

Influence of polymerization conditions on melt crystallization of partially aliphatic polyimides

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A homologous series of polyimides (PIs) was prepared in *N*-methyl-2-pyrrolidone (NMP) from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and α,ω -diaminoalkanes containing 4–10 carbon atoms. For this series the well known odd-even effect was found. Whereas the PIs based on even numbered aliphatic diamines all rapidly crystallize from the melt, the PIs based on 1,7-diaminoheptane (C7) and 1,9-diaminononane (C9) stay amorphous upon cooling from the melt. The chemical structure of the synthesized PIs was confirmed by solid state ¹³C n.m.r. and FTi.r. spectroscopy.

The PI based on BPDA and 1,8-diaminooctane (DAO) was selected for a study on the relation between chain architecture and crystallization behaviour. This specific polymer was both prepared in NMP and in *m*-cresol. In NMP the poly(amic acid) intermediate was expected to generate a more branched PI structure than in *m*-cresol, where this intermediate has never been detected. Furthermore, for both the NMP and the *m*-cresol synthesized PI the residual amine endgroups were blocked, since it is known that these endgroups may generate branching and/or crosslinking. The endcapped poly(BPDA-DAO) synthesized in *m*-cresol exhibited the most optimal crystallization behaviour, which is in line with its expected, predominantly linear character. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polyimides (PIs) are well known as high-performance materials in view of their excellent mechanical properties and thermal stability. Although completely aromatic polyimides are commercially available, the rigidity of the backbone, which renders these materials amorphous, limits the processability in the melt. However, the commonly used two-step synthesis allows processing at the precursor stadium, i.e. poly(amic acid), and (all-aromatic) polyimides can be obtained as films or fibres¹. The need for more processable polyimides was evident and many research groups have focused on different chemical modifications in order to obtain semi-crystalline thermoplastic polyimides.

In the search for chemically modified polyimides, the dianhydrides used are mostly aromatic and the character of the diamines is varied, the aim being to find a good compromise between acceptable processing conditions without degradation and retaining the thermal and mechanical properties at temperatures as high as possible. The following are examples of the many different published chemical modifications that lead to semi-crystalline thermoplastic polyimides.

By using aromatic dianhydrides and aliphatic diamines, flexible segments are introduced into the main chain and T_g and T_m are lowered which makes these semi-crystalline materials processable in the melt. This proved to be a successful approach since these semi-crystalline polyimides exhibit interesting properties^{2–4}. Jin *et al.* have shown that

by replacing the aromatic diamines by alicyclic diamines, thermal stability is maintained and semi-crystalline materials can be obtained with T_g -values up to 340°C^{5,6}. Incorporation of bulky groups such as adamantane⁷ and diamantane⁸ via their diamino derivatives led to new semi-crystalline polyimides with high T_g values and good thermal stability.

In aprotic polar solvents, as e.g. *N*-methylpyrrolidone (NMP), the two-step synthesis consists of the reaction of a dianhydride and a diamine, generating the intermediate poly(amic acid), which is then ring-closed in the imidization step. A number of side reactions can occur on different levels in the synthesis, leading to architectural and chemical imperfections in the final polyimides. Thermal or chemical conversion of the poly(amic acid) results in the formation of many different chemical species such as isoimides, imides, diacids, dianhydrides, etc.^{9,10}. Spectroscopic techniques have been most commonly used in order to understand the thermal imidization of all-aromatic polyimides^{9,10}. During the synthesis, some salt formation occurs in the poly(amic acid) stadium, leading to the formation of diamides which upon heating will release free amino endgroups. It has been shown by a spectroscopic study on model compounds that upon thermal treatment, imine based crosslinks can be formed by the nucleophilic attack of a free amino endgroup on an imide carbonyl¹¹. The same conclusion can be drawn from a study on polyimides obtained from aromatic dianhydrides and aliphatic diamines using appropriate model compounds¹². The undesired side reactions resulting in branching or even partial crosslinking, can be largely suppressed by endcapping the free amino endgroups with a

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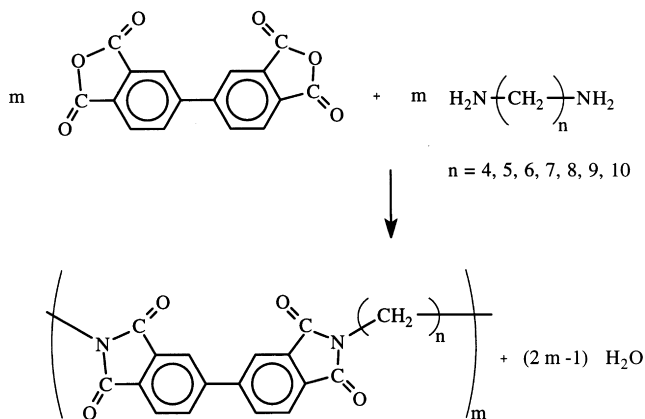


Figure 1 Scheme of polycondensations of BPDA with homologous series of α, ω -diaminoalkanes

suitable reagent, as will be shown. The side reactions related to the salt formation can also be limited if the polycondensation is performed in *m*-cresol, where the poly(amic acid) form is not a stable intermediate and has never been detected.

Alternative routes for the preparation of partially aliphatic polyimides are the high pressure synthesis from salts as described by Itoya *et al.*¹³ and the Pd-catalyzed carbonylation of bis(*o*-iodo esters) and diamines as described by Perry *et al.*¹⁴.

Based on earlier results of Kricheldorf *et al.*³, Hsiao *et al.*¹⁵ and Koning *et al.*⁴, this work will concentrate on the synthesis of polyimides based on 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and aliphatic α, ω -diaminoalkanes. As a good crystallizability from the melt of these semi-crystalline polyimides is expected, a systematic study of the polycondensations using BPDA and a homologous series of α, ω -diaminoalkanes in NMP and in *m*-cresol is proposed, as represented in Figure 1. Since an influence of the presence of amino endgroups on the crystallization behaviour is expected because of possible branching and/or crosslinking (*vide supra*), both endcapped and non-endcapped polyimides will be prepared. The effect of the supposed branching/crosslinking on the crystallization behaviour will be studied.

EXPERIMENTAL

Materials

3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) (Chriskev Co., 99.5% pure), all diamines (Aldrich, purities ranging from 95 to 99%), benzoylchloride (UCB) and xylene (Merck) were used as received, and phthalic anhydride (Merck) was recrystallized from chloroform. *N*-methyl-2-pyrrolidone (NMP) and *m*-cresol (Aldrich) were distilled (from calciumhydride in the case of NMP) prior to polymerization.

Polymerization in NMP

In a typical experiment, a three necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet, was brought under a dry nitrogen atmosphere. 16.8 mmol (1 eq) of diamine was dissolved in 50 ml of NMP, followed by the addition in one portion of 5.00 g (17.0 mmol, 1.01 eq) solid BPDA, which had been dried for 3 h at 180°C. The reaction mixture was cooled by an ice-water bath and the poly(amic acid) formation was accomplished under stirring overnight. The apparatus was then equipped with a Dean-Stark

separator, 15 ml of xylene was added and the solution was heated by an oil bath to 160°C in order to distill the water, released during the imide ring formation, by means of the xylene/water azeotrope. The imidization proceeded for 2.5 h, and after the optional addition of 1 ml of benzoylchloride (50 mol% compared to the initial number of amino groups) in order to endcap the remaining free amino groups, heating was continued for an additional 30 min. The polyimide crystallized from the solution upon cooling, was filtered, washed carefully with methanol and dried under vacuum at 180°C for 3 h and at 100°C overnight.

Polymerization in *m*-cresol

In a typical experiment, a three-necked flask, equipped with a mechanical stirrer, Dean-Stark separator and nitrogen inlet and outlet, was brought under a dry nitrogen atmosphere. 16.8 mmol (1 eq.) of diamine was dissolved in 150 ml of *m*-cresol and 5.00 g (17.0 mmol, 1.01 eq.) of solid BPDA was added in one portion at room temperature. The mixture was heated by an oil bath, and the temperature was gradually raised from room temperature to 180°C over a period of 3 h. Subsequently, phthalic anhydride was added (40 mol% compared to the initial number of amino groups) if endcapping of the remaining free amino groups was desired. The cooled reaction mixture was then poured into a tenfold excess of ethanol in order to precipitate the polymer, which was filtered, washed carefully with methanol and dried at 130°C under high vacuum (less than 1 mbar).

Characterization

FTi.r. spectra were taken in KBr on a Perkin Elmer System 2000 apparatus and solid state n.m.r. spectra were recorded on a Bruker 250 AC spectrometer equipped with a multinuclear X/¹H dual-channel probe head for CP MAS experiments.

The concentration of the primary amine endgroups was determined by titrating a PI solution in phenol with a 0.05 molar HCl solution in phenol/ethylene glycol.

Solution viscosimetry was performed with an Ubbelohde viscosimeter at 80°C on 0.008 g ml⁻¹ solutions in *m*-cresol.

D.s.c. experiments were performed on a Perkin Elmer DSC 7 using nitrogen as the purge gas. All samples were prepared in perforated aluminum pans and were submitted to a similar temperature program: heating from 25°C to a temperature 20°C higher than the corresponding melting temperature at 10°C min⁻¹, 2 min isothermal at that temperature, cooling to 60°C at 10°C min⁻¹, 2 min isothermal at 60°C, and a second heating run identical to the first.

T.g.a. experiments were performed on a Perkin Elmer TGA 7 in a helium atmosphere and the samples were heated at 10°C min⁻¹.

RESULTS AND DISCUSSION

Synthesis

Partially aliphatic polyimides were prepared from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and the following diamines: 1,4-diaminobutane (DAB); 1,5-diaminopentane (DAP); 1,6-diaminohexane (DAH); 1,7-diaminoheptane (DAHe); 1,8-diaminooctane (DAO); 1,9-diaminononane (DAN) and 1,10-diaminodecane (DAD). Primary amine endgroups of the PIs synthesized in NMP were optionally blocked by reaction with benzoyl chloride, whereas the amines present in the PIs prepared in *m*-cresol were reacted with phthalic anhydride, if desired.

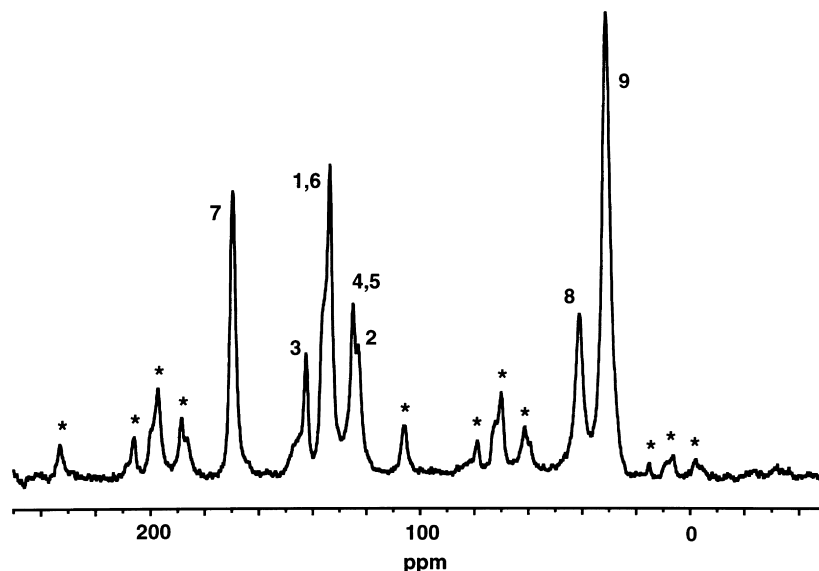


Figure 2 Solid state ^{13}C n.m.r. spectrum of the polyimide based on BPDA and DAO. The numbering of the carbon atoms is explained in *Figure 3*. *Spinning side bands

Molecular characterization

The synthesized polymers were characterized by FTi.r. spectroscopy. The following absorption bands, in cm^{-1} , were found in all spectra: 3461, 3070, 2932, 2856, 2359, 1853, 1770, 1706, 1622, 1438, 1422, 1393, 1364, 1261, 1189, 1106, 1050, 905, 842, 742, 692, 675, 621, 545. As all polymers have a similar molecular structure, the position of the absorption bands is the same. An increase in the number of methylene groups can be confirmed by a higher intensity of the absorption bands corresponding with the stretching and bending vibrations of the methylene unit. The absorptions at 1706 and 1770 cm^{-1} are typical imide absorption bands.

Table 1 Experimental and calculated¹⁶ chemical shifts in the solid state ^{13}C n.m.r. spectrum of the PI based on BPDA and DAO

| Nr. C-atom in <i>Figure 3</i> | Experimental chemical shifts (ppm) | Calculated chemical shifts (ppm) |
|-------------------------------|------------------------------------|----------------------------------|
| C1 | 131.7 | 135.4 |
| C2 | 121.1 | 125.7 |
| C3 | 140.6 | 142.4 |
| C4 | 123.1 | 128.2 |
| C5 | 123.1 | 127.2 |
| C6 | 131.7 | 133.9 |
| C7 | 167.6 | — |
| C8 | 39.1 | — |
| C9 | 29.4 | — |

The presumed chemical composition of the PIs given in *Figure 1* was confirmed by a solid state ^{13}C n.m.r. analysis. A typical spectrum is given in *Figure 2*.

In *Table 1*, the experimentally obtained chemical shifts of the PI based on BPDA and DAO are compared with calculated values. The carbon atoms are numbered as in *Figure 3*.

The spectra of all synthesized PIs were comparable, except for the relative intensity of the aliphatic carbon atoms C₈ (approximately 39 ppm) and C₉ (approximately 29 ppm), as expected. The sequence of the experimental chemical shifts of the aromatic carbon atoms, as well as the absolute value of these shifts, are in good agreement with the calculated shifts¹⁶. Note that the shifts of C₇, C₈ and C₉ cannot be calculated¹⁶. Other peaks present in the solid state ^{13}C n.m.r. spectrum shown in *Figure 2* are first- and second-order spinning side bands.

Thermal analysis

In spite of their partially aliphatic character, all PIs of this homologous series are remarkably stable. With t.g.a. in a helium atmosphere and heated at $10^\circ\text{C min}^{-1}$, no weight loss is observed up to approximately 375°C . This information is important for reliable melt crystallization studies. Note that the 10% weight loss level is observed around $480\text{--}500^\circ\text{C}$ for all materials. A typical t.g.a. thermogram is given in *Figure 4* for the polyimide based on BPDA and DAO.

Table 2 summarizes the data obtained from d.s.c.

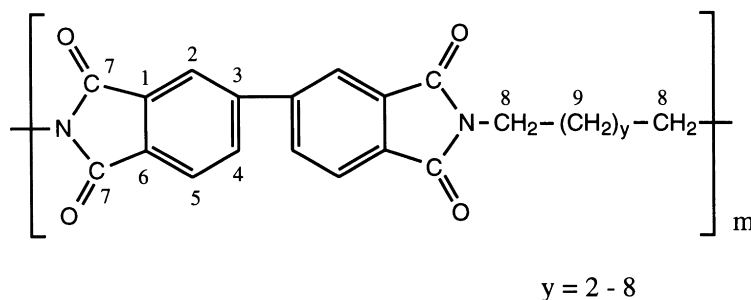


Figure 3 Repeating unit of polyimide based on BPDA and α, ω -diaminoalkanes

experiments and viscosity measurements on the polyimides synthesized in NMP and endcapped with benzoylchloride.

Using NMP as the polymerization medium, all partially aliphatic polyimides were obtained as semi-crystalline materials exhibiting a clear melting and crystallization behaviour, although polyimides prepared with DAHe and DAN (7 and 9 methylene groups) do not crystallize from the melt at a cooling rate of $10^{\circ}\text{C min}^{-1}$ (no crystallization peak visible in the cooling run). As an illustration, in Figures 5 and 6 the d.s.c. thermograms of poly(BDPA-DAO) ($n = 8$) and poly(BDPA-DAN) ($n = 9$) are given, respectively. Note the sharp crystallization peak and the small super-cooling $\Delta T = T_m - T_c$ in Figure 5, typical for a relatively fast crystallization. On the contrary, the odd numbered DAN based polyimide only crystallizes during the second heating run (Figure 6).

In addition to poly(BDPA-DAO), the other 'even numbered' polyimides, based on DAH ($n = 6$) and DAD ($n = 10$), readily crystallize from the melt. No reliable values of T_{m2} , T_{g2} and ΔH_c can be given for poly(BDPA-DAB) ($n = 4$), owing to the extremely high melting point, causing degradation in the melt during the d.s.c. experiment.

Melting points in the first and second heating run correspond well (except for poly(BDPA-DAB)). This is indicative of almost absent NH_2 initiated branching and/or

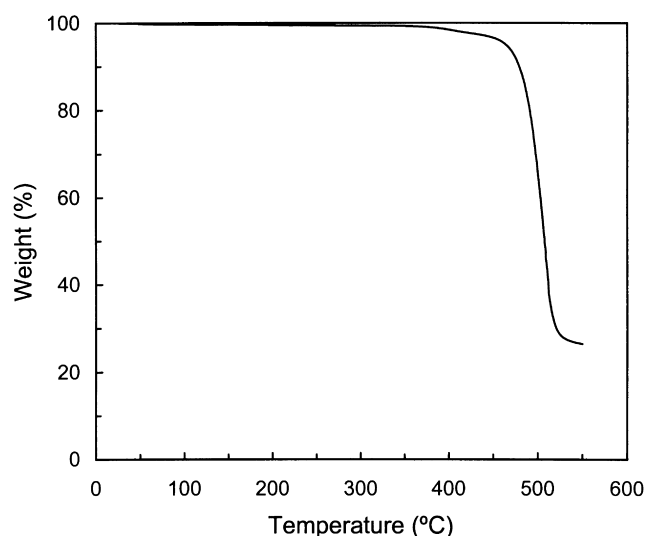


Figure 4 t.g.a. thermogram of poly(BDPA-DAO). Weight loss in helium atmosphere as a function of temperature. Heating rate $10^{\circ}\text{C min}^{-1}$

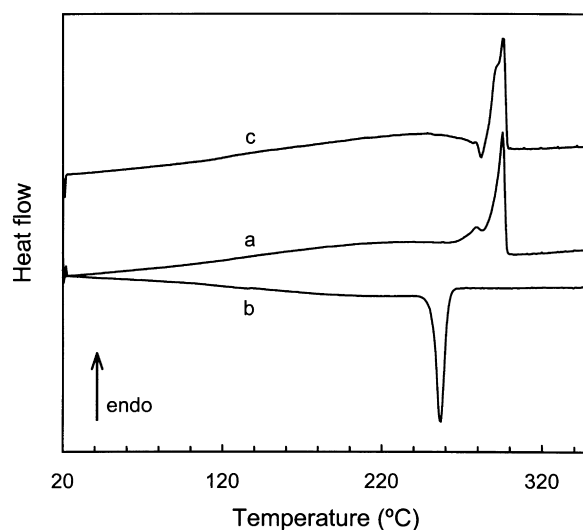


Figure 5 d.s.c. thermogram of poly(BDPA-DAO) ($n = 8$), synthesized in NMP and endcapped with benzoylchloride. Heating/cooling rate $10^{\circ}\text{C min}^{-1}$: (a) first heating; (b) cooling; (c) second heating

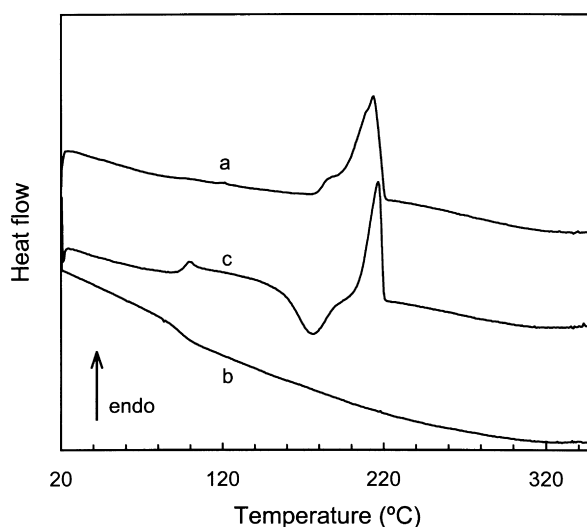


Figure 6 d.s.c. thermogram of poly(BDPA-DAN) ($n = 9$), synthesized in NMP and endcapped with benzoylchloride. Heating/cooling rate $10^{\circ}\text{C min}^{-1}$: (a) first heating; (b) cooling; (c) second heating

Table 2 Inherent viscosities, thermal transitions and melting enthalpies obtained from first (1) and second (2) heating curves of a homologous series of polyimides based on BPDA and α, ω -diaminoalkanes, synthesized in NMP and endcapped with benzoylchloride ($n =$ number of CH_2 groups in the diamine)

| Polyimide (n) | η_{inh} (dl g^{-1}) | T_{g2} ($^{\circ}\text{C}$) | T_{m1} ($^{\circ}\text{C}$) | ΔH_{m1} (J g^{-1}) | T_{m2} ($^{\circ}\text{C}$) | ΔH_c (J g^{-1}) |
|-------------------|-------------------------------------|---------------------------------|---------------------------------|---------------------------------------|---------------------------------|------------------------------------|
| BPDA-DAB (4) | — ^a | — ^b | 438 | 64 | — ^b | — ^b |
| BPDA-DAP (5) | 0.46 | 158 ^d | 331 | 41 | 330 | 35 |
| BPDA-DAH (6) | 0.26 | 137 ^d | 349 | 40 | 349 | 38 |
| BPDA-DAHe (7) | 0.31 | 125 | 258 | 55 | 258 | — ^c |
| BPDA-DAO (8) | 0.29 | 113 ^d | 293 | 61 | 293 | 41 |
| BPDA-DAN (9) | 0.25 | 94 | 214 | 42 | 217 | — ^c |
| BPDA-DAD (10) | 0.30 | 87 ^d | 249 | 46 | 249 | 35 |

Melting temperatures are defined as the maximum of the melting endotherm

ΔH_c = enthalpy of crystallization upon cooling

^a: insoluble in *m*-cresol at 80°C

^b: unreliable values because of degradation in the melt during first heating

^c: crystallization not observed

^d: T_g measured after quenching from the melt in the case of a melt crystallizable polyimide

crosslinking and thermal stability, as expected for these 'amine-blocked' PIs.

Contrary to the other 'odd numbered' PIs, the DAP ($n = 5$) based polymer does also crystallize from the melt. Here the effect of the relatively short odd numbered diamine residue is probably overruled by the crystallization promoting biphenyl unit.

No firm indications were found that these partially aliphatic PIs, based on BPDA, show liquid crystalline behaviour in the melt. This is in agreement with conclusions of Itoya *et al.*¹³ and Inoue *et al.*¹⁷. Note that the small and narrow exothermic peak around 300°C in the cooling curve of poly(BPDA-DAO) (Figure 5) might suggest that this PI shows thermotropic behaviour. However, additional experiments failed to reproduce this peak, which rather has to be considered as a spark.

Currently we are studying the crystallization kinetics of this homologous series of partially aliphatic PIs. The results will be compared to those of Hsiao *et al.*¹⁵ who carefully studied the crystallization of the PI based on BPDA and 1,12-diaminododecane ($n = 12$).

When the glass transition temperature T_g and the melting temperature T_m are plotted as a function of the number of CH_2 groups of the diamine residue in the repeating unit (n), T_g seems to decrease in a linear way if n is enhanced from 5 to 10, whereas the T_m versus n plot exhibits the well known 'odd-even' effect, as shown in Figure 7^{4,18}.

Influence of polymerization conditions on melt crystallization

The results of the thermal analyses discussed so far all concern polyimides synthesized in NMP, of which the

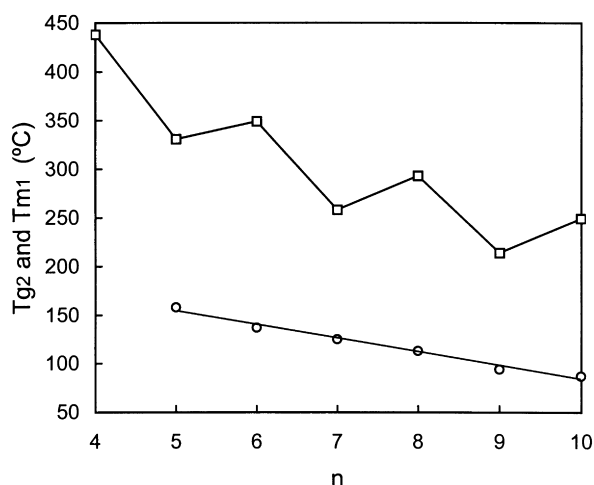


Figure 7 T_{g2} (○) and T_{m1} (□) of NMP synthesized and benzoylchloride endcapped polyimides based on BPDA and α, ω -diaminoalkanes, as a function of the number of CH_2 groups of the diamine residue in the repeating unit (n)

Table 3 Influence of polymerization solvent and endcapping on the DSC data for poly(BPDA-DAO) ($n = 8$) of Table 2

| Solvent | End cap | $[\text{NH}_2]$ (meq g^{-1}) | T_{g2} (°C) | T_{m1} (°C) | ΔH_{m1} (J g^{-1}) | T_{m2} (°C) | T_c (°C) | ΔH_c (J g^{-1}) |
|------------------|---------|--|------------------|------------------|--|------------------|---------------|---------------------------------------|
| NMP | yes | 0.006 | 113 | 293 | 61 | 293 | 257 | 41 |
| NMP | no | 0.068 | 126 | 294 | 61 | 279 | 211 | 25 |
| <i>m</i> -cresol | yes | 0.009 | 108 | 297 | 41 | 298 | 252 | 34 |
| <i>m</i> -cresol | no | 0.019 | 124 | 291 | 27 | 271 | 229 | 18 |

All T_g values were measured after quenching from the melt.

$[\text{NH}_2]$ = concentration of NH_2 endgroups obtained by titration.

T_c = crystallization temperature (maximum of crystallization exotherm upon cooling)

amine endgroups have been blocked as completely as possible.

Now, the influence of the polymerization solvent (NMP versus *m*-cresol) and the endcapping on the d.s.c. results is considered. The data have been collected in Table 3 for BPDA-DAO ($n = 8$).

In the introduction it was already mentioned that at elevated temperatures, e.g. in the melt or during drying, amine endgroups of one PI chain can react with imide carbonyl groups along another PI chain, with formation of branched or even crosslinked products.

Using NMP, in the poly(amic-acid) stadium, some salt formation occurs between NH_2 endgroups and carboxylic acid sidegroups. In the imidization step, the salt-free amic-acid groups will release water and are transformed into the desired imide groups. However, amic-acid groups existing in the $[-\text{COO}^- \text{ } ^+\text{NH}_3-]$ form are transformed into a diamide group after removal of water, and the as synthesized PI will have a branched character.

After this imidization step, the benzoylchloride endcapping agents are added, which can only react with the NH_2 groups present at that time. At high temperature, e.g. in the melt, the diamide will be transformed into an imide¹², upon elimination of an amine terminated PI chain. This latent amine was not trapped by the endcapper benzoylchloride, and immediately after being generated it will react with an imide-carbonyl¹². So, the branched structure generated in the poly(amic-acid) stadium will be retained. Therefore, it can be concluded that, at least after being heated up, the PIs synthesized in NMP inevitably will have a branched (or even partially crosslinked) character.

However, poly(amic-acid) related branching is impossible in *m*-cresol, since in this polymerization medium this intermediate has never been observed, and is, at most, very 'short-lived'. In this case, probably no latent amines are present after endcapping of the more linear PI with phthalic anhydride (the more reactive benzoylchloride reacts with the solvent *m*-cresol), and the blocking of NH_2 endgroups is probably preventing (or at least to a large extent limiting) branching or crosslinking at elevated temperatures. In other words, the PI as synthesized in *m*-cresol is probably more linear than the NMP synthesized counterpart, and will stay more linear even after being molten. One should note that, by accident, the 'non endcapped' *m*-cresol PI of Table 3 had been treated with benzoylchloride. Since nearly all benzoylchloride reacts with the solvent, this polymer still contains relatively high amounts of NH_2 endgroups and is to be considered, therefore, as 'non endcapped' material.

With this in mind, the results of Table 3 have to be discussed. It is obvious that both in NMP and in *m*-cresol the endcapping of the NH_2 endgroups was quite efficient, since the amino endgroup concentration in both cases is very close to the detection limit of 0.005 meq g^{-1} . In the first heating curve, the melting points of all four

poly(BPDA-DAO) samples are quite similar. The higher enthalpies of melting ΔH_{m1} for the NMP synthesized PIs, both endcapped and non-endcapped, are related to the different crystallization procedure for the as-synthesized polymers. The *m*-cresol synthesized PIs have to be precipitated in ethanol, whereas the NMP route allows the polymers to crystallize very slowly from solution upon cooling, generating a higher crystallinity.

Upon cooling from the melt, the endcapped PIs exhibit a much higher crystallization temperature, as well as a significantly higher enthalpy of crystallization, both for the *m*-cresol and NMP synthesized polymers. This is in line with the expected, crystallization disturbing, branching and crosslinking phenomena in the melt for non- or incompletely endcapped PIs. This branching and/or crosslinking also results in an upward shift of the glass transition temperatures and in a downward shift of the melting points during second heating. Upon crystallization from the melt, the most perfect crystals seem to be obtained for the endcapped PI, synthesized in *m*-cresol. This PI can be obtained in a nearly linear form, contrary to the endcapped PI prepared in NMP, where poly(amic acid) initiated branching cannot be totally avoided.

CONCLUSIONS

Polyimides based on 3,3',4,4'-biphenyldicarboxylic dianhydride (BPDA) and 'even numbered' aliphatic diamines with 4, 6, 8 or 10 methylene groups readily crystallize from the melt at a cooling rate of $10^{\circ}\text{C min}^{-1}$, contrary to the corresponding PIs based on 'odd numbered' diamines (7 and 9 methylene groups).

The crystallization from the melt is facilitated if branching and crosslinking reactions in the melt are limited by blocking the amine endgroups, and most perfect crystals seem to be obtained for blocked, predominantly linear PIs prepared in *m*-cresol. For the PIs synthesized in NMP, a branched or even slightly crosslinked architecture cannot be avoided, since the amine blocking reaction is applied to already branched polymers containing latent amines, which are set free and regenerate branching at elevated temperatures. These non-linear PIs clearly exhibit a disturbed crystallization behaviour from the melt compared to the more linear counterparts.

The endcapped polyimide based on BPDA and 1,8-diaminooctane seems to have the optimum balance with respect to processability (thermally stable up to approximately 375°C , T_m around 300°C) and crystallizability.

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