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Synthesis and properties of α,ω-diaminoalkane based poly(amide-imide)s

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Abstract

Several regular thermoplastic poly(amide-imide)s (PAIs) were synthesized from the diacid chloride derivatives of *N*,*N*′-alkane-α,ω-diylbis(trimellitimide)s and α,ω-diaminoalkanes. The PAI synthesized from the 1,4-diaminobutane (DAB) based bis(trimellitimide) and 1,4-diaminobutane (PAI[4,4]) yielded semi-crystalline testbars upon injection moulding, but the high melting point of ca. 346°C caused degradation during processing. Surprisingly, all 1,6-diaminohexane (DAH) based PAI[6,6], prepared from the DAH based bis(trimellitimide) and DAH, with a first heating T_m of 257°C, did not even crystallize from the melt at a cooling rate of 20°C/min in the DSC. The same lack of crystallizability from the melt was observed for all 1,3-diaminopropane and for all 1,9-diaminononane based (odd) poly(amide-imide)s PAI[3,3] and PAI[9,9]. The PAI[6,4], based on *N*,*N*′-butane-α,ω-bis(trimellitimide) and DAH, with an attractive T_m of 289°C, shows an intermediate crystallization behaviour from the melt: amorphous after injection moulding, but limited crystallization from the melt at a cooling rate of 20°C/min. Copoly(amide-imide)s, from the DAB based bis(trimellitimide) and mixtures of DAB and DAH, showed intermediate melting points of 290°C (for 50 mol% DAB) to 317°C (for 75 mol% DAB) and a better crystallizability with increasing mole percentage DAB, which is ascribed to the wider crystallization window ($T_m - T_g$) with increasing DAB content and to the more linear ('all-*trans*') configuration of DAB with respect to DAH. In spite of their amorphous character the injection moulded PAIs show some attractive physical properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Semi-aliphatic poly(amide-imide)s; Crystallization; Thermal and mechanical properties

1. Introduction

Poly(amide-imide)s (PAIs) are polymers carrying both amide and imide bonds in the main chain. A widely applied way of preparing all aromatic PAIs is by a low temperature polycondensation reaction of an aromatic diamine with trimellitic anhydride chloride (TMAC) [1–4], or with diacid chlorides containing preformed imide rings [5–8]. In Ref. [8], the activated *N*,*N*′-bis(trimethylsilyl) derivative of an aromatic diamine is applied instead of the diamine itself. The polymerization with TMAC in frequently used aprotic polar solvents like NMP and DMAc requires either chemical imidization (with e.g. acetic anhydride and pyridine) or ring-closure at high temperature of the preformed poly(amic-acid). Both imidization procedures may result in undesirable side reactions like partial crosslinking, which is undesirable in polymers intended for moulding applications. Moreover, since a diamine molecule can either react with two TMAC anhydrides, with two TMAC carboxylic acid chlorides, or with both one TMAC anhydride and one TMAC carboxylic acid chloride, this route does not guarantee a regular chain structure, which is inevitable (but not always sufficient) if semi-crystallinity is demanded. On the other hand, the reaction of an imide containing diacid chloride and a diamine usually takes place at low temperatures, and PAIs with a highly regular and even symmetrical chain structure can be obtained, the latter if the imide containing diacid chloride has a symmetric structure itself.

An example of a commercially available, all aromatic PAI is Torlon™, which is based on the monomers TMAC and 4,4′-methylene dianiline (MDA). This high performance polymer has an irregular chain structure, which explains its amorphous character. Torlon™ has excellent physical properties up to high temperatures, but due to the high glass transition temperature (T_g) of 275°C, melt processing is extremely difficult. Usually, a low molecular weight prepolymer is processed in the melt, followed by a long 'baking' or 'curing' procedure resulting in higher molecular weights and, accordingly, satisfactory mechanical properties. Melt

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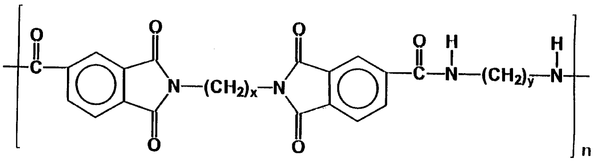
processability would be improved if the T_g is reduced, e.g. by applying aliphatic diamines instead of the usual aromatic diamines. If, however, applications up to high temperatures are required, these partially aliphatic, low T_g PAIs should be semi-crystalline.

Several (partially) aliphatic PAIs with much lower glass transition temperatures than Torlon™ have been reported in both open and patent literature. Without the aim of being complete we briefly mention some available reports here. Lee et al. [9] describe fully aliphatic PAIs derived from the reaction of nitrilotriacetic acid and several aliphatic diamines like 1,6-diaminohexane and 1,8-diaminooctane. Campbell and Hill [10] describe PAIs from aliphatic tricarboxylic acids like 1,2,3-propanetricarboxylic acid and 1,3,5-pentanetricarboxylic acid. Other papers describe the reaction product of either trimellitic anhydride (TMA) or aromatic dianhydrides with aliphatic ω-amino acids as a base monomer, which is reacted with an aromatic diamine furnishing partially aliphatic PAIs [11–16]. In all these papers the imide rings, always present in the diacids, had been preformed before the polycondensation reaction, which is the preferred route in view of the advantage mentioned earlier in Section 1. Ref. [11] mentions the possibility of reacting, e.g. (the acid chloride derivative of) 4-carboxy-phthalimide hexanoic acid with 1,6-diaminohexane, yielding a PAI with a very high aliphatic character. For most semi-aliphatic PAIs described above [9–16], satisfactory crystallization from the melt, which is a prerequisite if the low T_g PAIs are to be applied as high performance polymers, is rather an exception than a rule. Semi-aliphatic PAIs have also been prepared from TMA(C) and aliphatic diamines, without the incorporation of aliphatic ω-amino acids. One of the finest examples, where the imide bonds are performed in a first step to avoid side reactions, and where fully ordered semi-aliphatic PAIs with a high aliphatic character are obtained, is given by a patent of the Pennwalt Corporation [17]. In the first step, a diimide-diacid intermediate is formed from one mole of an aliphatic diamine and two moles of TMA. The resulting N,N'-alkane-α,ω-diyl-bis(trimellitimide) is subsequently converted to its acid chloride derivative, which in a final step is polymerized with an equimolar amount of an aliphatic diamine. Applied diamines are a.o. 1,3-diaminopropane, 1,6-diaminohexane and 1,9-diaminononane. The patent describes that all 1,6-diaminohexane (DAH) based PAI has a softening point of around 260°C, but that compression moulding of this material at 280°C results in a clear film. This is an indication that the DAH based semi-aliphatic PAI crystallizes poorly, or not at all from the melt. Although the Pennwalt patent claims PAIs based on α,ω-diaminoalkanes with 2–18 methylene groups, 1,4-diaminobutane (DAB) based PAIs are not given in the examples. This triggered us, since in the past it was reported that, with respect to 1,6-diaminohexane based stepgrowth polymers, the 1,4-diaminobutane based stepgrowth polymers exhibit not only higher transition temperatures (T_g and T_m), which is as expected, but also that the crystallization from the melt of the DAB based polycondensates quite often outperforms that of the corresponding DAH based polymers. Often both the crystallization rate and the degree of crystallinity of the DAB based polymers is higher, and accordingly their physical properties are usually more interesting. Advantages of DAB over DAH have been found for polyamide 4.6 versus 6.6 [18] (faster crystallization and better properties), aromatic–aliphatic polyimides [19] (higher T_m for DAB based PI), aromatic–aliphatic poly(ester-imide)s [20] (higher thermal transitions and higher crystallinity), polyamides 4.10 and 4.12 versus 6.10 and 6.12 [21] (faster crystallization and better properties), and very recently for fully aliphatic poly(ester-amide)s, based on either DAB, adipic acid and butanediol or DAH, adipic acid and butanediol [22] (faster crystallization, higher thermal transitions and better physical properties).



Scheme 1.

The question for us was whether DAB based PAIs would, apart from their expected higher thermal transitions, have benefits over the DAH based PAIs, either with respect to their crystallization from the melt or with respect to their physical properties. This paper will give an answer to this question. We will also pay attention to the influence of chain regularity on the crystallization behaviour of these semi-aliphatic PAIs. The specific structure of the regular PAIs studied in this paper is given in Scheme 1.

In the rest of this paper, a PAI based on an aliphatic diamine containing *y* methylene groups and an N,N'-alkane-α,ω-diyl-bis(trimellitimide) containing *x* methylene groups is indicated as PAI[*y*,*x*]. This nomenclature is more or less in line with that for polyamides made from diamines and diacids.

2. Experimental

2.1. Materials

Trimellitic anhydride chloride (TMAC) was obtained from Aldrich, and was purified by dissolving it in toluene, after which insoluble impurities like trimellitic anhydride were removed by filtration. Trimellitic anhydride (TMA, 97% pure) and phthalic anhydride (99+%) were purchased from Aldrich and used as received. 1,4-Diaminobutane (99.5%) was obtained from DSM, 1,3-Diaminopropane (>99.5%) and 1,6-diaminohexane (>99.5%) were from Janssen Chimica, and 1,9-diaminononane (>98%) was from Fluka. All diamines were used as received. *N*-methyl-2-pyrrolidone (NMP) was from Janssen Chimica, and was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves until use. Triethylamine was purchased from Merck in a >99% pure form, and also distilled over CaH_2 prior to use. Lithium chloride (Merck, >98% pure) was dried (48 h, 100°C, vacuum) before use. Dimethylformamide (DMF, Baker), xylene and methanol (Riedel de Haen), toluene and thionyl chloride (Merck), benzoyl chloride (Janssen), sodium hydroxide (Merck), deuterated dimethylsulphoxide (DMSO-D6) and 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich) were used without purification.

2.2. Synthesis of poly(amide-imide) (PAI) from equimolar amounts of 1,4-diaminobutane and TMAC

In a 250 ml flask, 3.6 g (0.0409 mol) of 1,4-diaminobutane (DAB) and 4.5 g of triethylamine (TEA) were dissolved in 150 ml NMP under nitrogen. The mixture was cooled to −15°C, after which 8.6 g (0.0409 mol) of purified TMAC (dissolved in 30 ml toluene) were added slowly to the stirred solution. After 1 h at − 15°C, the mixture was heated up and stirred at 60°C for 3 h. Conversion of the formed poly(amic-acid) to the poly(amide-imide) PAI was performed by heating the mixture for 6 h at 140°C, during which the reaction water was removed by azeotropic distillation using toluene. The resulting orange coloured solution was filtered to remove TEA·HCl crystals, and the filtrate was poured into 1200 ml of methanol. The precipitated PAI was isolated by filtration, washed three times with methanol, and dried overnight in vacuum at 80°C. The yield of the polymerization was roughly 30 wt%. The PAI was characterized by FTIR (imide carbonyl absorptions at 1774 and 1705 cm^{-1}, amide absorptions at 3295, 1640 and 1540 cm^{-1}) and ^{13}C NMR.

2.3. Synthesis of *N,N′*-alkane-α,ω-diylbis(trimellitimide)s from TMA and α,ω-diaminoalkanes

All *N,N′*-alkane-α,ω-diylbis(trimellitimide)s were synthesized in analogy with the following specific example for the 1,4-diaminobutane (DAB) based bis-(*N*-trimellitimide).

A 2 l flask was charged with 333.15 g (0.85 mol) of trimellitic anhydride (TMA) and 950 ml NMP. A solution of 74.93 g (0.85 mol) of DAB in 300 ml of NMP was added dropwise at room temperature under stirring. The stirred reaction mixture was heated at 70°C for 5 h, after which 100 mol of xylene was added to the clear solution. The solution was further heated to reflux for an additional 5 h, during which the reaction water was removed azeotropically using a Dean–Stark trap. Upon cooling, a white crystalline product separated from the final reaction solution. This product was isolated by filtration, washed with methanol and dried overnight under vacuum at 80°C. 361 g of the DAB based bis-(*N*-trimellitimide) were obtained. The structure of the compound was confirmed by FTIR (imide carbonyl absorptions at 1774 and 1700 cm^{-1}), ^1H- and ^{13}C NMR, melting point (T_m observed is 340–350°C, literature value is 343–345°C [23]), and elemental analysis: C: calculated 60.55 wt% and found 60.3 wt%; H: calculated 3.7 wt% and found 3.6 wt%; N: calculated 6.42 wt% and found 6.5 wt%.

Note: the 1,3-diaminopropane and 1,9-diaminononane based bis-(*N*-trimellitimide)s did not separate from the final reaction mixture upon cooling. Here, distilled water was added as precipitating agent.

2.4. Synthesis of diacid chloride derivatives of *N,N′*-alkane-α,ω-diylbis(trimellitimide)s

All diacid chloride derivatives of the *N,N′*-alkane-α,ω-diylbis(trimellitimide)s were synthesized in analogy with the following specific example for the DAB based bis-(*N*-trimellitimide). Under a nitrogen atmosphere, 175 g (0.401 mol) of *N,N′*-butane-α,ω-diylbis(trimellitimide) were mixed with 400 ml of thionyl chloride in a 1 l flask. The reflux cooler connected to the reactor was connected to a gas absorption trap (40 g NaOH in 200 ml of water). 2 ml of *N,N*-dimethylformamide were used as a catalyst. The mixture was stirred at reflux (80°C) for 22 h. After completion of the reaction the excess of $SOCl_2$ was distilled off. At the end of the distillation *n*-hexane was added to the mixture, and subsequently distilled off in order to assure complete elimination of residual traces of $SOCl_2$, which was checked by holding wet pH paper in the outgas. The white product was washed with *n*-hexane and dried overnight at 80°C under nitrogen. The diacid chloride was collected in a 186 g yield. The FTIR spectrum of the product showed the characteristic imide doublet at 1774 and 1703 cm^{-1} and the characteristic –COCl carbonyl absorption around 1750 cm^{-1}. The product was further characterized by elemental analysis: C: calculated 55.83 wt% and found 55.4 wt%; H; calculated 2.98 wt% and found 3.0 wt%; N: calculated 5.92 wt% and found 5.9 wt%; Cl: calculated 14.98 wt% and found 14.7 wt%.

2.5. Synthesis of poly(amide-imide)s (PAIs) from diacid chloride derivatives of *N,N′*-alkane-α,ω-diylbis(trimellitimide)s and α,ω-diaminoalkanes

All polymerizations of this kind were performed in a way similar to the procedure described in the following example concerning the all DAB based PAI[4,4].

In a 2 l flask, 15.91 g (0.1805 mol) of DAB and 36.53 g (0.361 mol) of triethylamine were dissolved in NMP containing 2 wt% LiCl. The solution was cooled to −15°C, after which 85 g (0.1796 mol) of the diacid chloride derivative of *N,N′*-butane-α,ω-diylbis(trimellitimide), dissolved in NMP/2 wt% LiCl, were added drop by drop. Also added were 0.2537 g (0.001805 mol, 1% with respect to the total number of amine groups) of the chain stopper benzoyl chloride. The total amount of NMP used was 1500 ml. The reaction mixture was stirred vigorously while maintaining the temperature at −15°C for 30 min. Then the temperature was allowed to rise to room temperature in 2 h.

To complete the reaction the mixture was stirred for another 4 h at 60°C, resulting in a PAI solution containing small crystals of TEA·HCl. The polymer solution was added dropwise to methanol, after which the white fibrous precipitate was isolated by filtration, washed thoroughly with methanol, and (after grinding to a fine powder) dried in a vacuum oven for 48 h at 120°C and 16 h at 160°C to remove the last traces of NMP. The yield was 84.2 g (96%) of PAI[4,4]. The PAI was characterized by FTIR spectroscopy (imide carbonyl absorptions at 1774 and 1706 cm^{-1}, amide absorptions at 3296, 1645 and 1540 cm^{-1}), solution viscosity measurements in *m*-cresol at 80°C, dynamic viscosity, GPC with universal calibration (SEC/DV in hexafluoroisopropanol), ^{1}H- and ^{13}C NMR, thermogravimetric analysis, DSC analysis, WAXS and a limited mechanical/physical analysis.

2.6. Synthesis of model compounds for ^{13}C NMR analysis

A model compound containing two imide rings was synthesized from DAB and phthalic anhydride. The procedure was similar to the one described for the preparation of *N*,*N*′-butane-α,ω-diylbis(trimellitimide) from DAB and TMA.

A second model compound containing two amide groups was synthesized from DAB and benzoyl chloride. 16.87 g (0.12 mol) of benzoyl chloride were added slowly to 5.29 g (0.06 mol) of DAB and 12.5 g of TEA, dissolved in 100 ml of NMP. The reaction mixture was stirred for 30 min at 0°C, and was then allowed to heat up slowly to room temperature. Subsequently the mixture was heated at 60°C for 3 h. The yellow solution was filtered to remove TEA·HCl crystals, and then poured into toluene. The white precipitate (13.8 g) was dried under vacuum for 24 h at 60°C.

2.7. Characterization of the poly(amide-imide)s

FTIR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer in KBr discs. ^{1}H- and ^{13}C NMR spectra were recorded on a 200 MHz Bruker BACS 120. The ^{13}C NMR spectra were recorded in hexafluoroisopropanol, where deuterated acetone, present in a sealed capillary within the NMR tube, was used as a spectral reference. Dynamic Viscosity measurements were performed using a Rheometric RMS 800 mechanical spectrometer (using parallel plates). Size Exclusion Chromatography with universal calibration, using polystyrene standards, was performed on a HP-1090M, equipped with a diode array detector and a Viscotek differential viscosimeter detector (model 200). Thermogravimetric analyses were carried out under He with a Perkin Elmer TGA 7 (heating rate 20°C/min). DSC traces were recorded under N_2 on a Perkin Elmer DSC 7 (heating/cooling rate 20°C/min). Melting points of the bis(trimellitimide)s were measured using a transmitted-light polarizing microscope (Jena) equipped with a Linkam THM-600 hot stage. WAXS diffractograms were obtained with a Philips PW 1730 diffractometer, using CuKα radiation. After drying (105°C, 16 h) some PAIs were injection moulded on an Arburg 5, 20–30°C above their melting points. Bending and tensile tests were performed on dry as moulded bars on a Zwick 1445 (ASTM D790 and ASTM D638, respectively). Izod notched impact tests were performed with a Zwick 5102 (ASTM D256).

3. Results and discussion

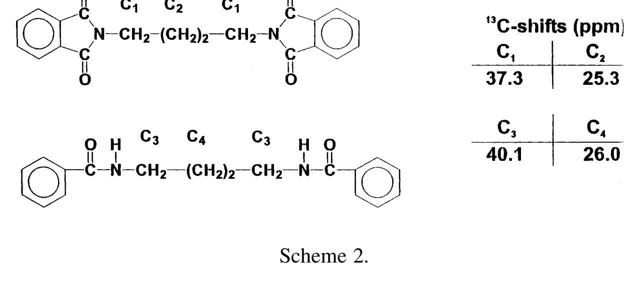
3.1. Synthesis of *N*,*N*′-alkane-α,ω-diylbis(trimellitimide)s and their diacid chloride derivatives

N,*N*′-alkane-α,ω-diylbis(trimellitimide)s and their diacid chloride derivatives were synthesized as described in Section 2. The FTIR spectra of the 1,3-diaminopropane (DAP), 1,4-diaminobutane (DAB), 1,6-diaminohexane (DAH) and 1,9-diaminononane (DAN) based bis(trimellitimide)s only differed in the strength of the methylene absorptions, and the spectra showed the characteristic imide absorptions around 1774 and 1700 cm^{-1}. In addition the ^{1}H- and ^{13}C NMR spectra were in agreement with the expected molecular structure. Elemental analysis was performed on the DAB based bis(trimellitimide), which showed excellent agreement between calculated and found wt% for C (60.55 resp. 60.3 wt%), H (3.7 resp. 3.6 wt%) and N (6.42 resp. 6.5 wt%). The melting points of the four different bis(trimellitimide)s were in agreement with the values reported by Kricheldorf et al. [23] (given here between parentheses): T_m *N*,*N*′-propane-α,ω-diylbis-(trimellitimide) = 284–292°C (not given in Ref. [23]); T_m *N*,*N*′-butane-α,ω-diylbis(trimellitimide) = 340–350°C (343–345°C [23]); T_m *N*,*N*′-hexane-α,ω-diylbis-(trimellitimide) = 322–325°C (321–322°C [23]); T_m *N*,*N*′-nonane-α,ω-diylbis(trimellitimide) = 216–220°C (204–205°C [23]). The diacid chloride derivatives of the four bis(trimellitimide)s were characterized by FTIR. All spectra showed the characteristic imide doublet at 1774 and 1703 cm^{-1} and the –COCl carbonyl absorption around 1750 cm^{-1}. The DAB based bis(trimellitimide) diacid chloride was also characterized by elemental analysis, which showed excellent agreement between the calculated and found wt% for C (55.83 resp. 55.4 wt%), H (2.98 resp. 3.0 wt%), N (5.92 resp. 5.9 wt%) and Cl (14.98 resp. 14.7 wt%). These analyses point to a high purity of the diacid chloride derivatives of the bis(trimellitimide)s, which is a prerequisite for their application as a monomer in a step-growth polymerization reaction with diamines.

3.2. Synthesis of poly(amide-imide)s and their molecular characterization

The direct synthesis of a PAI from equimolar amounts of TMAC and DAB may result in either 'head-to-tail', 'head-to-head', or in 'tail-to-tail' coupling, resulting in 'heterotriads' (amide-imide) or 'homotriads' (amide-amide or imide-imide), respectively. In TMAC the reactivity of anhydride differs from that of the acid chloride. E.g. it has been shown that, for the drop by drop addition of 4,4′-methylene dianiline (MDA) to an excess of TMAC, the acid chloride functionality reacts about 15 times faster than the anhydride functionality [24]. So, if the symmetrical diamine is added to an excess of TMAC, it can be expected that amide formation is favoured as long as sufficient acid chloride groups are present. When the acid chlorides become exhausted, then the amines have no alternative and will predominantly react with anhydrides with formation of amic-acid structures (which after ringclosure are transferred into imides). This procedure is expected to result in a more or less ordered structure (predominantly 'head-to-head' and 'tail-to-tail': amide-amide-imide-imide-amide-amide-imide-imide(…). On the contrary, our synthetic route, involving the addition of TMAC to the DAB, is expected to result in a more random, less ordered structure of the polymer chain, since at the beginning of the polymerization reaction the amine groups are exposed to both a large excess of acid chloride and of less reactive anhydride. An FTIR analysis showed the presence of both amide and imide bonds in this polymer (see Section 2). The randomness of this PAI can be checked with ^{13}C NMR spectroscopy (see later).

The synthesis of *N*,*N*′-alkane-α,ω-diylbis(trimellitimide)s, followed by the polycondensation of their acid chloride derivatives with (various mixtures of) aliphatic diamines, will guarantee the formation of a highly regular, ordered PAI chain structure ((amide-amide-imide-imide)$_n$). Moreover, the use of monomers with preformed imides will prevent undesired branching and crosslinking reactions, which may occur during the imidization of a poly(amic-acid). FTIR analysis of all DAB based PAI showed the presence of both amide and imide absorption (see Section 2). Again ^{13}C NMR spectroscopy is the method to study the chain regularity. To facilitate the interpretation of the spectra, two model compounds were synthesized, of which the chemical structure and their measured ^{13}C carbon shifts are given in Scheme 2.



^{13}C-shifts (ppm)	
C$_1$	C$_2$
37.3	25.3
C$_3$	C$_4$
40.1	26.0

Scheme 2.

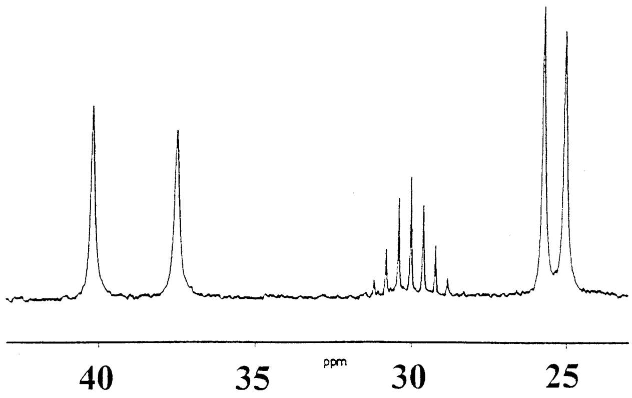


Fig. 1. Methylene carbon region of ^{13}C NMR spectrum of the regular PAI[4,4], recorded in hexafluoroisopropanol (heptet around 30 ppm is from deurterated acetone).

For a regular, all DAB based PAI[4,4] (Both *x* and *y* in Scheme 1 are equal to 4), exactly four different methylene carbon absorptions are expected in the ^{13}C NMR spectrum, viz. C1, C2, C3 and C4 in Scheme 2. On the other hand, a random structure having 'head-to-tail' (amide-imide) as well as 'head-to-head' (amide-amide) and 'tail-to-tail' (imide-imide) triads is expected to show at least two additional methylene absorptions next to C1–C4, and probably even more, since in theory in a 'head-to-tail' structure all four methylenes may have chemical shifts different from the C1–C4 shifts observed for the methylenes in a regular chain structure. The methylene parts of the ^{13}C NMR spectra of both the *N*,*N*′-butane-α,ω-diylbis(trimellitimide)/DAB-based PAI and the TMAC/DAB-based PAI (both recorded in hexafluoroisopropanol) are given in Figs. 1 and 2, respectively. The spectrum of the former PAI, as expected, points to a highly regular chain structure (four different single methylene carbon absorptions with the expected shifts given in Scheme 2), whereas the spectrum of the latter is in agreement with a more random chain structure (Instead of four single CH$_2$ peaks, the peaks around 26 and 40 ppm have become doublets). So, our synthetic route resulted in an irregular TMAC/DAB based PAI. The heptet around 30 ppm, present in both spectra, is from

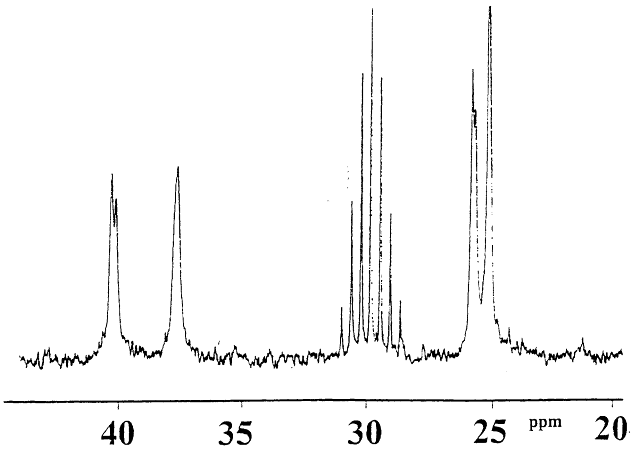


Fig. 2. Methylene carbon region of ^{13}C NMR spectrum of the irregular PAI synthesized from equimolar amounts of TMAC and DAB, recorded in hexafluoroisopropanol (heptet around 30 ppm is from deuterated acetone).

deuterated acetone, which was used as a spectral reference in a sealed tube present in the NMR tube.

As expected, the ^{13}C NMR spectrum of the regular PAI[6,4], synthesized from the diacid chloride derivative of the DAB based bis(trimellitimide) and 1,6-diaminohexane (DAH), shows five different single methylene absorption peaks at 40.9 (corresponding to C3 in Scheme 2), 37.7 (corresponding to C1), 26.0 (corresponding to C4), 25.2 (corresponding to C2 in Scheme 2) and at 28.4 ppm, the latter being the extra absorption for the middle two methylenes in the DAH residue (C5) (Spectrum not shown here).

For the regular all DAB based PAI, the M_n as determined by SEC/DV proved to be 12,000 g/mol. The intrinsic viscosity of this very same PAI, determined in *m*-cresol at 80°C, was 0.91 dl/g. The intrinsic viscosities of the other regular PAIs used in this study were of the same order of magnitude. In addition to the regulation of the linear chain length, the use of the endcapping agent benzoyl chloride has the advantage of capping amine chain ends, thereby preventing these from reacting with carbonyl groups of other PAI chains, which would result in branching and/or crosslinking.

3.3. Bulk characterization of the PAIs by WAXS, thermogravimetric analysis (TGA), melt viscosity, DSC and mechanical testing

WAXS analysis: In the introduction it was already mentioned that, in order to be suitable for high performance applications, our partially aliphatic PAIs with their expected relatively low T_g should be semi-crystalline. A WAXS study revealed that the as-synthesized random PAI, synthesized from an equimolar mixture of TMAC and DAB, only shows a very low degree of crystallinity (see the diffractogram of Fig. 3, which hardly shows the characteristic sharp crystalline peaks). On the other hand, the X-ray diffractogram of the as-synthesized well ordered PAI[4,4] shows large, well defined crystalline peaks, pointing to an estimated degree of crystallinity of ca. 50% (see Fig. 4).

Thermogravimetric analysis (TGA): The carefully dried regular PAIs were submitted to a TGA test (heating rate 20°C/min under He). The (not shown) TGA curve of PAI[6,4], being a representative polymer, shows no weight loss at all up to ca. 380–390°C. Above 400°C a serious weight loss is observed.

Melt viscosity: The fact that TGA of the regular poly(amide-imide)s of the PAI[*y*,*x*] type does not show any weight loss up to ca. 380°C does not guarantee that no chain scission into relatively large, non volatile parts occurs, which would have disastrous consequences for the mechanical properties of the PAIs. The measurement of the melt viscosity as a function of residence time indicates whether processing in the melt would be possible without chain scission, which would also influence the crystallization from the melt, since low molecular weight polymers crystallize much more readily than highly viscous polymers. For a high melting PAI[4,4] sample ($T_m = 346$°C, see DSC results), the dependence of the melt viscosity η^* of the frequency ω was measured as a function of time at 355°C. The recorded values of η^* at $\omega = 150$ rad/s after 2.5, 5 and 8 min in the melt were 300, 15 and 3 Pas, respectively, indicating an enormous reduction of the molecular weight. Obviously, PAI[4,4] cannot be processed in the melt without severe degradation. PAI[6,4] has a T_m of 289°C (see DSC results). Also for this polymer η^* was recorded as a function of ω for several residence times, this time at 300°C. For a relatively high molecular weight PAI[6,4] ($[\eta]_{m\text{-cresol},80°\mathrm{C}} = 1.05$ dl/g) the following melt viscosities at 150 rad/s were obtained after 2.5, 5 and 10 min at 300°C: 1000, 1500 and 1800 Pas, respectively. So,

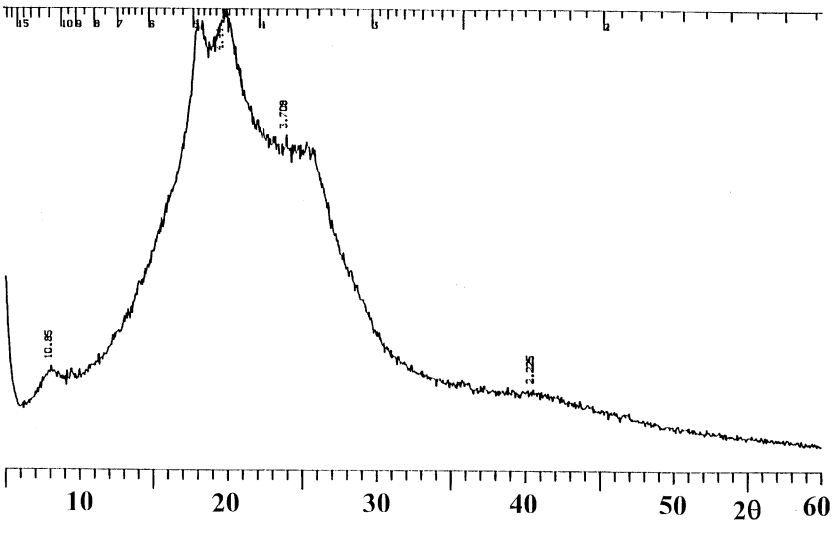


Fig. 3. WAXS diffractogram of the as synthesized, irregular PAI based on equimolar amounts of TMAC and DAB.

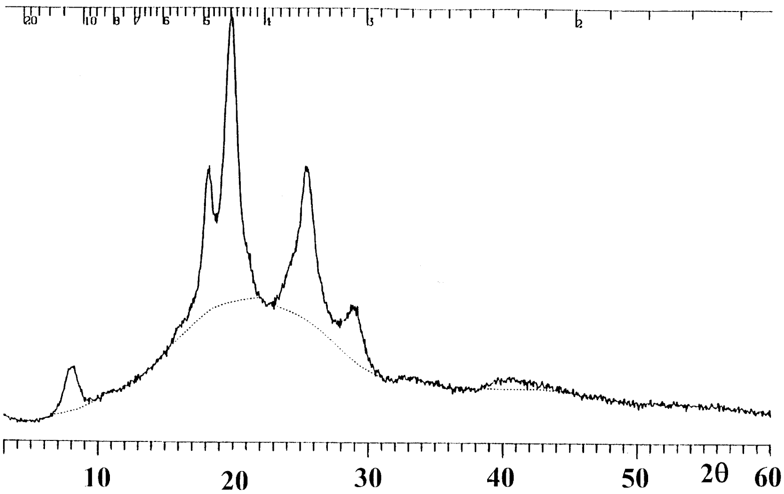


Fig. 4. WAXS diffractogram of the as synthesized, regular PAI[4,4].

around 300°C the semi-aliphatic PAIs seem to be stable enough for processing in the melt without degradation. The viscosity even somewhat increases with increasing residence time, most likely due to postcondensation and/or crosslinking reactions in the melt.

DSC analysis: The as synthesized random PAI, synthesized from equimolar amounts of TMAC and DAB, shows a modest melting endotherm in the first heating curve around 178°C. However, no crystallization takes place from the melt upon cooling at a rate of 20°C/min. The second heating curve only shows a T_g around 140°C, and no melting endotherm is observed. This behaviour is in agreement with the non-ordered molecular structure of this PAI, and implies that this type of PAI is not suitable for high performance injection moulding applications.

Table 1 shows the DSC data for the regular PAI[4,4]. The first heating curve melting point of this PAI ($T_{m,1}$) is around 346°C, the polymer readily crystallizes from the melt at a cooling rate of 20°C/min, and the second heating curve shows both a T_g ($T_{g,2} = 158°C$) and a melting point ($T_{m,2} = 344°C$). The heat of melting at first ($\Delta H_{m,1}$) and second heating ($\Delta H_{m,2}$) are in excellent agreement, and the crystallization enthalpy is of the same order of magnitude, which is characteristic for a well crystallizable polymer.

A melting point of 346°C implies a processing temperature of at least 350–360°C. The earlier discussed melt viscosity measurements at 355°C learned that such high processing temperatures would result in chain scission, which would surely affect the crystallization from the melt (see below). A regular PAI with a lower T_m, and accordingly a better melt processability, would be the all 1,6-diaminohexane (DAH) based PAI[6,6], or the PAI synthesized from the DAB based bis(trimellitimide) and DAH, PAI[6,4]. In agreement with the patent literature [30], PAI[6,6] has a softening or melting point around 260°C (For the as synthesized PAI[6,6] we found a T_m of 257°C), and this polymer did not show any crystallization from the melt upon cooling, nor did it crystallize during second heating (see Fig. 5 and Table 1). This is surprising, and we will comment on this phenomenon later on. It is obvious that PAI[6,6] is not suitable as a high temperature engineering plastic, since its T_g is only 119°C. The polymer prepared from the diacid chloride derivative of the DAB based bis(trimellitimide) and DAH, PAI[6,4], shows an intermediate

Table 1
DSC crystallization data for poly (amide-imides) ($\Delta T = 20°C/min$). x and y = number of CH_2 groups in bis-trimellitimide, resp. in diamine residue

Entry	PAI	x	y	$T_{m,1}$ (°C)	$\Delta H_{m,1}$ (J/g)	T_c (°C)	ΔH_c (J/g)	$T_{g,2}$ (°C)	$T_{m,2}$ (°C)	$\Delta H_{m,2}$ (J/g)	($T_{m,2} - T_g$) (°C)
1	[4,4]	4	4	346	60	278	59	158	344	58	186
2	[4/6,4]	4	4/6 = 75/25	317	49	240	37	153	314	35	161
3	[4/6,4]	4	4/6 = 65/35	303	39	–	–	148	299	21[a]	151
4	[4/6,4]	4	4/6 = 50/50	290	33	–	–	150	289	2[a]	139
5	[6,4]	4	6	289	53	–[b]	–[b]	140	285	27[b]	145
6	[3,3]	3	3	249	7	–	–	169	–	–	80[c]
7	[6,6]	6	6	257	42	–	–	119	–	–	138[c]
8	[9,9]	9	9	170	44	–	–	87	–	–	83[c]

[a] Crystallization during second heating curve only.

[b] Very broad and small exotherm during cooling, major part of crystallization during second heating.

[c] $T_{m,1} - T_g$.

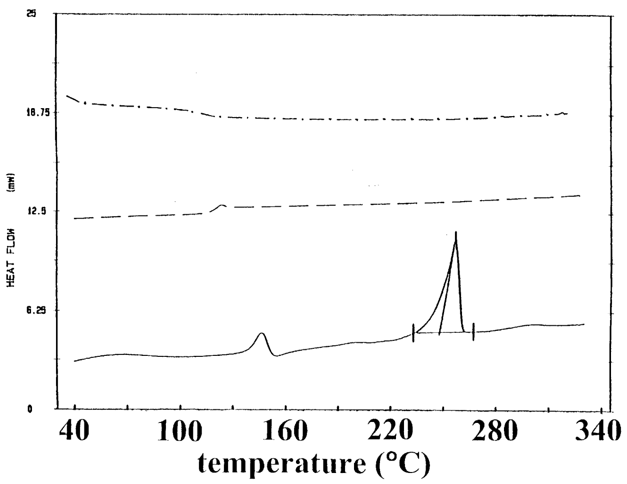


Fig. 5. DSC curves for PAI[6,6] (heating/cooling rate 20°C/min): (—) = first heating; (– · –) = cooling; (– – –) = second heating

crystallization behaviour between PAI[4,4,] and PAI[6,6]: the T_m of the as synthesized polymer is 289°C (which would allow injection moulding around the acceptable temperature range of 320–330°C, which is quite common for e.g. the aliphatic polymide 4.6, with a T_m of ca. 290°C), PAI[6,4] shows a very broad and small exotherm upon cooling at 20°C/min, and the crystallization proceeds further up to a relatively low degree of crystallinity during second heating (see Fig. 6 and Table 1). It is obvious that the crystallization rate of PAI[6,4] is too low for applications as a high temperature engineering plastic, since it is expected that injection moulding of this poorly crystallizing polymer, implying a very fast cooling, will result in an amorphous polymer with a T_g of only 140°C (see item mechanical properties). On the other hand, it is clear that PAI[6,4] crystallizes faster from the melt than the PAI[6,6], which does not contain any DAB at all.

In addition to the DAB and DAH based PAIs, two regular PAIs with an odd number of carbon atoms, both in the diamine and in the bis(trimellitimide) residue, were synthesized, viz. PAIs[3,3] and PAI[9,9]. Just like PAI[6,6], these regular PAIs did not crystallize from the melt (see Table 1). An important conclusion from the foregoing is the following: the crystallizability from the melt of semi-aliphatic PAIs, with the general regular chain structure given in Scheme 1, is raised with increasing content of DAB. So, since the all DAB based PAI has a too high T_m, and the crystallization from the melt of PAI[6,4] is too slow, a good compromise with respect to crystallizability from the melt and (not too high) melting point might be a ‘copoly(amide-imide)’ (coPAI) synthesized from the DAB based bis(trimellitimide) and mixtures of DAB and DAH. Table 1 shows that the melting points of the as synthesized coPAIs are indeed significantly lower than that of PAI[4,4]. CoPAIs from the DAB based bis(trimellitimide) and 50/50 and 65/35 DAB/DAH mixtures do not crystallize from the melt, but they do show some crystallization during second

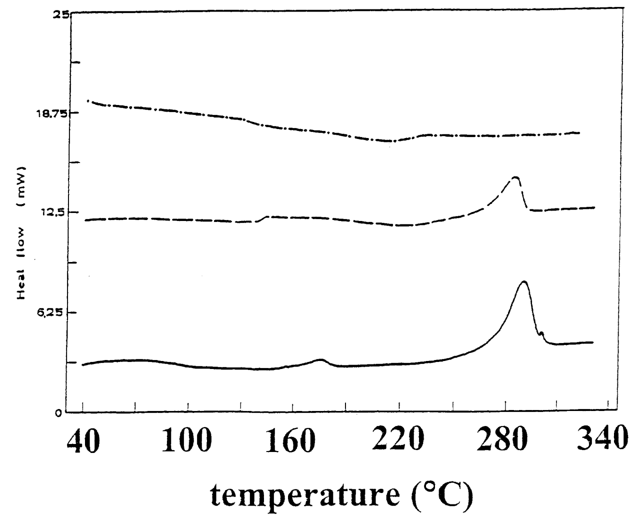


Fig. 6. DSC curves for PAI[6,4] (heating/cooling rate 20°C/min): (—) = first heating; (– · –) = cooling; (– – –) = second heating.

heating, the melting enthalpy being higher for the higher DAB content. The coPAI based on the 75/25 DAB/DAH mixture even crystallizes from the melt at a cooling rate of 20°C/min, but the crystallizability is definitely worse than that of the all DAB based PAI[4,4]. In Fig. 7 the ($T_{m,1}$) and ($T_{g,2}$) values of the coPAIs are given as a function of the mol% DAH in the DAB/DAH mixture, which is polymerized with the diacid chloride derivative of the *N*,*N*′-butane-α,ω-diylbis(trimellitimide). So, Fig. 7 concerns the

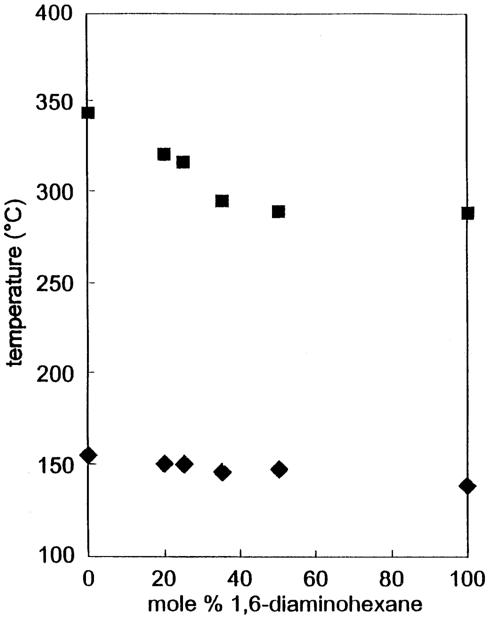


Fig. 7. Melting points (■) and glass transition temperatures (◆) as a function of the mol% DAH in the DAB/DAH mixture, used for the polymerization with the diacid chloride derivative of *N*,*N*′-butane-α,ω-diylbis(trimellitimide) to coPAI[4/6,4]. T_m determined from first heating curve, T_g determined from second curve (ΔT = 20°C/min).

copoly(amide-imide)s PAI[4/6,4]. Just like the series PAI[4,4], PAI[6,4] and PAI[6,6], the coPAIs[4/6,4] show a better crystallizability (either during cooling or during second heating) with increasing DAB content. The results in Table 1 show that the so called crystallization window ($T_m - T_g$), which is the temperature range in which a polymer crystallizes, generally increases with increasing DAB content of the PAIs. It has been described that crystallization from the melt occurs more readily for polymers with wider crystallization windows [25], which thus might explain the better crystallizability with increasing DAB content. Another reason for the faster crystallization might be related to the configuration of the alkane residue. The relatively short DAB residue is less flexible than the longer DAH residue, and the chances of a deviation from the all-*trans* configuration is probably lower in the case of four methylenes than in the case of six. So, a higher DAB content might result in a more straight polymer chain, which is expected to be favourable for crystallization.

The results of the dynamic viscosity measurements also have to be mentioned here. The good crystallization performance of PAI[4,4] (and probably also of the DAB rich coPAI[4/6,4] (DAB/DAH = 75/25)) is probably over-estimated in view of molecular degradation in the DSC to a low viscous polymer, which crystallizes much faster than a highly viscous polymer. For the PAIs with lower melting points degradation in the melt is limited or (for T_m values around 300°C) even absent, and more reliable crystallization data are obtained. Probably the best indication that an increased DAB content really enhances the crystallization from the melt, without the necessity to take into account possible degradation reactions, is the comparison of PAI[6,4] and PAI[6,6] (entries 5 and 7 in Table 1). These polymers with similar intrinsic viscosities both have been heated to 330°C in the first heating curve and were submitted to the same temperature program. Therefore, the observed differences in crystallizability from the melt must be related to differences in the chemical structure.

Mechanical properties: The dynamic viscosity measurements have shown that PAI[4,4] will undergo degradation during processing at (T_m + 20°C). Nevertheless the polymer was injection moulded, and the mechanical properties are as follows: flexural modulus = 4200 ± 200 MPa, notched Izod impact = 0.5 ± 0.1 kJ/m^2 and maximum flexural strength = 42 ± 7 MPa The bars are opaque and the recorded modulus is extremely high, both phenomena pointing to a reasonable degree of crystallinity (even after injection moulding). On the other hand the bars are extremely brittle, which is caused by the mentioned molecular degradation. It is obvious that PAI[4,4] is useless as a high performance engineering plastic. The dynamic viscosity measurements on PAI[6,4] showed that this polymer probably can be moulded around 300–310°C without serious degradation problems. These injection moulded bars are fully transparent, pointing to an amorphous character, which is as expected in view of the results of the crystallization study. The following properties were found (between parentheses the brochure values for the all-aromatic PAI Torlon™ have been given): tensile modulus = 2900 ± 30 (4800) MPa, tensile strength at yield = 100 ± 1 (192) MPa, tensile strength at break = 80 ± 10 (117) MPa. Tensile elongation at break = 50 ± 30(15)%, flexural modulus = 3200 ± 20 (5000) MPa, maximum flexural strength = 156 ± 1 (241) MPa, and notched Izod impact = 6.6 ± 0.2 (11.1) kJ/m^2. The good properties of the moulded bars indicate that no serious molecular degradation had taken place during processing, but the amorphous character and the relatively low T_g (140°C) limit the possibilities for this PAI in engineering plastics applications. The coPAI[4/6,4] (DAB/DAH 75/25) crystallizes more readily from the melt than PAI[6,4], but less readily than PAI[4,4] (see Table 1). Since the T_m of this coPAI is some 30°C lower than that of PAI[4,4], less degradation during injection moulding is expected. However, the injection moulded bars of coPAI[4/6,4] (DAB/DAH 75/25) were transparent, and a WAXS analysis of the bars did not show any sign of crystallinity. This implies that also for this coPAI the maximum use temperature is limited by the relatively low T_g of 153°C. On the other hand, the tensile properties of the copoly(amide-imide) (modulus = 3100–3300 MPa, strength at break = 80–85 MPa) and the notched Izod impact value (3–6 kJ/m^2) are quite acceptable, indicating that degradation phenomena are much less pronounced than in the case of PAI[4,4]. The all-aromatic Torlon™, however, is the PAI with the superior mechanical properties. The only drawback of this high performance polymer with respect to our semi-aliphatic PAIs remains its bad processability.

4. Conclusions

It was investigated whether semi-aliphatic, thermoplastic poly(amide-imide)s are interesting alternatives for the all-aromatic high performance polymer Torlon™, which is based on TMAC and 4,4′-methylene dianiline, and for which melt processability is extremely difficult. In order to be suitable for high performance applications, a semi-crystalline character is required, since the relatively low T_gs of the partially aliphatic PAIs, favourable for melt processing, would limit high temperature applications if these materials would be fully amorphous.

Our study has shown that the application of partially aliphatic poly(amide-imide)s as engineering plastics seems to be a bridge too far. The all DAB based PAI[4,4] crystallizes from the melt, but during the required high processing temperature (T_m = 346°C) degradation to low molecular weight polymer is inevitable. The all DAH based PAI[6,6], with a much lower T_m (257°C), does not crystallize from the melt, and the PAI[6,4] (T_m = 289°C) based on the diacid chloride derivative of *N,N′*-butane-α,ω-diylbis(trimellitimide) and DAH, shows a very low degree of crystallinity at a cooling rate of 20°C/min, but is totally amorphous after injection moulding. Copoly(amide-imide)s with a high DAB content crystallize more readily than PAIs with a lower DAB content, e.g. during second heating in the DSC (20°C/min). This is thought to be related to a wider crystallization window for the PAIs with a higher DAB content, and to the more straight polymer chains for DAB rich PAIs, since a diamine containing four carbon atoms will have less cis-configurations than a diamine containing six carbons. Only if the rate of crystallization of PAI[6,4] or the copoly(amide-imide)s can be enhanced significantly, e.g. by raising both the nucleation density and the spherulitic growth rate, then these materials might become interesting candidates for the high performance market. A study on the crystallization kinetics and on the enhancement of the nucleation density is in progress.

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