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THERMOPLASTIC COPOLY(ESTER IMIDE)S DERIVED FROM PBT, TRIMELLITIC ANHYDRIDE, AND 1,4-DIAMINOBUTANE

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ABSTRACT

Starting from 1,4-diaminobutane and trimellitic anhydride, α,ω-diaminobutanebis(trimellitimide) was synthesized and subsequently esterified with methanol. Thermal polycondensation with dimethyl terephthalate in mol ratios from 0 to 100% and 1,4-butanediol yielded the corresponding series of random copoly(ester imide)s based on poly(butylene terephthalate) (PBT). Differential scanning calorimetry and wide-angle x-ray scattering showed that all poly(ester imide)s are semicrystalline with degrees of crystallinity up to 50% (depending on the comonomer content). Compared to pure PBT, the rate of crystallization, however, is strongly decreased if the content of the comonomer is higher than 20%. Annealing is necessary to crystallize these materials. The melting temperatures (T_ms) of the copoly(ester imide)s display the usual melting point depression of copolymers: by increasing the content of the comonomer, the melting temperatures initially decrease but increase when the content of the comonomer is increased further. The glass transition temperatures

(T_gs) increase linearly with increasing content of the comonomer. The maximum T_m (258°C) and the maximum T_g (100°C) were obtained for the homopoly(ester imide) derived from *N,N'*-butane-α,ω-diyl-bis(trimellitimide) and 1,4-butanediol. Some mechanical properties were determined on injection-molded testbars of three poly(ester imide)s containing various amounts of *N,N'*-butane,α,ω-diyl-bis(trimellitimide). They were compared to those of pure PBT and poly(ethylene terephthalate).

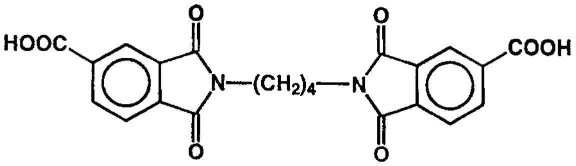
INTRODUCTION

This work is part of a broader study with the general intention to explore the possible application of aliphatic 1,4-diaminobutane (DAB) as a monomer for various polycondensates compared to the commercialized polyamide 4.6 for which large-scale manufacturing of DAB was originally initiated.

The first DAB-based polyimides were recently prepared [1, 2]. These partially aliphatic polyimides proved to be injection moldable and exhibited some very interesting physical properties. In addition, a study on DAB-based poly(amide imides) has been performed in our laboratory, the first results of which will be reported in a future publication. Another possibility implies the incorporation of DAB in commercial polyesters like poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). A direct partial substitution of DAB for 1,4-butanediol in PBT was demonstrated by Gaymans et al. [3]. After reacting one equivalent of DAB with two equivalents of dimethyl terephthalate (DMT), the resulting diamide was copolycondensed (up to 50 mol%) with DMT and 1,4-butanediol under the formation of random copoly(ester amide)s. Compared to pure PBT, these materials exhibit higher T_gs, T_ms, and torsional moduli. In addition, the crystallinity and the rate of crystallization remain high. The present work was aimed at synthesizing copoly(ester imide)s based on PBT and DAB. Instead of the diamide prepared by Gaymans et al., we synthesized *N,N'*-butane-α,ω-diyl-bis(trimellitimide) (4-BTI) (Structure 1) from DAB and trimellitic anhydride (TMA). The synthesis has been described by Kricheldorf et al. [4].

Because of its easy synthesis from relatively cheap starting materials, this monomer-type could be an alternative for recently introduced aromatic monomers, e.g., 4,4'-biphenyl dicarboxylic acid or 2,6-naphthalene dicarboxylic acid.

Whereas Kricheldorf et al. reacted these *N,N'*-alkane-α,ω-diylbis(trimellitimides) with various bisphenols under the formation of predominantly aromatic LC-poly(ester)imides [4], we polycondensed mixtures of DMT and the dimethylester



STRUCTURE 1.

of 4-BTI with 1,4-butanediol (BD) to yield the copoly(ester imide)s of Structure 2 (x = 0–1).

0–100% of the terephthalic acid of PBT was replaced by 4-BTI. The influence of the comonomer content on crystallization behavior, and the thermal and mechanical properties have been studied. In several patents homopoly(ester imide)s based on bis(trimellitimides) and 1,2-ethanediol or 1,4-butanediol are reported [5–7]. Some copoly(ester imide)s with terephthalic acid as comonomer were also mentioned [8], but no special attention was directed toward poly(ester imide)s derived from the DAB-based bis(trimellitimide).

EXPERIMENTAL

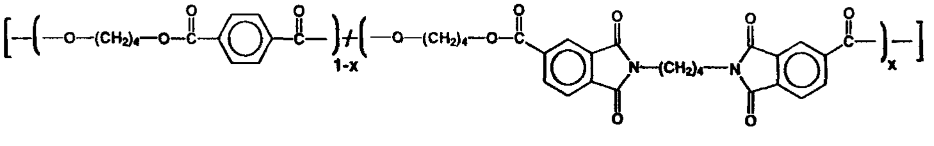
Materials

For the syntheses of the monomers and the polymers the following chemicals were used without further purification: 1,4-butanediol (BASF, 99.7%, mp 20°C), 1,4-diaminobutane (DSM, 99–99.5%, mp 28°C), dimethyl terephthalate (Hüls, 99%, mp 140–142°C), methanol (Riedel de Haen, 99.7%, bp 64–65°C), thionyl chloride (Merck, >99%, bp 76°C), and trimellitic anhydride (Aldrich, 97%, mp 165–169°C). The catalyst was a solution of tetrabutoxy titane (TBT, Hüls) in 1,4-butanediol. 1,3-Phenylene bisoxazoline (PBO) was obtained from Takeda Chemical and used without further purification. Solvents for syntheses and recrystallizations were *N*-methylpyrrolidone (NMP, Janssen Chimica), *N*,*N*-dimethylformamide (DMF, Baker), and toluene (Riedel de Haen). NMP was dried by distillation over calcium hydride under reduced pressure. The other solvents were used without further purification.

N,*N*′-Butane-α,ω-diyl-bis(trimellitimide) (4-BTI) and Its Dimethylester

1.8 mol of DAB (158.7 g) was dissolved in 2.6 L of dry NMP. 3.75 mol of TMA (726.3 g) was added portionwise at room temperature under stirring. The resulting suspension was heated to 80°C for 2 hours. The formed amic acid precipitated and was not soluble under these conditions. 500 mL of toluene was then added, and the reaction mixture was heated up to 150°C. The suspension immediately became a clear solution. Water was distilled azeotropically by using a Dean-Stark trap, and heating was continued until the removal of water was completed (ca. 8 hours). The product crystallized upon cooling and was isolated by filtration. The crude bis(trimellitimide) was recrystallized from ca. 6 L of DMF.

4-BTI: Yield 93%, mp 351–353°C (Lit. 343–345°C [4]).



STRUCTURE 2.

Subsequently, 1.7 mol of 4-BTI (741.9 g) was refluxed in 1.5 L of thionyl chloride (containing a catalytical amount of DMF) until the evolution of sulfur dioxide and hydrogen chloride had almost ceased (ca. 4 hours). The excess of thionyl chloride was removed by distillation. Then toluene was added to the residues and subsequently distilled off (3 times) to remove traces of thionyl chloride. Methanol (2 L) and pyridine (50 mL) were added, and the mixtures were refluxed for 16 hours. After cooling the crude products were isolated by filtration and recrystallized from 4 L of DMF.

4-BTI-dimethyl: Yield 84%, mp 224-226°C, 200 MHz ^{1}H-NMR (DMSO-d_6), δ = 1.64 (t, 4H); 3.61 (t, 4H); 3.91 (s, 6H); 7.96 (d, 2H); 8.17 (s, 2H); 8.34 (dd, 2H) ppm.

Polycondensations

Polycondensations were carried out at small-scale as well as upscaled. In a typical small-scale experiment a mixture of DMT, 4-BTI-dimethyl (collectively 100 mmol, for molar ratios see Table 1), BD (150 mmol), and the catalyst solution were weighed into a 50 mL-cylindrical glass reactor equipped with a mechanical stirrer and a distillation bridge. The reaction mixture was stirred at 190-220°C under a slow stream of nitrogen whereby most of the methanol was distilled off. If the amount of the high melting 4-BTI-dimethylester was increased up to 80 mol%, it became more difficult to keep the reaction mixture liquid during the transesterification step. These reactions were carried out with a larger excess of BD. Then the temperature was raised to 230°C, and vacuum (<0.8 mbar) was applied. The temperature was raised gradually to 240-280°C (in general 20°C above the T_m of each

TABLE 1. Properties of Poly(ester)imides Based on DMT, 4-BTI, and 1,4-Butanediol. Thermal Data Were Taken from DSC Measurements: T_{m_1}, ΔH_{m_1} = first heating after annealing. T_{g_2}, T_{m_2}, ΔH_{m_2} = second heating. T_{end} = polycondensation end temperature.

Code[a]	T_{end}/t, °C/min	η_{rel}[b]	e_c, meq/g	T_{g_2}, °C	T_{m_1}, °C	ΔH_{m_1}, J/g	T_{m_2}, °C	ΔH_{m_2}, J/g
PBT (100/0)	245	2.04	<0.005	45	233	54.2	224	36.1
PEI-4 (90/10)	245/20	1.83	<0.005	53	225	48.3	211	28.2
PEI-4 (80/20)	245/20	2.08	0.010	59	209	36.2	196	24.7
PEI-4 (70/30)	245/40	1.76	0.009	62	200	32.1	186	21.6
PEI-4 (60/40)	250/60	1.69	0.013	69	201	27.7	185	2.5
PEI-4 (50/50)	250/60	1.64	0.015	75	212	20.7	–	–
PEI-4 (40/60)	255/90	1.68	0.033	82	225	26.9	–	–
PEI-4 (30/70)	260/45	1.85	0.035	88	234	37.7	–	–
PEI-4 (20/80)	270/85	1.70	0.046	92	244	39.4	–	–
PEI-4 (10/90)	270/40	1.68	0.044	96	250	43.5	234	2.64
PEI-4 (0/100)	280/30	1.65	0.072	99	258	49.2	244	18.3

[a] The values in parentheses represent the DMT/BTI mol ratios.

[b] Measured in *m*-cresol.

polymer) and polycondensation was continued for some hours. Upon cooling, the highly viscous melt solidified and the yellowish or brownish polymer was removed from the reactor. Upscaling was performed following a similar procedure. Yields >90% were obtained in all experiments.

Characterization

The melting points of the monomers were determined using a transmitted-light microscope (Jena) with a Linkam (THM-600) hot stage. ^{1}H-NMR spectra were recorded with a 200 MHz Bruker BAC S 120 using 5 mm-o.d. sample tubes. The relative viscosities of the polymers were measured at 25°C in *m*-cresol using 1 wt% solutions. The content of carboxylic acid end groups of the polymers was determined by titration to bromocresol green indicator in *o*-cresol/chloroform using a standardized solution of potassium hydroxide in ethanol. Differential scanning calorimetry (DSC) traces were recorded on a Perkin-Elmer DSC-7 in aluminum pans at a heating or cooling rate of 20°C/min under nitrogen. Dynamic or isothermal thermogravimetric analyses (TGA) were carried out with a Perkin-Elmer TGA-7 under helium at a heating rate of 20°C/min. Wide-angle x-ray scattering (WAXS) diffractograms were obtained on a Philips PW 1820 diffractometer using Ni-filtered CuKα radiation. Dynamic viscosity measurements were obtained using a Rheometric RMS 800 mechanical spectrometer. Injection-molded test bars were submitted to bending and tensile tests on a Zwick 1445 apparatus at room temperature (ASTM D790 and ASTM D638, respectively), an Izod notched impact test on a Zwick 5102 apparatus at room temperature (ASTM D256), and a Limiting Oxygen Index test (ASTM D 2863). The tensile tests were conducted with 25 mm/min. The molecular weights of the injection-molded samples were determined by size exclusion chromatography on a HP-1090M, equipped with a UV-diode array detector. The solvent/eluent was *m*-cresol. The intrinsic viscosities of the eluates were measured on-line with a Viscotek differential viscometer detector (model 200), and the absolute molecular weights were calculated according to the universal calibration method using PS standards.

RESULTS AND DISCUSSION

Syntheses

All poly(ester)imides of this work were prepared by the same synthetic approach. *N,N'*-Butane-α,ω-diylbis(trimellitimide) (4-BTI) was synthesized from TMA and DAB. In the first step the amic acid intermediate was synthesized, which subsequently was ring-closed by azeotropic removal of water. Since melt polycondensation was preferred, the diacid was converted into the diacid chloride by means of thionyl chloride. It was subsequently esterified with methanol in the presence of a small amount of pyridine as esterification catalyst. Purification of the diacid chloride was not necessary.

The resulting dimethylesters of 4-BTI and DMT were polycondensed in different mol ratios with 1,4-butanediol in the melt including transesterification at 190–220°C under elimination of methanol followed by polycondensation at temperatures up to 280°C (depending on the T_m of the individual polymer, see Table 1) with elimination of 1,4-butanediol. Tetrabutoxy titane (TBT) was used as catalyst. The DMT/BTI mol ratios, reaction conditions, relative viscosities, content of carboxyl end groups (e_c), and thermal phase transitions are summarized in Table 1. The thermal phase transitions will be discussed in detail in the next section.

The relative viscosities of the 4-BTI based poly(ester imide)s fell into the range between 1.64 and 2.08. Values of about 2 are normally obtained for PBT after melt polycondensation. This corresponds to M_ns around 20,000 g/mol and a P_n of approximately 100. In the case of our poly(ester imide)s, however, it is difficult to estimate the absolute molecular weights from the relative viscosities because of the unknown influence of the different chain structures.

From Table 1 it can be seen that increased levels of carboxylic end groups (e_c) are obtained when melt temperatures $\geq 255\,°C$ have to be applied in the final state of polycondensation. With respect to solid-state postcondensation and hydrolysis resistance, this is generally undesirable. A possible explanation for the observed high e_c values is a random ester-linkage scission by a β-CH-hydrogen transfer reaction generating open chain oligomers with carboxylic end groups [9–11] which can be observed for PBT already in the temperature range of processing ($T \geq 245\,°C$). Furthermore, the elimination of THF from butanediol end groups has to be taken into account.

Upscaling of the copoly(ester imide)s synthesis was carried out to 300 g for three samples with increasing amounts of the 4-BTI comonomer (respectively 20, 70, and 100%). The reaction conditions and some properties are summarized in Table 2.

Compared to the small-scale experiments, the relative viscosities of our upscaled poly(ester imide)s were lower (compare Tables 1 and 2). Attempts were made to further increase the molecular weights by solid-state postcondensation (SSPC), which is a convenient way to prepare high molecular weight polyesters [11]. Granules of the poly(ester imide)s were postcondensed under high vacuum (0.2–0.5 mbar), 15–20 °C below their respective melting temperatures. From Table 2 it can be seen that the relative viscosities of PEI-4 $(80/20)_{IM}$ and PEI-4 $(30/70)_{IM}$ significantly increase upon SSPC. In addition, a decrease of the carboxyl content was detected in the case of PEI-4 $(80/20)_{IM}$.

TABLE 2. Reaction Conditions, Relative Viscosities, Carboxylic Acid Content, and Thermal Data of Poly(Ester)imides Prepared in Larger Quantities for Injection Molding. For the Meaning of Symbols, see Table 1

Code[a]	T_{end}, °C	η_{rel}[b]	e_c, meq/g	T/t_{SSPC},[c] °C/h	η_{rel}[b]	e_c, meq/g	T_{g_1}, °C	T_{m_1}, °C	ΔH_{m_1}, J/g
PEI-4 $(80/20)_{IM}$	240	1.87	0.012	190/24	2.30	0.005	74	210	49.2
PEI-4 $(30/70)_{IM}$	250	1.61	0.014	220/46	1.80	0.014	95	236	47.8
PEI-4 $(0/100)_{IM}$	265	1.56	0.080	220/48	1.54	0.086	101	249	60.9

[a] The values in parentheses represent the DMT/BTI mol ratios.

[b] Measured in *m*-cresol.

[c] T/t_{SSPC} = temperature and time of solid-state postcondensation.

In the case of PEI-4 $(0/100)_{IM}$, neither an increase of the relative viscosity nor a decrease of the carboxyl content could be detected under various conditions (T = 220, 235°C; t = 8, 24, 48 hours). This is due to the relatively higher carboxyl content obtained after the melt polycondensation. As mentioned before, a high concentration of carboxyl end groups slows down solid-state postcondensation or even prevents it [11]. An alternative approach in this case could be to chain extend PEI-4 $(0/100)_{IM}$ by using a carboxyl-addition-type chain extender according to a method proposed by Inata [12]. Instead of 2,2′-bis(2-oxazoline), which was reported by Inata as an effective chain extender for PET with high e_c values, we performed some experiments using the 1,3-phenylene bisoxazoline (PBO) because of its higher thermal stability. Five gram samples of PEI-4 $(0/100)_{IM}$ were mixed with 0.8 wt% (theoretical amount) up to 4 wt% PBO for 5 minutes at 265°C in a double-screw mini-extruder. A significant decrease of the e_c (from 0.080 meq/g down to 0.001 meq/g) was detected when 4 wt% PBO was used, but no increase of the viscosity was observed. By using 2 wt% PBO, an e_c value of 0.020 was obtained and, in addition, a slight increase of the relative viscosity up to 1.62. These results indicate that PBO was very effective in reducing the carboxyl end group concentration whereas its usefulness as a real chain extender was limited in our case.

Thermal Properties, Crystallinity, and Crystallization Behavior

All poly(ester imide)s were subjected to DSC measurements at a heating and cooling rate of 20°C/min after drying at 140°C overnight. In general, the first heating curve of each as-synthesized poly(ester imide) showed multiple endothermic transitions (one or two weak endotherms and one broad melting endotherm) indicating crystallites of different sizes and perfection analogous to most semicrystalline polymers. After annealing for 2 hours 10–15°C below the maximum of the broad melting endotherm of each sample, the stronger transitions became sharper and were shifted to a somewhat higher temperature whereas the weaker endotherms disappeared completely. In addition, the melting enthalpies calculated from the areas under the endotherms increased, indicating a greater perfection of the crystallites and a higher degree of crystallinity. In order to allow a reliable comparison between all polymers, all T_ms and ΔH_ms taken from the first heating curve (see Table 1) were determined after the aforementioned annealing procedure.

The glass transition temperatures could not be detected in all cases in the first heating curve, but they appeared very clearly in the second heating run after cooling from the melt with 20°C/min. Therefore the T_gs listed in Table 1 were taken from the second heating curve.

In Fig. 1 the T_gs and T_ms of the 4-BTI-based poly(ester imide)s are given versus the comonomer content.

The T_ms of the poly(ester imide)s of both series display the usual melting point depression of copolymers. When the content of the 4-BTI comonomers is increased, these decrease first, but increase when the comonomer content is increased further. As expected, the melting enthalpies follow the same tendency. The glass transition temperatures of the poly(ester imide)s increase linearly with increasing mol percentage of the 4-BTI comonomer.

Repeated heating and cooling cycles proved that the crystallization rate appears to be very slow when 4-BTI is incorporated as comonomer in PBT (which is

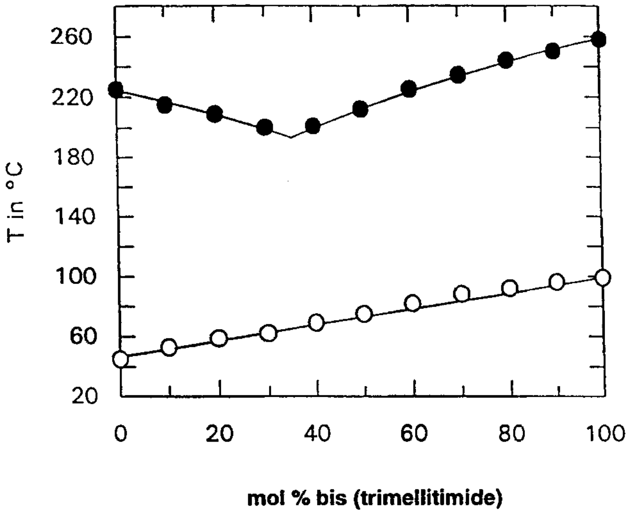


FIG. 1. T_gs (○) and T_ms (●) of the 4-BTI-based poly(ester)imides as a function of the 4-BTI content.

known as one of the fastest crystallizing polyesters). A significant recrystallization from the melt upon cooling with 20 °C/min was observed only up to a concentration of 20 mol% (Fig. 2). At higher comonomer concentrations no recrystallization, or a very slow and incomplete recrystallization (upon second heating), was detected. An example is given in Fig. 3. In other words, the crystallization rate (compared to PBT) is strongly reduced when more than 20 mol% of 4-BTI is incorporated in PBT. A qualitative comparison showed that these copoly(ester imide)s crystallize even much slower than the slowly crystallizing PET.

In order to determine the maximum attainable degree of crystallinity of the poly(ester)imides, melt-pressed samples with various amounts of 4-BTI (respectively

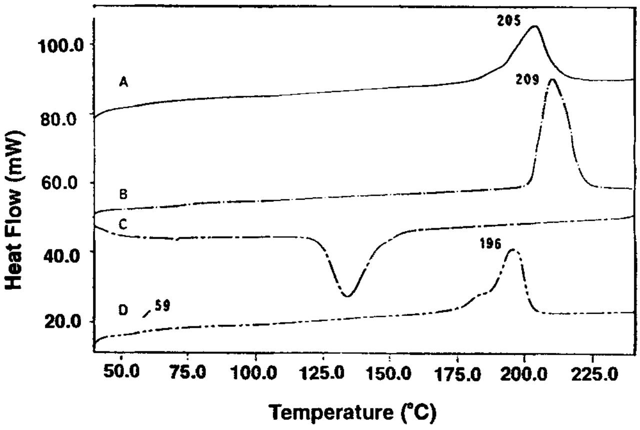


FIG. 2. DSC measurements of PEI-4 [80/20]: First heating after drying at 140°C overnight (A), first heating after annealing (see text) (B), cooling (C), second heating (D).

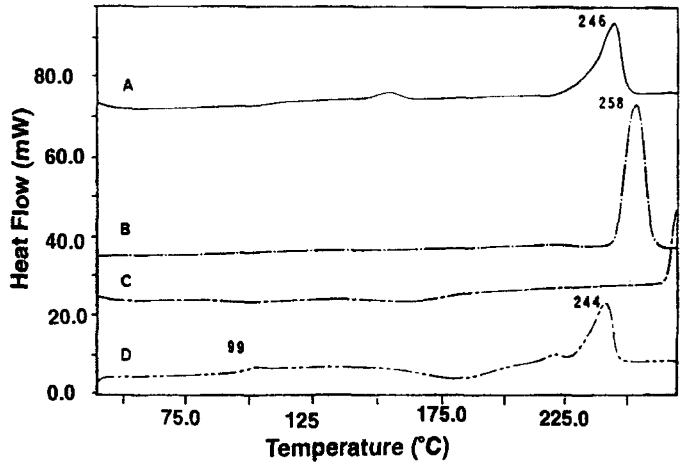


FIG. 3. DSC measurements of PEI-4 [0/100]: First heating after drying at 140°C overnight (A), first heating after annealing (B), cooling (C), second heating (D).

20, 40, 60, 80, and 100 mol%) were characterized by wide-angle x-ray scattering (WAXS) and compared to pure PBT. After melt pressing, the samples containing more than 20 mol% 4-BTI were amorphous. They were first precrystallized at 140°C/4 h and then annealed 10–15°C below their respective melting temperatures for 2 hours. For a proper comparison, the semicrystalline sample containing 20 mol% 4-BTI was annealed in a similar way. The WAXS patterns are given in Fig. 4.

All poly(ester)imides have in common that a reasonable degree of crystallinity can be achieved after annealing. The degree of crystallinity was estimated using the patterns of completely amorphous samples as references. Relative values are about 20% (low comonomer content), 30–40% (medium comonomer content), and 40–50% for samples with a high comonomer content. Significant differences exist between the diffractogram of PBT and those of the poly(ester imide)s. It is evident that the homopoly(ester imide) PEI-4 (0/100) and the copoly(ester imide)s with high comonomer concentration adopt a new crystal structure with complete rejection of the PBT units from the crystals (compare Fig. 4A with 4D, E, and F). The change of the crystal lattice can be observed at some intermediate copolymer composition (Fig. 4C and D). At lower comonomer concentrations the PBT and homopoly(ester imide) units can cocrystallize under the formation of a mixed crystal (Fig. 4C). In the case of very low comonomer concentrations, a strongly deformed PBT lattice seems to be present (Fig. 4B).

Thermal Stability and Melt Viscosity

Before processing, it is necessary to check the thermal stability as well as the rheological properties such as melt viscosity and phase angle.

The thermal stability of the poly(ester imide)s was investigated by thermogravimetric analysis (TGA). In Fig. 5 the dynamic TGA curves of PEI-4 (30/70) and PEI-4 (0/100) are given and compared to that of PBT.

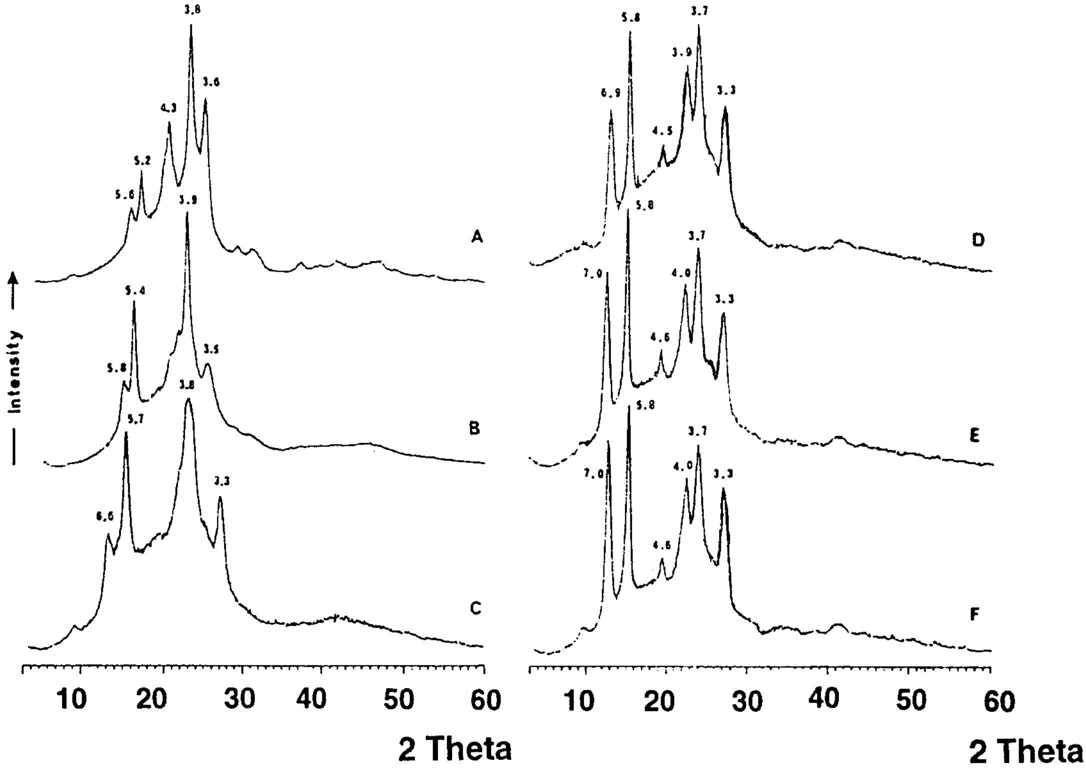


FIG. 4. WAXS diffractograms of PBT (A), PEI-4 [80/20] (B), PEI-4 [60/40] (C), PEI-4 [40/60] (D), PEI-4 [20/80] (E), and PEI-4 [0/100] (F). Except PBT, all samples were annealed.

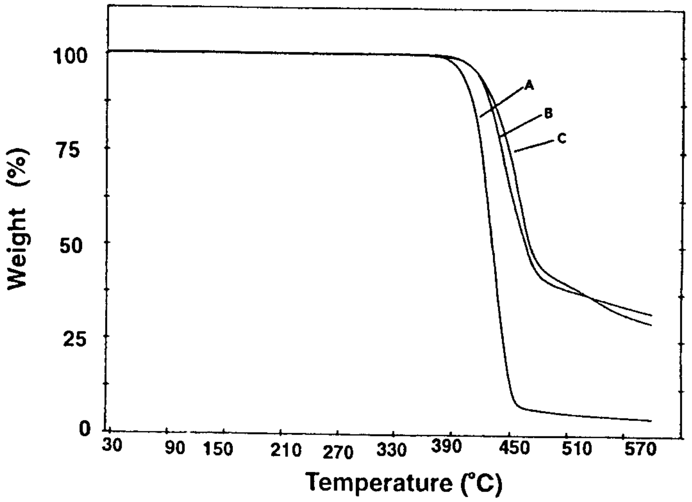


FIG. 5. Dynamic TGA measurements of PBT (A), PEI-4 [30/70] (B), and PEI-4 [0/100] (C) with 20°C/min under helium.

For the poly(ester imide)s a significant weight loss (≥5%) occurs above 400°C in an inert atmosphere. Compared to PBT, the thermal stability is somewhat better due to the incorporation of heat-resistant imide groups into the polymer chain. Isothermal TGA measurements up to 290°C for 15 minutes (under helium) did not show any weight loss for all poly(ester imide)s. So processing in the melt is possible as far as the thermal stability is concerned.

In Figs. 6-8 the isothermal dynamic viscosity η^* and the phase angle are given as functions of the angular frequency ω for the three poly(ester imide)s PEI-4 $(80/20)_{IM}$, $(30/70)_{IM}$, and $(0/100)_{IM}$ prepared in larger quantities. The measurements were carried out at the anticipated processing temperatures for all samples.

The measurements were carried out 20-30°C above the melting temperatures determined by DSC (after annealing). In general, the values for η^* are between 10^2 and 10^4 Pas. Such values will normally not lead to injection molding difficulties. The highest melt viscosity was determined for PEI-4 $(80/20)_{IM}$. The melt viscosities of the other two samples were lower due to somewhat lower molecular weights. This tendency is also represented by the solution viscosities (see Table 2). η^* of PEI-4 $(80/20)_{IM}$ hardly changes with the residence time whereas a slight increase of η^* can be observed for PEI-4 $(30/70)_{IM}$. This can be interpreted as a slight increase in molecular weight due to postcondensation. PEI-4 $(0/100)_{IM}$ shows a slight decrease of η^* with the residence time, indicating a slight decrease in molecular weight at 265°C. Processing temperatures above 265°C should be avoided for that reason. However, dynamic viscosity measurements clearly showed that in all three cases η^* is nearly independent of ω. In addition, the phase angles at low angular frequencies are close to 90°, indicating no branching at these temperatures. Both results indicate

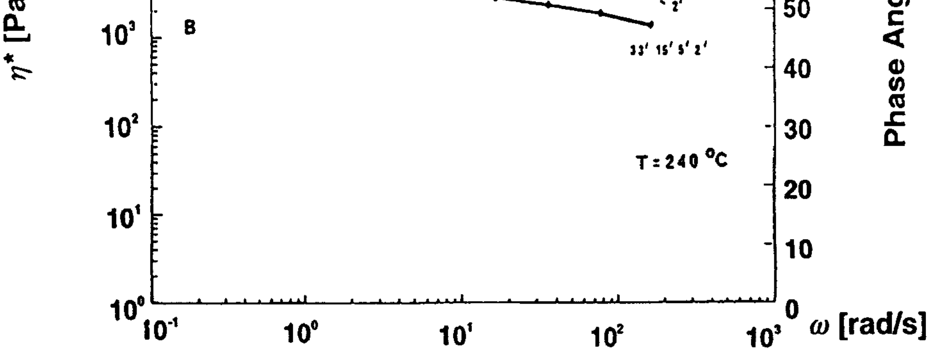


FIG. 6. Phase angle Δ (A) and melt viscosity η^* (B) versus angular frequency ω at 240°C for PEI-4 [80/20] IM for residence times in the melt of 2, 5, 15, and 33 minutes.

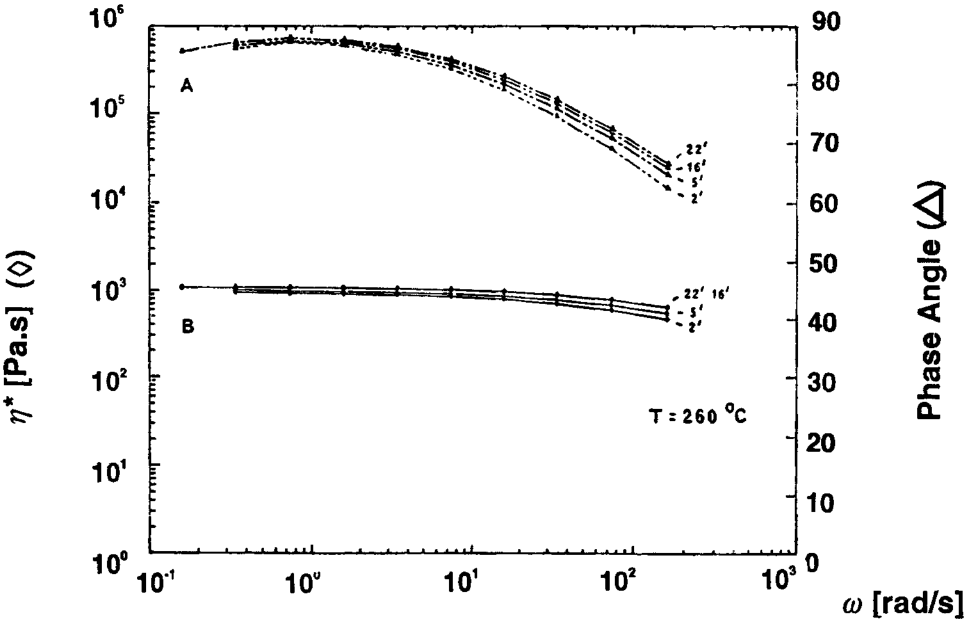


FIG. 7. Phase angle Δ (A) and melt viscosity η* (B) versus angular frequency ω at 260°C for PEI-4 [30/70] IM for residence times in the melt of 2, 5, 16, and 22 minutes.

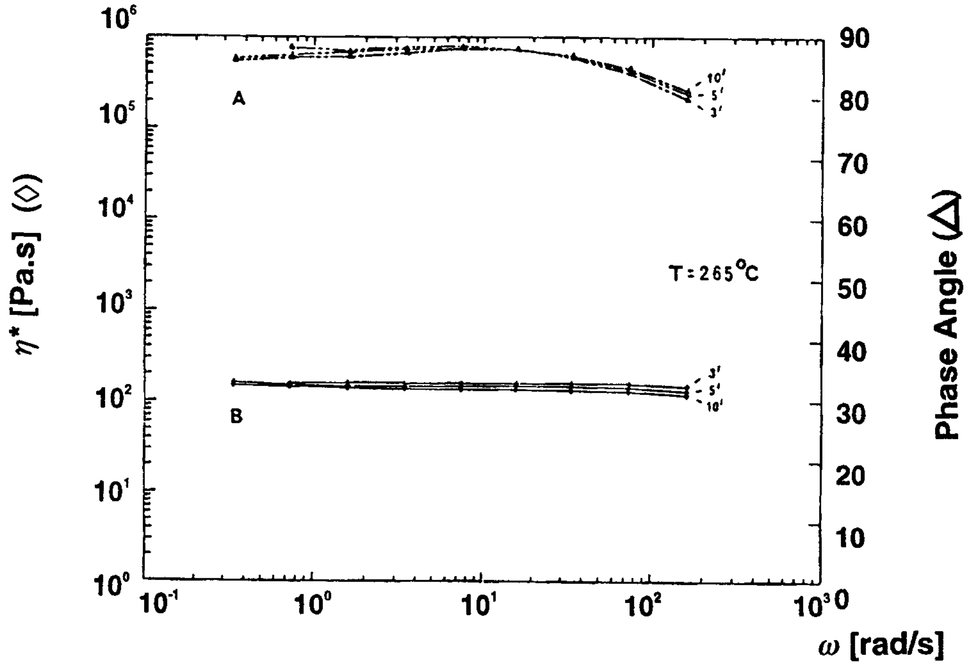


FIG. 8. Phase angle Δ (A) and melt viscosity η* (B) versus angular frequency ω at 265°C for PEI-4 [0/100] IM for residence times in the melt of 3, 5, and 10 minutes.

TABLE 3. Injection Molding Conditions for Poly(Ester)imides

Sample	Melt temperature range, °C	Injection pressure, MPa	Injection speed, s	Mold temperature, °C
PEI-4 $(80/20)_{IM}$	220-230	30	0.29	110
PEI-4 $(30/70)_{IM}$	240-250	30	0.23	80
PEI-4 $(0/100)_{IM}$	220-230	30	0.29	80

that the poly(ester imide)s show a nearly ideal Newtonian, i.e., viscous and nonelastic behaviour, and that injection molding is possible.

Processing

The three poly(ester)imides PEI-4 $(80/20)_{IM}$, $(30/70)_{IM}$ and $(0/100)_{IM}$ were injection molded into tensile and Izod impact test bars. In the case of PEI-4 $(0/100)_{IM}$, 2 wt% PBO was added to reduce the relatively high content of carboxylic acid end groups. The injection molding conditions are given in Table 3, and the results will be discussed below.

Physical Characterization of the Injection-Molded Poly(ester)imides

In Table 4 the relative viscosities, content of carboxyl end groups, molecular weights, and thermal properties are given for the injection-molded poly(ester imide)s. In Table 5 the results of tensile, bending, and impact tests, as well as limiting oxygen indices (LOI), are summarized and compared to PET and PBT.

Compared to the values before injection molding (see Table 2), hardly any decrease of η_{rel} and e_c could be detected for PEI-4 $(80/20)_{IM}$, indicating very good stability in the melt. In contrast to that, a decrease in η_{rel} and an increase in e_c is detected for PEI-4 $(30/70)_{IM}$ due to the higher processing temperature. The relative viscosity of PEI-4 $(0/100)_{IM}$ after injection molding is comparable to that of PEI-4 $(30/70)_{IM}$. Due to the addition of PBO, no decrease but a slight increase of the relative viscosity and a significant decrease of e_c were detected after injection mold-

TABLE 4. Relative Viscosities, Carboxyl Content, Molecular Weights, and Thermal Data of Injection-Molded Poly(Ester)imides

Code	η_{rel}[a]	e_c, meq/g	M_n[a]	M_w/M_n	T_g, °C	T_m, °C	ΔH_m, J/g
PEI-4 $(80/20)_{IM}$	2.27	0.010	22,400	2.38	67	200	25.3
PEI-4 $(30/70)_{IM}$	1.61	0.039	14,600	2.20	85	225[b]	15.4[b]
PEI-4 $(0/100)_{IM}$	1.59	0.008	13,200	2.05	100	245[b]	30.6[b]

[a] Measured in *m*-cresol.

[b] Recrystallization upon reheating in the DSC.

TABLE 5. Mechanical Properties and Limiting Oxygen Index of 4-BTI-Based Poly(Ester)imides[a] and PET and PBT

Properties	PEI-4 $(80/20)_{IM}$	PEI-4 $(30/70)_{IM}$	PEI-4 $(0/100)_{IM}$	PBT	PET
Tensile test:					
σ_{yield}, MPa	53	65	76	52	81
σ_{break}, MPa	14	36	43		
ε_{break}, %	21	94[b]	100[c]	200	70
Bending test:					
Modulus, MPa	2300	2515	2800	2340	2830
$\sigma_{flex,max}$, MPa	89	108	125	83	114
Impact test:					
$Izod_{notch}$, kJ/m^2	5.1	4.1	3.8	3.5	3
LOI, %	24	25	25	22	

[a] Unless otherwise noted, the standard deviations were <10%.

[b] ±20%.

[c] ±30%.

ing. The absolute molecular weights were determined according to the universal calibration technique using polystyrene standards. The M_w/M_n values are close to the theoretical value for an ideal polycondensate in all cases (= 2). For comparison, the molecular weight of a commercial injection-molded PBT sample was also determined (η_{rel} = 2.00; e_c = 0.0505 meq/g; M_n = 17,800; M_w/M_n = 2.20).

PEI-4 $(80/20)_{IM}$ was crystallized from the melt when the mold temperature was kept slightly above 100°C. The degree of crystallinity, however, was relatively low (about 15%, estimated by WAXS). PEI-4 $(30/70)_{IM}$ and PEI-4 $(0/100)_{IM}$ were amorphous after injection molding. No crystallinity was induced by shear or could be induced by increasing the mold temperature. In contrast to PEI-4 $(80/20)_{IM}$, the mold temperatures had to be lowered to values slightly below T_g to obtain a material with sufficient stiffness immediately after the injection-molding process. In contrast to the small-scale PEI-4 (30/70) (see Table 1), a recrystallization upon reheating in the DSC was observed for the injection-molded PEI-4 $(0/100)_{IM}$. This is possibly due to the somewhat lower molecular weight of the injection-molded sample and/or by shear-induced orientation of the molecules in the injection-molded parts.

Tensile, bending, and Izod impact tests were performed. The test bars were neither conditioned nor dried in order to exclude any annealing effects. Some tendencies are clearly detectable. Both tensile and flexural properties are enhanced with increasing content of the 4-BTI comonomer, although M_n is decreased. It should be kept in mind that both PEI-4 (30/70) and (0/100) are amorphous, while PEI-4 (80/20) still exhibits some 15% crystallinity. Surprising and not yet understood is the significant drop of the elongation at break from 200 down to 20% when only 20 mol% 4-BTI is incorporated into the PBT chains. The best notched Izod impact resistance was found for PEI-4 $(80/20)_{IM}$, although the values do not differ significantly. The determined mechanical properties of the fully amorphous PEI-4 $(0/100)_{IM}$ are more comparable to those of PET than to those of PBT.

In order to obtain a first impression about the flame retardancy properties of the poly(ester imide)s, the injection-molded samples were submitted to a LOI test. A slight improvement of the flame retardancy, observed as a small but significant raise in LOI, was achieved by the incorporation of semiaromatic imide structures in PBT (see Table 5).

CONCLUSIONS

By incorporation of *N,N'*-butane-α,ω-diyl-bis(trimellitimide) units into PBT the relatively low glass transition temperature (45°C) can be raised remarkably up to 100°C when the terephthaloyl units are completely substituted by the comonomer. This value is located between that of PET (75°C) and that of poly(ethylenenaphthalate) (PEN, 122°C). In addition, a melting temperature between 245 and 260°C is obtained (depending on the thermal history), which is comparable to the melting temperatures of PET (252°C) and PEN (264°C), but significantly higher than that of PBT (225°C). Compared to pure PBT, the crystallization rate is strongly reduced when the comonomer content exceeds 20 mol%. However, it is possible to achieve degrees of crystallinity of about 40–50% by annealing. The poly(ester imide)s containing the DAB-based bis(trimellitimide) could be easily processed thanks to a sufficient thermal stability (somewhat better than that of PBT) and a nearly ideal Newtonian behavior of the polymer melts. Injection-molded test bars were obtained either as semicrystalline when 20 mol% comonomer was incorporated or as fully amorphous for higher comonomer concentrations. With the exception of a relatively poor elongation at break (compared to PBT), the tensile, impact, and flexural properties of the poly(ester)imides are comparable to, or even better than, those of pure PBT or PET, even when the products are amorphous after injection molding. The results of a study on the enhancement of the crystallizability will be published in a forthcoming paper, which will also deal with a comparison of the crystallization behavior of copoly(ester imide)s based on *N,N'*-ethane-α,ω-diyl-bis(trimellitimide), *N,N'*-butane-α,ω-diyl-bis(trimellitimide), and *N,N'*-hexane-α,ω-diyl-bis(trimellitimide).

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