aliphatic chain segments into the main chain. Several  $\alpha,\omega$ -diaminoalkanes have been used as aliphatic diamines, while six different well-known aromatic dianhydrides have been used, aiming at an excellent balance between processability and material properties. The general structure of the polyimides prepared is given in Figure 2. Poly(BTDA-DAB) based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA,  $\text{R} = \text{C}=\text{O}$ ) and 1,4-diaminobutane (DAB,  $n = 4$ ), exhibiting the best properties-processability trade-off, has been investigated in more detail.

## EXPERIMENTAL

### Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) (Allco, 99% pure), 4,4'-oxydiphthalic anhydride (ODPA) (Oxychem, 99% pure), 3,3',4,4'-diphenylsulfone-

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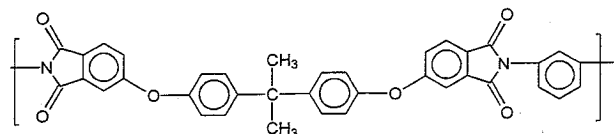
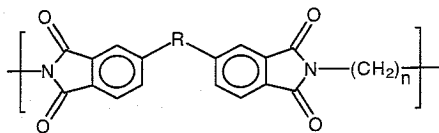
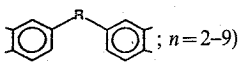


Figure 1 Structure of Ultem

Figure 2 General structure of the polyimides prepared ( $R=C=O$ ,  $SO_2$ ,  $O$ ,  $-$ , or the dianhydride is PMDA with instead of

tetracarboxylic dianhydride (DSDA) (Chriskev, 99% pure), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) (Oxychem, 99% pure), pyromellitic dianhydride (PMDA) (Alco, 99% pure) and phthalic anhydride (PA, Janssen, > 99% pure) were used as received. Bisphenol-A-bisether-4-phthalic dianhydride, the Ultem dianhydride, was donated by Professor Eastmond of the University of Liverpool. It was at least 99% pure and used as received. DAB was manufactured by DSM (99–99.5% pure). 1,6-Diaminehexane (Baker) and all other diamines (Janssen) were used without further purification. Ultem 1000 was obtained from General Electric Plastics. *N*-Methylpyrrolidone (NMP) was purified by distillation under reduced pressure from calcium hydride and stored over 4 Å molecular sieves. *m/p*-Xylene was used as received (Janssen).

#### Synthesis of poly(BTDA-DAB)

Under a dry nitrogen atmosphere a solution of the dianhydride (0.1632 mol) and of the chain stopper phthalic anhydride (0.0016 mol, i.e. 0.5 mol% with respect to the total number of amine groups of the diamineobutane) in NMP (450 cm<sup>3</sup>) was added dropwise to a solution of DAB (0.1632 mol) in NMP (200 cm<sup>3</sup>). During the addition of the dianhydride solution the temperature of the reaction mixture was kept between 0°C and 5°C. Considerable gelation occurred during the addition of the dianhydride, which gradually disappeared on stirring at 20°C for 4 h. The solution was stirred for a further 16 h at 23°C, after which the poly(amic acid) formation was assumed to be completed. To the poly(amic acid) solution in NMP, 20 cm<sup>3</sup> of *m/p*-xylene was added, after which the mixture was heated to reflux (160°C) for ~4 h. During this period the water, formed by the ring-closing reaction, was removed azeotropically from the solution. After cooling the resulting polyimide solution to room temperature, the formed polyimide either crystallized from solution or was precipitated with methanol. The polymer was filtered off, washed with methanol and dried under reduced pressure at 60°C. The polyimide was obtained as a fine powder (after crystallization) or as small granules (after precipitation) in a 95% yield ( $T_g=175^\circ\text{C}$ ;  $T_m=277^\circ\text{C}$ ). Elemental analysis: C (found): 67.38, 67.11 and 66.80 wt%

(calculated 67.38 wt%); H (found): 3.54, 3.68 and 3.88 wt% (calculated 3.74 wt%); N (found): 7.29, 7.53 and 7.46 wt% (calculated 7.49 wt%). I.r. analysis shows imide absorption bands at 1715 and 1775 cm<sup>-1</sup>. All other polyimides listed in Table 1, as well as a 300 g scale poly(BTDA-DAB) sample, were prepared following the same general procedure.

#### Moulding and characterization of the polyimides

Poly(BTDA-DAB) and Ultem 1000 were injection moulded at 330 and 370°C, respectively. The mould temperature was 110°C. The moulded testbars were submitted to a toughness test ( $G_c$  measurement according to the method of Plati and Williams<sup>15</sup>), a notched Izod impact test (ASTM D 256), a Limiting Oxygen Index (LOI) test (ASTM D2863) and a water uptake test (immersed in water, 24 h, 23°C; ASTM D570). Torsional modulus tests ( $G'$  versus  $T$ ) were carried out with a home-built dynamic mechanical analyser. A d.s.c. study was carried out with a Perkin-Elmer DSC-7, and a t.g.a. study was carried out with a Perkin-Elmer TGA-7 analyser. X-ray scattering experiments were performed with a Philips PW 1820 diffractometer and a Statton camera, using CuK $\alpha$  radiation in both cases. The

Table 1 Glass transition temperatures and melting points of the polyimides as synthesized

Dianhydride	Diamine	$T_g$ (°C)	$T_m$ (°C)
PMDA	DAB	—	> $T_{decomp.}$
	DAH	—	> $T_{decomp.}$
	DAN	115	271
BPDA	DAB	184	415
	DAH	150	336
ODPA	DAB	160	340
	DAH	123	228/276
	DAN	91	—
BTDA	DAE	220	399
	DAPr	185	244
	DAB	175	277 <sup>a</sup>
	DAPe	158	220
	DAH	140	250
	DAH <sub>e</sub>	129	183
	DAO	117	203
	DAN	97	138
DSDA	DAB	193	347
	DAH	157	292/310
	DAN	123	217/251
Bisphenol-A-bisether DA	DAB	145	—

<sup>a</sup>The melting enthalpy is 36 J g<sup>-1</sup>

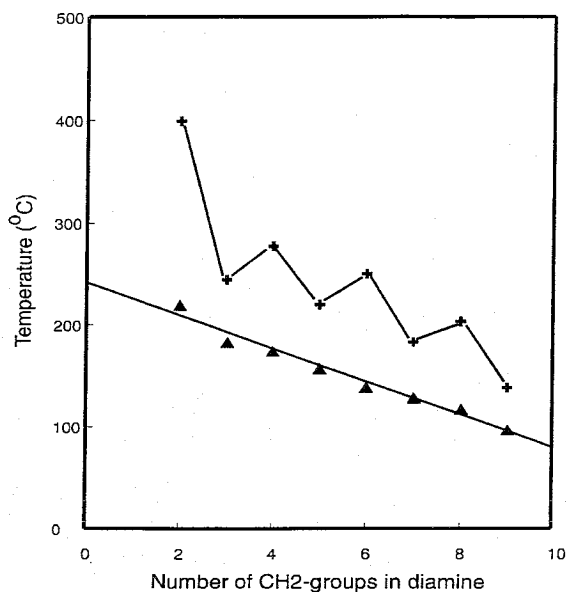


Figure 3  $T_g$  (▲) and  $T_m$  (+) versus the number of  $\text{CH}_2$  units present in the diamine residue of poly(BTDA- $\alpha,\omega$ -diaminoalkane)s

molecular weights of Ultem 1000 and of the 300 g scale poly(BTDA-DAB) sample were determined by s.e.c. on a HP-1090M, equipped with a u.v.-diode array detector. The solvent/eluent was a 0.01 M solution of LiBr in *m*-cresol. The intrinsic viscosity of the eluates was measured on-line with a Viscotek differential viscosimeter detector (model 200) and the (absolute) molecular weight was calculated according to the universal calibration method using polystyrene standards. Details concerning the s.e.c. experiments will be published elsewhere.

## RESULTS AND DISCUSSION

### Synthesis of the polyimides

In our study we have synthesized in a two-step process a series of polyimides from five of the commercially available dianhydrides as well as the bisphenol-A-bisether-4-phthalic dianhydride (the 'Ultem dianhydride'), and eight aliphatic diamines, namely 1,2-diaminoethane (DAE), 1,3-diaminopropane (DAPr), DAB, 1,5-diaminopentane (DAPe), 1,6-diaminohexane (DAH), 1,7-diaminoheptane (DAHe), 1,8-diaminooctane (DAO) and 1,9-diaminononane (DAN). The poly(amic acid)s are prepared in NMP (~10 wt%) using a slightly modified McGrath method<sup>16</sup>. The condensation is performed by using an azeotropic mixture with xylene, furnishing the polyimides after crystallization from NMP solution, filtration and washing with methanol in yields of ~95%. Some of the polyimides do not crystallize from the NMP solution upon cooling and have to be precipitated with methanol. The polymers prepared, their  $T_m$  values and their  $T_g$ s are given in Table 1.

In this first series of experiments no optimizations are performed. Nevertheless, from Table 1 it is obvious that the use of DAB results in polymers with significantly higher  $T_g$ s than those made out of DAH, irrespective of the dianhydride used. The polyimides from DAE, to the contrary, possess transition temperatures that are too high to allow for processing without degradation. The thermal transitions of the as-synthesized BTDA based polyimides are plotted in Figure 3. As expected the  $T_g$

decreases linearly with increasing number of  $\text{CH}_2$  units ( $n$ ) in the aliphatic diamine residue. The graph of  $T_m$  versus  $n$  also shows the well-known odd-even effect, which has earlier been reported by Kricheldorf *et al.*<sup>12</sup> for partially aliphatic poly(ester imide)s. This odd-even relationship also nicely demonstrates that the polyimide from BTDA and DAB is highly favourable.

Some of the transitions of our polyimides can be compared with data reported previously. For poly(PMDA-DAN) ( $n=9$ ) the reported  $T_g$  is 110°C<sup>4</sup>, whereas we obtained 115°C. For BTDA based polyimides Blackley<sup>6</sup> reports the data given in Table 2. The corresponding values for our polyimides are also given.

In general, the  $T_g$ s of our polyimides agree well with the values reported. The melting points of the BTDA based polyimides, however, do not entirely agree with our data, which is probably related to a different crystallization history of the samples (see below). Considering both Table 1 and Figure 3, and keeping in mind that processing of partially aliphatic polymers above 400°C will cause severe degradation, poly(BTDA-DAB) ( $R=\text{C}=\text{O}$  and  $n=4$  in Figure 2) exhibits the highest values of  $T_g$  and  $T_m$  which would still allow melt processing. Other polyimides have either lower thermal transitions or have melting points which are too high for melt processing without significant degradation.

Poly(BTDA-DAB) is the partially aliphatic polyimide of choice for injection moulding and is investigated in more detail. The desired molecular weight for processing is adjusted by using PA as a monofunctional monomer. In order to come to a complete endcapping of all amines and to diminish further chain extension and/or crosslinking during processing, an additional amount of PA is added after the imidization step, while the polyimide is still dissolved. Without going into detail, we state here that PA is effective in limiting the molecular weight, but is not capable of completely endcapping the amine end groups under the reaction conditions used here. The molecular weight of the poly(BTDA-DAB) powder after drying at 60°C has been determined according to the universal calibration technique using polystyrene standards. The molar mass data of the as-synthesized powder are:  $\bar{M}_n=11\,000$  and  $\bar{M}_w/\bar{M}_n=4.0$ , which is higher than the theoretical value for an ideal polycondensate (2.0), but quite normal for polyimides<sup>2</sup>. Just before injection moulding, the polyimide powders are dried at 180°C for 16 h. This treatment changes the  $\bar{M}_n$  slightly but the  $\bar{M}_w$  significantly to 14 000 and 91 000, respectively. After the injection moulding procedure, the  $\bar{M}_n$  has been raised to 17 000 and the  $\bar{M}_w$  to 200 000. Obviously, the non-endcapped amine groups give rise to chain extension and/or crosslinking during drying at elevated temperature and during processing, as suggested above. As a control sample, Ultem 1000 has been submitted to the same s.e.c. procedure. For this poly(ether

Table 2 Comparison of  $T_g$  and  $T_m$  of partially aliphatic polyimides as reported by Blackley<sup>6</sup> and our own data (in parentheses)

Polyimide	$n$	$T_g$ (°C)	$T_m$ (°C)
poly(BTDA-DAPr)	3	170–178 (185)	300 (244)
poly(BTDA-DAH)	6	138–147 (140)	250 (250)
poly(BTDA-DAO)	8	99–110 (117)	180 (203)
poly(BTDA-DAN)	9	93–100 (97)	160 (138)

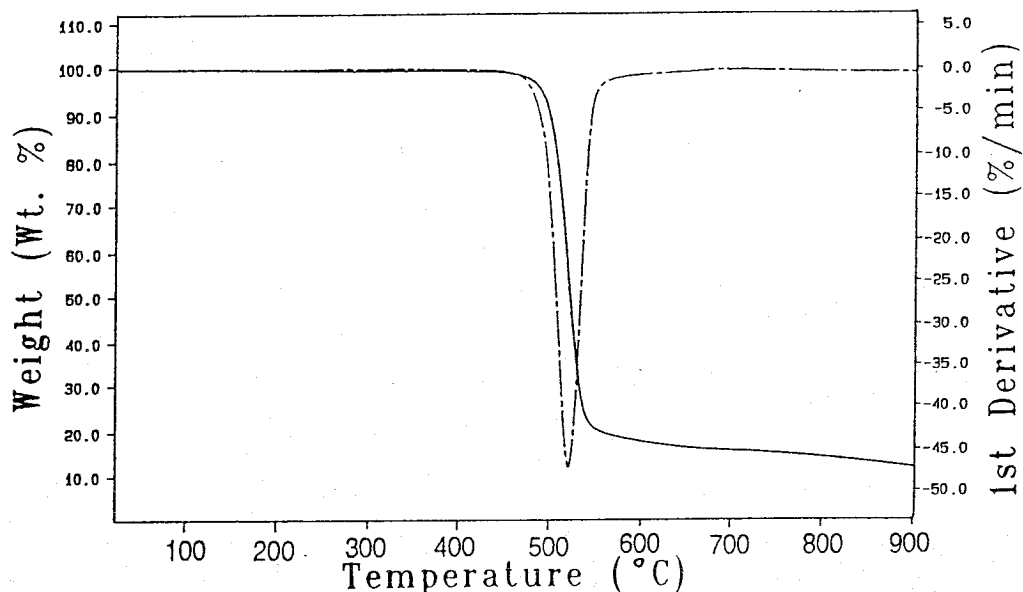


Figure 4 Thermogravimetric analysis curve for poly(BTDA-DAB) with a heating rate of  $20^{\circ}\text{C min}^{-1}$  in a helium atmosphere

imide) we found  $\bar{M}_n = 16000$  and  $\bar{M}_w/\bar{M}_n = 2.7$ , which is quite close to the values obtained at the NASA Langley Research Center<sup>17</sup>. Drying Ultem for 16 h at  $180^{\circ}\text{C}$  does not change the molecular weight data significantly. Obviously, Ultem has been endcapped sufficiently. We will discuss the phenomenon of changing  $\bar{M}_n$  and  $\bar{M}_w$  in more detail in a forthcoming paper, and conclude this section with the remark that melt processing will result in some branching and/or crosslinking of our poly(BTDA-DAB).

In view of the possible melt processability, the most interesting partially aliphatic polyimide based on BTDA and DAB was submitted to elemental analysis. For three different samples, obtained from three different syntheses, the carbon content was determined to be 67.38, 67.11 and 66.80, respectively, while the calculated value is 67.38 wt%. The hydrogen content of the three samples was 3.54, 3.68 and 3.88, respectively, while the calculated value is 3.74 wt%. Finally, the nitrogen content of the three analysed samples was 7.29, 7.53 and 7.46, respectively, while the theoretical value is 7.49 wt%.

#### Thermal analysis of poly(BTDA-DAB)

Figure 4 shows the t.g.a. curve of poly(BTDA-DAB) by studying the weight loss under helium atmosphere as a function of temperature. Significant weight losses are only observed for temperatures exceeding  $420^{\circ}\text{C}$ . In addition a 15 min exposure of poly(BTDA-DAB) samples to  $330^{\circ}\text{C}$ , being the expected processing temperature, results in weight losses of only 0.1–0.5%. Some of the samples prepared show even weight losses close to 0.0%. In spite of its partially aliphatic character, the thermal stability of this polyimide is unexpectedly high and this thermal stability will allow melt processing of this material around  $\sim 330^{\circ}\text{C}$ .

#### D.s.c. analysis of the polyimides

The d.s.c. curves of the as-synthesized polyimide are given in Figure 5. The first heating curves of the as-prepared powder, of the injection-moulded polymer and of a testbar which was annealed after injection

moulding, are given in Figure 6. As can be seen in Figure 5, the as-prepared poly(BTDA-DAB) is semi-crystalline. For poly(BTDA-DAB), containing moderately rigid ketone functionalities, the  $T_g$  and the  $T_m$  are  $175^{\circ}\text{C}$  and  $277^{\circ}\text{C}$ , respectively (Table 1). This synthesized polyimide has a lower  $T_g$  than the fully aromatic, but in all stages completely amorphous Ultem 1000 ( $T_g = 217^{\circ}\text{C}$ ). Upon cooling the molten poly(BTDA-DAB) in the differential scanning calorimeter, no crystallization is observed. Even for a cooling rate of  $1^{\circ}\text{C min}^{-1}$  the second heating curve only shows a glass transition, indicating a completely amorphous character of the polyimide when obtained from a non-oriented melt. The phenomenon that a polymer crystallizes easily from solution but not from the melt has been observed for other, well-known polymers such as polycarbonate, poly(ether sulfone) and others. In Figure 6 the first heating curve of the injection-moulded poly(BTDA-DAB) shows a small melting peak. The heat of melting of this sample is  $\sim 4 \text{ J g}^{-1}$ , which is much lower than the heat of melting of the as-prepared sample ( $\sim 36 \text{ J g}^{-1}$ ). So, while unoriented poly(BTDA-DAB) chains, which are present in the as-prepared sample after melting, do not recrystallize (Figure 5), the chains of the injection-moulded polyimide seem to have enough pre-orientation to be able to crystallize from the melt. The existence of such a pre-orientation could be confirmed by X-ray studies (see later). Korshak *et al.*<sup>9</sup> have demonstrated that the crystallinity of as-prepared partially aliphatic polyimides can be raised significantly by annealing. In order to check this for our poly(BTDA-DAB), the following 'annealing' experiment was performed. An injection-moulded testbar was submitted to a torsional modulus measurement. During this test the bar was heated from room temperature to  $250^{\circ}\text{C}$  at a heating rate of  $1\text{--}2^{\circ}\text{C min}^{-1}$ . After cooling to room temperature this treatment was repeated. After this annealing treatment the bars were submitted to a d.s.c. experiment. The result is shown in Figure 6c. It is obvious that the degree of crystallinity has been increased with respect to the unannealed injection-moulded bar. The heat of melting of the annealed sample proved to be  $\sim 8 \text{ J g}^{-1}$ . It should

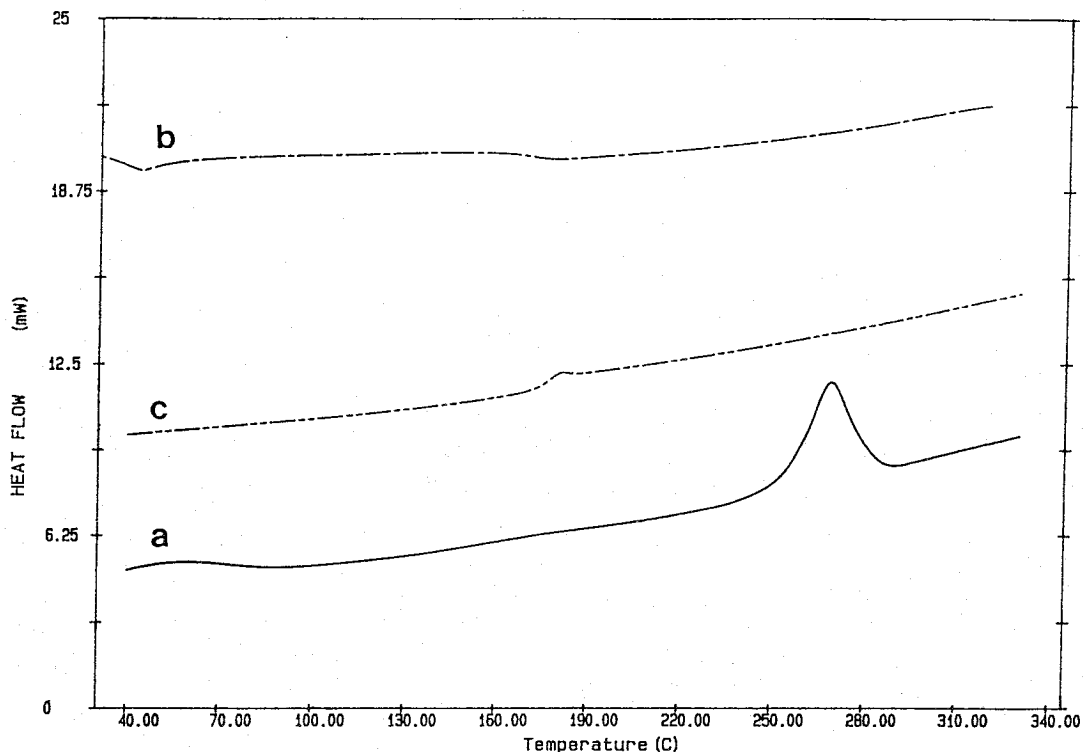


Figure 5 D.s.c. curves (heating rate  $20^{\circ}\text{C min}^{-1}$ ) for the as-prepared poly(BTDA-DAB): (a) first heating curve; (b) cooling curve; (c) second heating curve

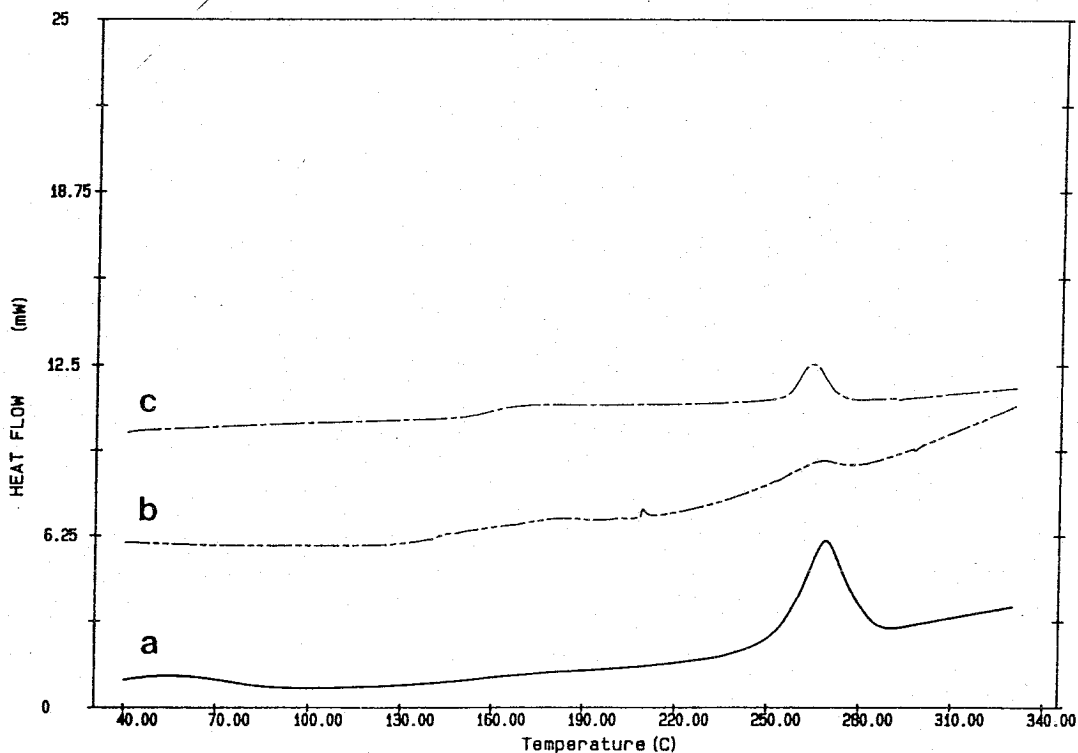


Figure 6 First heating d.s.c. curves (heating rate  $20^{\circ}\text{C min}^{-1}$ ) for poly(BTDA-DAB): (a) as-synthesized powder; (b) injection-moulded testbar; (c) annealed, moulded testbar

be noticed that the annealing procedure was not optimized.

#### X-ray analysis of poly(BTDA-DAB)

A 30–40% crystallinity for the as-prepared poly(BTDA-DAB) is estimated from the powder diffractogram of

this polyimide (Figure 7). A Statton photograph of the injection-moulded polyimide bar (Figure 8a) only shows two broad reflection bands, typically found for amorphous polymers or polymers with very small and imperfect crystals. These X-ray results are in good agreement with the d.s.c. results for an unannealed

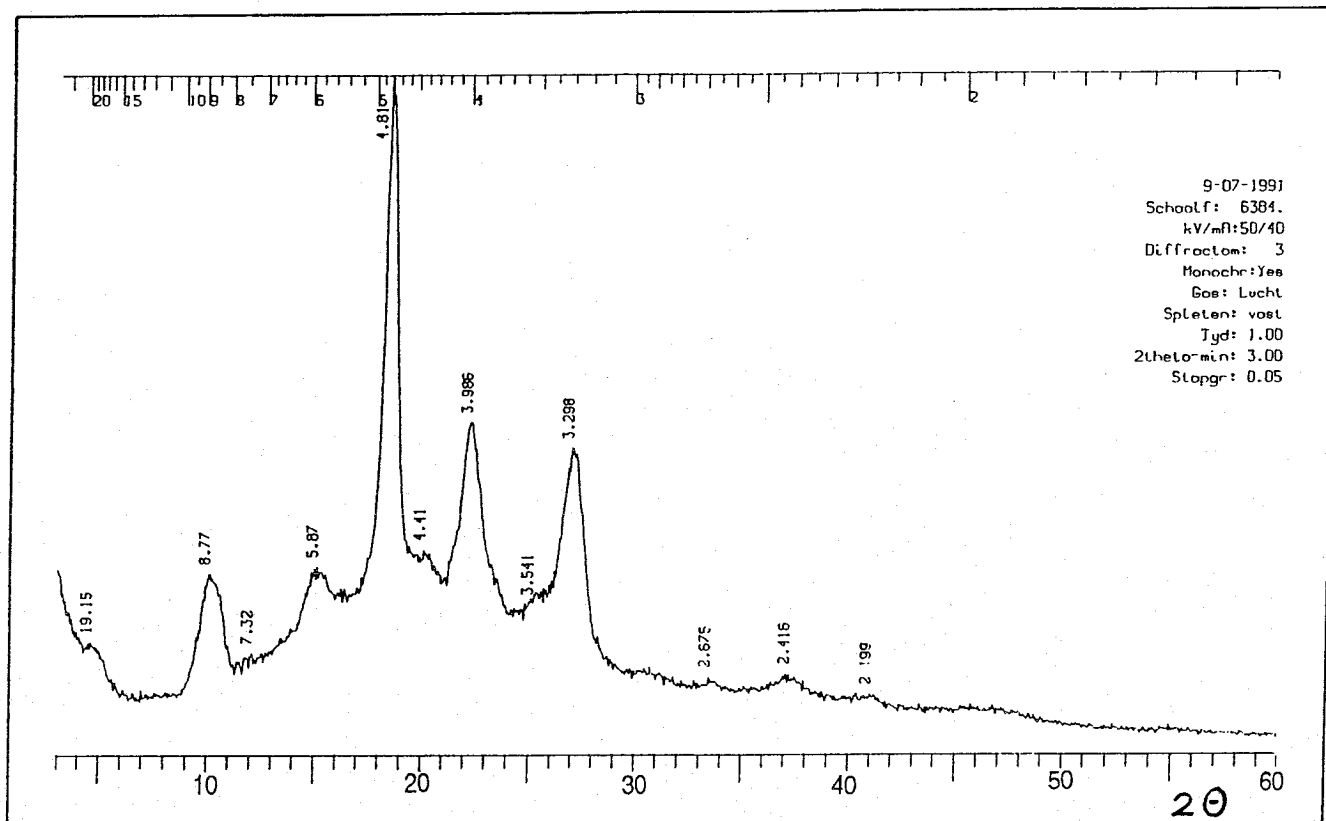


Figure 7 X-ray diffractogram of the as-prepared poly(BTDA-DAB) powder

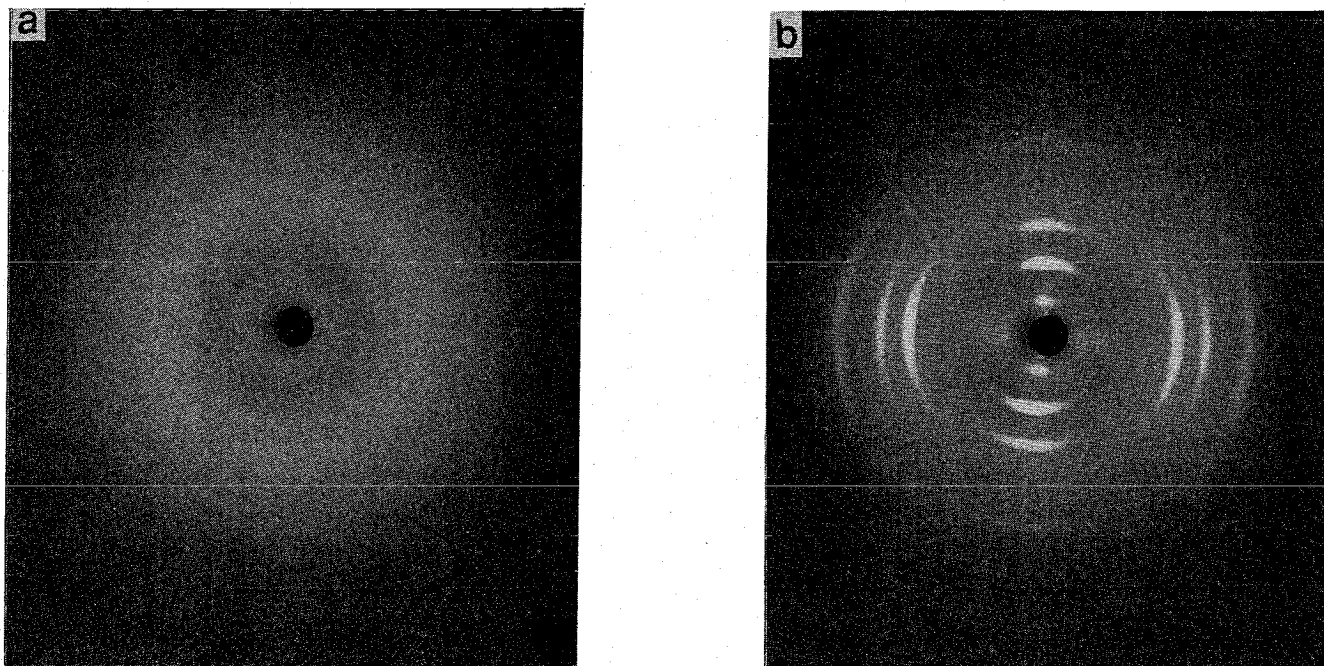


Figure 8 Statton X-ray diffraction patterns of injection-moulded poly(BTDA-DAB) (a) and of injection-moulded and annealed poly(BTDA-DAB) (b). Injection moulding direction is from the bottom of the picture to the top

injection-moulded bar, which only shows a very small melting peak (Figure 6b). Figure 8b shows the Statton photograph of the polyimide sample after annealing in the same way as described before. On top of the amorphous halos, crystalline reflections have appeared, again corresponding with the d.s.c. observations. The

relatively narrow reflection arcs show that a considerable molecular orientation is present in the annealed injection-moulded bar. Most probably the orientation is already present before annealing, but it is less visible due to the predominantly amorphous character of the polyimide before annealing. The meridional reflections in Figure 8b

Table 3 Material properties of poly(BTDA-DAB) and Ultem 1000

Polyimide	$G_c$ (kJ m <sup>-2</sup> )	Izod (kJ m <sup>-2</sup> )	$G'$ (23°C) (N mm <sup>-2</sup> )	LOI (%)	Water uptake (%)
Ultem 1000	4.1	3.4	1300	>40	0.3-0.4
Poly(BTDA-DAB)	3.8	2.9	1550	25.5	0.35

correspond with the reflections in Figure 7 which have  $d$  values of 19.15, 8.77, 5.87, 4.41 and 3.541 Å. These reflections are the first five orders of reflection to the planes perpendicular to the injection moulding direction. From the last four reflections (orders 2 to 5) an interplanar spacing of  $17.62 \pm 0.07$  Å can be derived. This corresponds closely to the length of the repeating unit of the polyimide. The  $d$  value of the first reflection deviates significantly, probably due to the strongly sloped background on which it is superimposed. The orientation of these reflections and their assignment, indicates that the molecules are oriented along the injection moulding direction.

#### Mechanical and physical properties

Some selected properties of poly(BTDA-DAB) are given in Table 3. As a reference we have used Ultem 1000, a commercially available melt processable polyimide.  $G_c$ , Izod impact and shear modulus ( $G'$ ) are determined in the injection moulding direction ( $//$ ). Table 3 shows that the  $G'$  modulus ( $//$ ) of poly(BTDA-DAB) is significantly higher than the corresponding value of Ultem 1000. After a first torsional modulus scan the samples are cooled down to room temperature, and a second torsional modulus run is carried out. In this second run the  $G'$  modulus at room temperature proves to be  $\sim 1.7$  kN mm<sup>-2</sup> for poly(BTDA-DAB), while no increase in modulus is observed if a similar 'double torsional modulus' treatment is applied to Ultem 1000. It is highly likely that this increase in modulus is caused by the observed enhanced degree of crystallinity after annealing. The Ultem 1000 samples are completely amorphous even after the annealing procedure. Furthermore, Table 3 shows that the toughness of the synthesized poly(BTDA-DAB) and of Ultem 1000, measured as  $G_c$  and as the notched Izod impact, is in the same order of magnitude, in spite of the significantly higher modulus of the poly(BTDA-DAB).

The water absorption of both polyimides is comparable. Because of its fully aromatic character, the LOI of Ultem is significantly higher than that of our partially aliphatic polyimide. Nevertheless, some of the synthesized poly(BTDA-DAB) samples proved to be intrinsically flame retardant at a thickness of 3.2 mm according to a standardized flame retardancy test (UL-94). This is probably related to the strongly char forming character of this polyimide. These preliminary results of poly(BTDA-DAB), obtained from an incompletely optimized synthesis, are very promising. Currently we are working on the preparation of perfectly linear partially aliphatic polyimides.

#### CONCLUSIONS

Several partially aliphatic polyimides have been prepared from six different dianhydrides and eight different  $\alpha,\omega$ -diaminoalkanes. Most of the polyimides prepared

crystallize readily from NMP solution upon cooling, or can be isolated after precipitation with methanol. The polyimide based on BTDA and DAB proved to have the optimum balance between thermal properties and processability. This polymer could be injection moulded, in spite of its partially branched structure. The non-nucleated crystallization of branched poly(BTDA-DAB) from the melt is very poor. Only if the rather stiff polyimide chains are oriented, e.g. by injection moulding, then a (low) degree of crystallinity is observed, which can be raised by annealing. A first screening of the thermal and mechanical properties of poly(BTDA-DAB) gave some very interesting results, in spite of the low degree of crystallinity.

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