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SYNTHESIS AND PROPERTIES OF POLYAMIDES, POLYIMIDES, AND A POLYAMIDE-IMIDE BASED ON TRIMETHYLENE GLYCOL-DI-*p*-AMINO BENZOATE

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ABSTRACT

New polyamides, polyimides, and a polyamide-imide containing ester linkages were prepared by the reaction of trimethylene glycol di-*p*-aminobenzoate with terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride, pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, and trimellitoyl chloride. The low temperature solution and interfacial polymerization techniques were utilized to prepare the above-mentioned polymers. The polymers thus prepared were found to be soluble in solvents like DMAC and DMSO and had inherent viscosities in the 0.15–0.60 range. The polyimides prepared formed transparent and flexible films.

INTRODUCTION

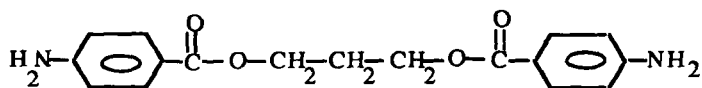
Aromatic polyamides, polyimides, and polyamide-imides have shown excellent thermal stability [1, 2] but their utilization seems to have been limited because of their insolubility in common solvents [3]. It has generally been accepted that the introduction of flexible linkages in aromatic polymer chains lowers the glass transition temperature and improves the solubility and other processing characteristics of the polymers [4–6]. Since trimethylene glycol di-*p*-aminobenzoate (TMAB) has the flexible linkage, the introduction of such a linkage in the polymer would improve polymer solubility. TMAB was first prepared by Baron et al. [7], and has been used as a curing agent by a number of investigators.

In the present paper we report the synthesis of new polyamides, polyimides, and a polyamide-imide containing ester linkages from trimethylene glycol di-*p*-amino-benzoate (TMAB) and terephthaloyl chloride (TCP), isophthaloyl chloride (IPC), adipoyl chloride (APC), pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic dianhydride (BTDA), and trimellitoyl chloride (TMC) by using low temperature polycondensation techniques and the properties of the resulting polymers.

EXPERIMENTAL

Materials

PMDA and BTDA were recrystallized from acetic acid. TCP and IPC were recrystallized from *n*-hexane. NMP, cyclohexanone, DMAC, and pyridine were purified by distillation. TMC was recrystallized from benzene and hexane. TMAB, obtained from Polysciences, Inc., was recrystallized from ethanol. All other materials used were purified before use.



TMAB

Viscosity measurements were made at 30°C by using a Ubbelohde viscometer.

Synthesis

Synthesis of Polyamides

Method 1: Solution Polymerization. In a three-necked round-bottomed flask equipped with stirrer, condenser, thermometer, and nitrogen gas inlet were placed TMAB (0.02 mol), NMP (200 mL), and calcium chloride (10 g). The reaction mixture was stirred and cooled to 0°C under an inert atmosphere. Dichloride (0.02 mol) was added in one portion and stirred rapidly at 0°C for 2 h.

After completion of the reaction, the polymer was recovered by precipitation by pouring the solution into water. The polymer was filtered, washed, and dried under vacuum at 60°C.

Method 2: Interfacial Polymerization. TMAB (0.01 mol) was placed in a high speed reactor followed by sodium hydroxide solution. The solution was stirred

for 10 min. A solution of dichloride in cyclohexanone (0.01 mol in 80 mL) was added and the whole solution was stirred rapidly for 20 min. The polymer formed was filtered, washed with ether, and dried at 60°C under vacuum.

Synthesis of Polyimides (Polyamic Acid)

TMAB (0.01 mol) and DMAC (35 mL) were placed in a three-necked round-bottomed flask equipped with condenser, thermometer, and nitrogen gas inlet. This solution was stirred on a magnetic stirrer and cooled to 0°C. Dianhydride (0.01 mol) was added in one portion and then the whole solution was stirred for 24 h at room temperature.

After completion of the reaction, the polymer was recovered by precipitation by pouring the resulting viscous solution into water. The polymer was filtered, washed with water, and dried under vacuum at 60°C.

Synthesis of Polyamide-Imide

TMAB (5 mmol) and DMAC were placed in a three-necked round-bottomed flask equipped with condenser, thermometer, and nitrogen gas inlet. This solution was stirred under a nitrogen atmosphere and cooled to -5°C. TMC (5 mmol) was added in one portion and the whole solution was stirred for 20 min. After this, pyridine (2 mL) was added dropwise at a rate that kept the temperature below 5°C. The reaction was continued overnight with stirring at room temperature.

After completion of the reaction, the polymer was recovered by precipitation by pouring the solution into water. The polymer was filtered, washed, and dried under vacuum at 60°C.

RESULTS AND DISCUSSION

Three new polyamides (Scheme 1) were prepared by the polymerization of TMAB with TPC, IPC, and APC by using both the solution and interfacial methods. The results obtained are given in Table 1.

Three new polyamides (Scheme 1) were prepared by the polymerization of TMAB with TPC, IPC, and APC by using both the solution and interfacial methods. The results obtained are given in Table 1.

The polyamide prepared from TMAB and TPC by the solution method was not soluble in polar solvents but was soluble in concentrated sulfuric acid. The same polymer prepared by interfacial polymerization was found to be partially soluble in DMAC, and hence low temperature interfacial polymerization was used to synthesize these relatively new polyamides. The polyamide prepared from TMAB and IPC was

TABLE 1. Synthesis of Polyamides

No.	Diacid chloride	Diamine	Method used	Yield, %	$[\eta]_{inh}$, dL/g
PA-1	TPC	TMAB	1	100	0.14 ^a
PA-2	TPC	TMAB	2	90	0.2 ^{a,b}
PA-3	IPC	TMAB	2	70	0.26 ^c
PA-4	APC	TMAB	2	60	0.11 ^a

^a0.5% solution in 96% H₂SO₄ at 30°C.

^bSoluble in DMAC, but the solution was turbid.

^c0.5% solution in DMAC at 30°C.

TABLE 2. Synthesis of Polyimides (polyamic acid)^a

No.	Dianhydride	Diamine	Yield, %	$[\eta]_{inh}$, dL/g ^b
PI-1	PMDA	TMAB	100	0.68
PI-2	BTDA	TMAB	100	0.56

^aIn DMAC at 0°C.

^b0.5% solution in DMAC at 30°C.

TABLE 3. Synthesis of Polyamide-Imide^a

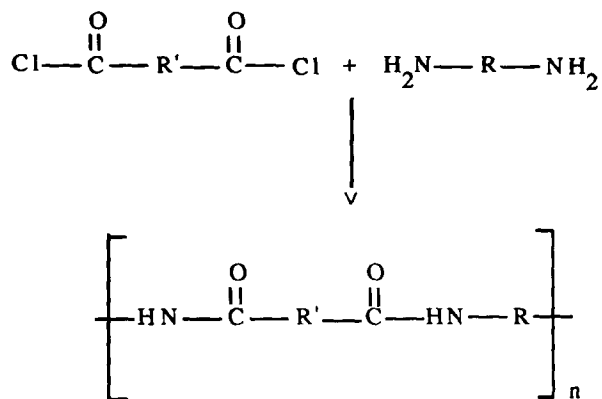
No.	Chloride	Diamine	Yield, %	$[\eta]_{inh}$, dL/g ^b
PAI-1	TMC	TMAB	100	0.42

^aIn DMAC.

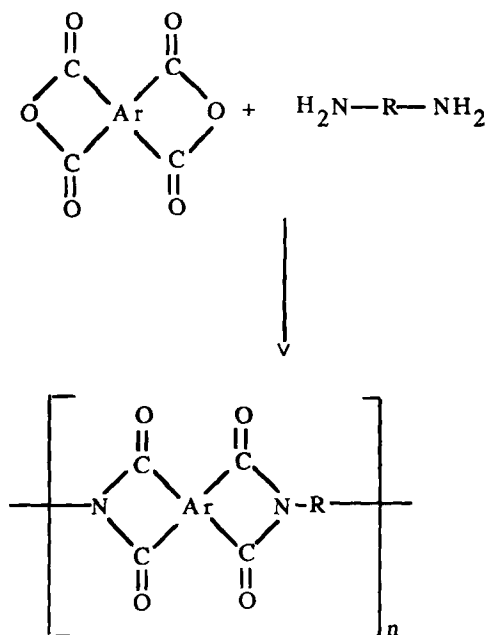
^b0.5% solution in DMAC at 30°C.

soluble in DMAC but that from TMAB and APC was insoluble in polar solvents. The inherent viscosities of these polymers were determined in concentrated sulfuric acid and DMAC, and they were in the 0.1–0.26 dL/g range, indicating that they are low molecular weight polymers.

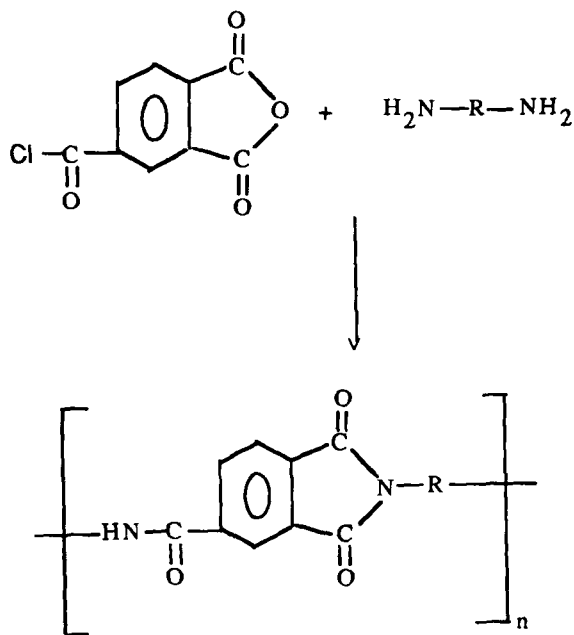
On the other hand, the polyimides (Scheme 2) prepared from TMAB with PMDA and BTDA were completely soluble in DMAC. The polymerization proceeded homogeneously. Since these two polymers were soluble in DMAC, the inherent viscosities



SCHEME 1.



SCHEME 2.



SCHEME 3.

were determined in DMAC and were found to be around 0.7 dL/g. The polymers obtained were in high yields (100%), as can be seen in Table 2.

The polyamide-imide (Scheme 3) prepared from TMAB and TMC was also soluble in DMAC, had 100% yield, and 0.4 dL/g inherent viscosity (Table 3).

Imidization of Polyamic Acid

The films of polyimides and polyamide-imide with inherent viscosities of more than 0.4 dL/g could be obtained by casting the polymer (polyamic acid) solution in DMAC on a clean glass plate using a doctor blade technique and heating at $150^\circ C$ under vacuum for 3 h to achieve complete imidization. The films obtained were transparent and flexible.

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