Investigation of polyimides containing naphthalene units: 1. Monomer structure and reaction conditions

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A series of novel polyimides with naphthalene units in the chain has been synthesized. The polyimides were prepared from 1,3- and 1,4-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene (III) and six diamines in *m*-cresol in the presence of various catalysts. The influence of monomer structure and the reaction conditions on polymer properties were investigated.

(Keywords: polyimides; naphthalene; dianhydride)

INTRODUCTION

Among the heterocyclic polymers, polyimides have remarkable high temperature resistance and good mechanical and electrical properties, but in most cases they are insoluble in organic solvents. A number of methods, including incorporation of flexible or non-symmetrical linkages in the backbone or using monomers with bulky substituents[1,2], have been used to improve their solubility while maintaining reasonably high temperature characteristics. In this study we used dianhydrides with carbonyl linkages which should lower polymer chain rigidity and naphthyl groups which should preserve the thermal stability of the polymer. The dianhydrides were used for the synthesis of soluble poly(naphthoylenebenzimidazoles)[3] and we expected soluble polyimides to be produced as well. A series of polyimides was prepared and the relationship between monomer structure and polymer properties was investigated. Also the influence of reaction conditions and catalysts on polymer viscosity was studied.

EXPERIMENTAL

Measurements

The i.r. spectra were recorded on a Specord M80 spectrophotometer. The reduced viscosities were measured in an Ubbelohde viscometer. The t.g.a. thermograms were recorded using a Q 1500D MOM Paulik and Erdey derivatograph. For the elemental analyses a 240C Perkin Elmer analyzer was used.

Materials

Terephthaloyl chloride and isophthaloyl chloride (Fluka) were recrystallized from n-hexane. Amines (Merck) and acenaphthene (Sojuzchim) were used without further purification as laboratory reagent grade chemicals. Solvents were distilled in the usual manner.

Anhydrides

The anhydrides were prepared[3] by a three-step reaction (*Scheme 1*). The first step was Friedel–Crafts acylation of acenaphthene to aryloyldiacenaphthenes (I), the second step was oxidation of aryloyldiacenaphthene to tetraacids (II) and the third was the dehydration of tetraacid to dianhydrides (III).

4,4′-Terephthaloyldiacenaphthene

In a flask fitted with a stirrer terephthaloyl chloride (20.3 g, 0.1 mol), dry aluminium chloride (28 g, 0.21 mol) and tetrachloroethane (250 cm^3) were placed, and then acenaphthene (0.84 g, 0.2 mol) in tetrachloroethane (250 cm^3) was added dropwise with simultaneous cooling (to maintain a temperature of 0°C) and stirring. The reaction was carried out for 6 h and the temperature was gradually increased to room temperature. The mixture was poured into ice, the organic layer was separated, washed with water and the product was precipitated using methanol. The precipitate was washed with methanol and then with boiling methylene chloride. The product obtained was 4,4′-terephthaloyldiacenaphthene (26 g, yield 59%); m.p. 240.5–242.5°C; C 87.03, H 4.91, O 8.06% (calculated C 87.67, H 5.02, O 7.3%).

4,4′-Isophthaloyldiacenaphthene

This compound was obtained by the procedure described above using isophthaloyl chloride (yield 57%); m.p. 189–190°C; C 87.13, H 4.97, O 7.9% (calculated C 87.67, H 5.02, O 7.3%).

1,4-Bis(1,8-dicarboxylic acid [or anhydride]-4-naphthaloyl)benzene

To a flask charged with 4,4′-terephthaloyldiacenaphthene (26 g, 0.059 mol) and acetic acid (520 cm^3), $Na_2Cr_2O_7$ (111 g) was added gradually. The reaction mixture was vigorously stirred and heated at the boiling point for 3 h and then poured into water (500 cm^3). The precipitate obtained was washed with water and then with acetic acid. I.r. analysis of the precipitate showed the presence of both carboxylic and anhydride groups. For complete dehydration the precipitate was boiled with acetic anhydride (60 cm^3) for 3 h. The dianhydride (22 g,

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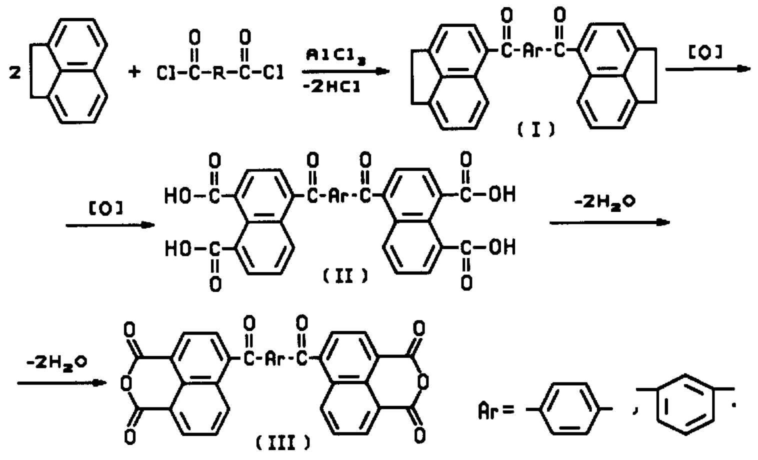


Scheme 1 Dianhydride synthesis

0.042 mol) was obtained (yield, relative to terephthaloyldiacenaphthene, 74%); C 73.80, H 2.72, O 23.48% (calculated C 73.0, H 2.67, O 24.33%).

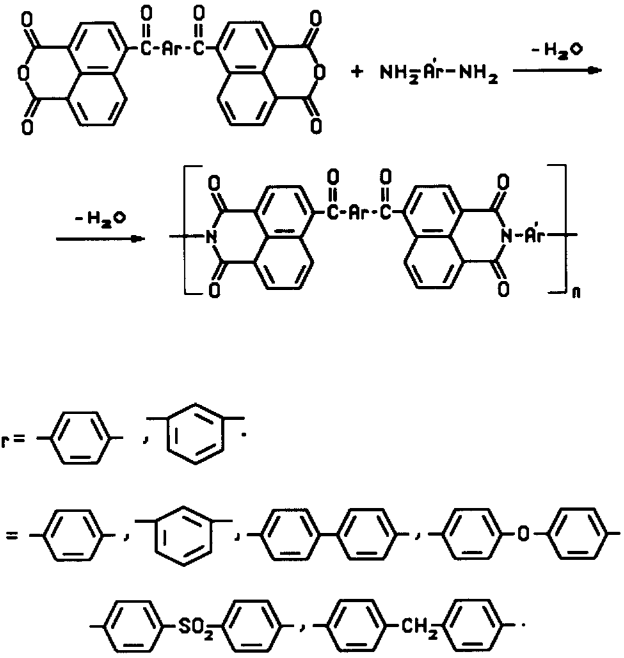
1,3-Bis(1,8-dicarboxylic acid [or anhydride]-4-naphthaloyl benzene

This compound was obtained by the procedure described above using 4,4′-isophthaloyldiacenaphthene (yield, relative to isophthaloyldiacenaphthene, 67%); C 72.25, H 2.87, O 24.88% (calculated C 73.0, H 2.67, O 24.33%).

Polymerization procedure

Dianhydride (1 mmol) and diamine (1 mmol) in *m*-cresol (10 cm^3) were placed with catalyst (2 mmol) in a flask equipped with a stirrer, reflux condenser and inlet for inert gas (argon). The mixture was stirred and heated to 190°C for 10 h, and then maintained at that temperature for 18 h. After this the solution was filtered, precipitated with methanol (200 m^3), and extracted in a Soxhlet with ethanol (*Scheme 2*).

The influence of the nature and amount of the catalyst and method and sequence of mixing was investigated (see later).



Scheme 2 Polycondensation reaction

RESULTS AND DISCUSSION

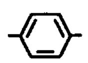
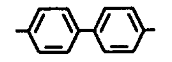
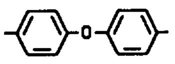
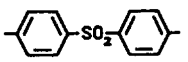
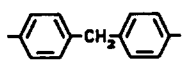
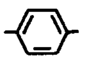
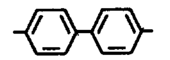
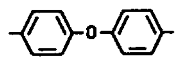
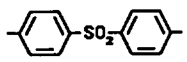
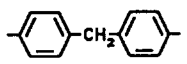
Influence of monomer structure

Table 1 presents the structures of the monomers and some properties of the polymers obtained following the procedure described above and using benzoic acid as catalyst. In the i.r. spectra of the polymers, absorption bands characteristic of aromatic polyimides for a six-membered imide ring, i.e. at 1692 and 1712 cm^{-1}, together with the band at 1660 cm^{-1} characteristic of a carbonyl group bonded to two aromatic rings, were observed. A weak absorption band seen at 3400–3500 cm^{-1} may indicate the presence of amine (chain end) or amide (uncyclized polyamic acid moieties) groups in the polymer. So we heated the polymer sample additionally at 300°C for 8 h to complete the cyclization. The i.r. spectra of the polymer samples before and after heating were the same which confirms that there are no uncyclized polyamic acid residues. Taking into consideration the influence of the catenation of the central ring in the dianhydrides on the reduced viscosity of the polyimides it may be seen that the higher values are exhibited by the polymers derived from 1,4-bis(1.8-dicarboxylic anhydride-4-naphthaloyl)benzene when the same diamines are compared. The structures of the diamines also influence the reduced viscosity of the polymers obtained. 1,4-Phenylenediamine with both dianhydrides gives polyimides having the higher viscosity than 1,3-phenylenediamine. In the series of two-ring diamines an influence of the linking group on the polymer solution viscosity was observed.

Influence of catalysts

Six-membered ring anhydrides are more stable and their reactivity towards an amine group is lower than their five-membered analogues. Hence it is necessary to use catalysts in reactions of such dianhydrides with diamines. Polyimides shown in *Table 1* were synthesized in the presence of benzoic acid (catalyst). In order to find more effective catalysts we have synthesized a series of polyimides from the dinaphthalene dianhydrides and

Table 1 Some properties of the polyimides

Monomers Dianhydride Ar (as in *Scheme 2*)	 Diamine Ar′ (as in *Scheme 2*)	Yield (%)	η_{red} (dl g^{-1})^a	Temperature of 10% weight loss in air (°C)
		93.0	0.48	450
		–	0.43	–
		84.0	0.66	435
		93.4	0.90	450
		–	0.18	500
		–	2.10	–
		91.0	0.42	470
		–	0.39	–
		87.3	0.57	450
		88.3	0.80	470
		–	0.18	485
		–	2.03	–

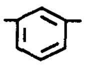
^{a}Concentration: 1 g per 100 ml in *m*-cresol, 27°C

4,4′-diaminodiphenyl ether using various catalysts. The influence of the catalysts on the reduced viscosity of the polymers is presented in *Table 2*.

The catalysts used have acidic or basic nature and include the phosphorus compounds used by Ogata and Higashi[4–7] in the synthesis of polyamides and polyesters. As can be seen, the polyimide with the lowest viscosity was obtained when condensation was carried out without catalyst. Benzoic acid is more effective as a catalyst in comparison with basic catalysts: isoquinoline, quinoline and imidazole used separately (nos 2 and 25 to nos 3, 4, 5 and 26, 27 in *Table 2*). The efficiency of the amine catalysts in increasing the polyimides reduced viscosities is in the following order: isoquinoline > quinoline > imidazole. It was observed that mixed catalysts, i.e. benzoic acid and amine catalysts give polyimides with higher reduced viscosities than when the catalysts are used separately (nos 6, 7 and 9 in *Table 2*). Polyimides 6, 7 and 9 were prepared in the presence of catalysts (2 mol of each compound with 1 mol of dianhydride). When the catalysts are used in the ratio of 1 mol of each compound to 1 mol of dianhydride (nos 8 and 10 in *Table 2*) the reduced viscosity of the polymers is almost 50% lower. Also the order the catalysts are added influences polymer viscosity. Adding isoquinoline to a reaction mixture containing dianhydride, 4,4′-diaminodiphenyl ether and benzoic acid after 9 h heating at 190°C (no. 11 in *Table 2*) gives a better result than when the order of addition is reversed (no. 12 in *Table 2*).

When isoquinoline was added to the reaction mixture of monomers and benzoic acid after heating for 9 h and then P_2O_5 was added after heating for 2.5 h, the reduced viscosity of the polymer (no. 13 in *Table 2*) was lower than that of the polymer without dehydrating agent. The addition of P_2O_5 after heating the mixture and for 2.5 h causes the decrease in the reduced viscosity (no. 23 in *Table 2*); P_2O_5 alone (no. 20 in *Table 2*) and with isoquinoline (no. 21 in *Table 2*) does not lead to polyimides with high viscosity. All the reactions were carried out in *m*-cresol except no. 24 where polyphos-

Table 2 Influence of catalysts on the polyimide reduced viscosity

No.	Dianhydride Ar (as in *Scheme 2*)	Catalyst[a]	Amount of catalyst[b]	η_{red} (dl g^{-1})[c]
1		None	–	0.26
2		BA	2	0.90
3		IQ	2	0.52
4		Q	2	0.32
5		IA	2	0.31
6		BA + IA	2 + 2	0.93
7		BA + IQ	2 + 2	1.37
8		BA + IQ	1 + 1	0.69
9		BA + Q	2 + 2	1.32
10		BA + Q	1 + 1	0.65
11		BA + IQ (0 and 9 h)	2 + 2	1.96
12		IQ + BA (0 and 9 h)	2 + 2	0.31
13		BA + Q + P_2O_5 (0 and 9 and 2.5 h)	2 + 2 + 2	0.79
14		TPP	2	0.26
15		TPP + Pyr	2 + 2	0.33
16		TPP + Q	2 + 2	0.30
17		TPP + C_2Cl_6 + Q	1.2 + 1.5 + 1.2	0.75
18		TPPO	2	0.24
19		TPPO + Q	2 + 2	0.57
20		P_2O_5	2	0.35
21		P_2O_5 + Q	2 + 2	0.34
22		BA + TPP	2 + 2	0.37
23		BA + P_2O_5 (0 and 2.5 h)	2 + 2	0.41
24		BA + Q in PPA as solvent	2 + 2	0.30
25		BA	2	0.80
26		IQ	2	0.52
27		IA	2	0.28

[a] BA, benzoic acid; IA, imidazole; IQ, isoquinoline; Q, quinoline; Pyr, pyridine; TPP, triphenylphosphine; TPPO, triphenylphosphine oxide; PPA, polyphosphoric acid

[b] Unit: mol on 1 mol of dianhydride

[c] Concentration: 1 g per 100 ml in *m*-cresol, 27°C

phoric acid was used as a solvent. In this case the polymer also exhibits low viscosity.

Ogata and Higashi used phosphorus compounds as catalysts in reactions of acids with amines and alcohols. We would like to prove if these catalysts act in the case of anhydrides. It was found that polyimides obtained in the presence of triphenylphosphine (no. 14 in *Table 2*) or triphenylphosphine oxide (no. 18 in *Table 2*) have the same reduced viscosity as in the absence of catalyst. Using mixed catalysts of phosphorus compounds with amine catalysts such as quinoline (nos 16 and 19 in *Table 2*) or pyridine (no. 15 in *Table 2*) causes little increase of the viscosity of the polymers; the value increases only to that observed when amine catalyst is used alone. Higher viscosity of the polymer was obtained when the reaction was carried out in the presence of triphenylphosphine, quinoline and hexachloroethane together (no. 17 in *Table 2*).

In conclusion, the following conditions influence the reduced viscosity of polyimides: nature of the catalysts; mole ratio of the catalyst and dianhydrides; and addition order of the catalysts.

The most effective catalyst used was benzoic acid (2 mol) with dianhydride (1 mol) added at the beginning of the reaction, with isoquinoline added after a few hours. All the results presented are important from a technological point of view and also give some information which may lead to reaction mechanisms for the various catalysts. Further work is in progress and proposed reaction mechanisms will be presented in due course.

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