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Synthesis and characterization of alternating copolyimides containing aliphatic spacers*

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SUMMARY

Alternating copolyimides and homopolyimides of pyromellitic dianhydride and benzophenonetetracarboxylic dianhydride containing aliphatic spacers have been synthesized by the solution polycondensation of N,N-bis(isocyanatoalkyl) - 1,2,4,5 - benzenetetracarboxylic - 1,2:4,5 - diimides and N, N-bis(isocyanatoalkyl) - 3,3',4,4' - benzophenonetetracarboxylic - 3,3': 4,4' - diimides with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) in dimethylacetamide. These polyimides are semicrystalline, thermally stable and soluble in polar aprotic solvents with inherent viscosities in the range 0.29 - 0.62 dL/g in m-cresol.

INTRODUCTION

Polymers are progressively invading areas of applications hithertofore dominated by metals or ceramics. One such area is thermally stable polymers. However, these polymers have poor solubility and processability. Various methods have been used to improve thermal stability and modify other physical properties. Copolymer synthesis is one of such methods. Various random copolyimides from different diamines and a dianhydride have been synthesized and employed for different applications [1-3]. The extent to which the properties could be modified depends upon the extent and type of the structural unit incorporated [4]. However, strictly alternating copolyimides of two dianhydrides with a diamine/diisocyanate have not been reported to our knowledge.

In our quest for the synthesis and application of novel diisocyanates, we have synthesized diisocyanates containing oxyethylene [5], imide [6], sulfone [7] and azomethine [8] moieties, and utilized them for the synthesis of various polymers . The synthesis of aliphatic diisocyanates containing built-in imide moiety [6] has given rise to a unique method for the preparation of alternating copolyimides of two different dianhydrides, e.g., PMDA and BTDA, separated by aliphatic spacers.

The present paper describes the synthesis of homopolyimides and alternating copolyimides of PMDA and BTDA by the reaction of imide-containing aliphatic diisocyanates with the same or different dianhydrides. The polyimides obtained

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**To whom offprint requests should be sent have been characterized by IR spectroscopy, viscosity measurements, X-ray and thermal studies.

EXPERIMENTAL

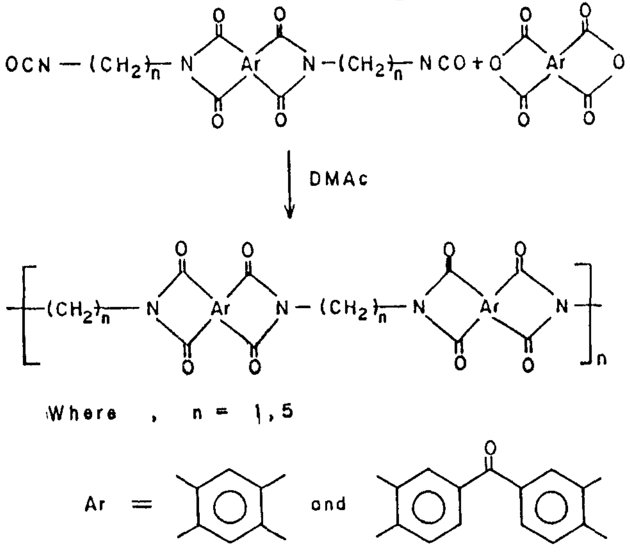
The diisocyanates N,N-bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and N,N-bis(isocyanatoalkyl)-3,3´,4,4´- benzophenonetetracarboxylic- 3,3´:4,4´-diimides were prepared by the procedure reported elsewhere [6].

Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride and sublimed in vacuum prior to use. Dimethylacetamide (DMAc) was kept over P_2O_5 and distilled prior to use. All other materials were of reagent grade and were used as received.

Synthesis of polyimides (I - VI).

Polyimides were prepared by the solution polycondensation reaction of the imide-containing diisocyanates with PMDA and BTDA (Scheme 1 and Table 1). In a 100 mL three necked flask fitted with a thermowell, nitrogen gas inlet, and $CaCl_2$ guard tube, was placed a solution of the diisocyanate (0. 01 mol) in 10 mL DMAc. To this solution at 0 °C was added the dianhydride (0.01 mol) in small portions over 1 h. The reaction mixture was stirred at this temperature for 30 min and then heated to 40 °C at which temperature it was held for 2.5 h. Then the temperature was gradually raised to 90 °C. Finally the reaction mixture was heated at 130 - 140 °C for 24 h.

The reaction mixtures were then poured into a large excess of methanol. The polymers that precipitated were isolated by filtration. These were washed with more methanol and dried at 150 °C under reduced pressure for 3 h.



SCHEME 1 SYNTHESIS OF POLYIMIDES (I-VI)

Table 1

Preparation of Polyimides (I - VI) and their inherent viscosities.[a]

Polyimides	Diisocyanates[b] (0.01 mol) Ar	n	Dianhydrides (0.01 mol)	Inherent viscosities η_{inh} (dL/g)
I	PMDA	1	PMDA	0.42
II	PMDA OR BTDA	1	BTDA OR PMDA	0.44
III	BTDA	1	BTDA	0.29
IV	PMDA	5	PMDA	0.62
V	PMDA OR BTDA	5	BTDA OR PMDA	0.49
VI	BTDA	5	BTDA	0.36

[a] Measured at a concentration of 0.5 g/dL in m-cresol at 30 °C.

[b] As per Scheme 1.

Table 2

Solubility of Polyimides.

Polyimides	DMSO	DMF	DMAc	NMP	HMPA	m-cresol	H_2SO_4
I	-	-	+	-	-	+	++
II	+	+	+	+	+	+	++
III	+	+	+	+	+	+	++
IV	+	+	+	+	+	+	++
V	+	+	+	+	+	+	++
VI	+	+	+	+	+	+	++

++ Highly soluble; + Soluble on standing; - insoluble

RESULTS AND DISCUSSION

Copolymers have gained importance because of their actual and potential applications in many fields. The synthesis of copolyimides of two different diamines (in different ratios) with a dianhydride to modify the thermal and other physical properties of the polymers has been documented [1-3]. These are randon copoyimides. However, strictly alternating polyimides of two different dianhydrides, say, PMDA and BTDA, separated by aliphatic spacers are not reported to our knowledge. In the present paper four homopolyimides and two alternating copolyimides containing aliphatic spacers have been synthesized as illustrated in Scheme 1 with a view to study the effect of alkyl spacers and copolyimide structure on thermal and other properties of the copolyimides. Inherent viscosities of these polyimides was determined in m-cresol at a concentration of 0.5 g/dL at 30 °C which varied from 0.25 - 0.62 dL/g (Table 1). The IR spectra of all polyimides showed characteristic absorption bands at 1780

cm^{-1} and 1745 cm^{-1} (imide-I), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III) and 720 cm^{-1} (imide-IV).

Unlike fully aromatic polyimides, these copolyimides have comparatively better solubility in various polar solvents such as , DMAc, DMF, NMP, HMPA, DMSO, m-cresol, and H_2SO_4 (Table 2). The solubility of copolyimides increases with the length of the aliphatic spacer. BTDA based polyimides (III and VI) have better solubility than PMDA based polyimides (I and IV). Similarly, copolyimides have better solubility than homopolyimides.

The X-ray diffractograms of the polyimides (I - VI) were determined by the powder method using nickel-filtered CuK_α radiations on a Philips PW-1730 Unit (Fig. 1). These indicate that the polyimides are semicrystalline in nature. Polyimides derived from PMDA have higher crystallinity than those derived from BTDA. Crystallinity decreases with the increase in the length of the aliphatic spacer. Polyimide I was most crystalline while polyimide VI was most amorphous. All other polyimides were intermediate in crystallinity.

Thermogravimetric analysis (TGA) of the polyimides was determined on a Netzsch 409 Thermal Analyzer in nitrogen

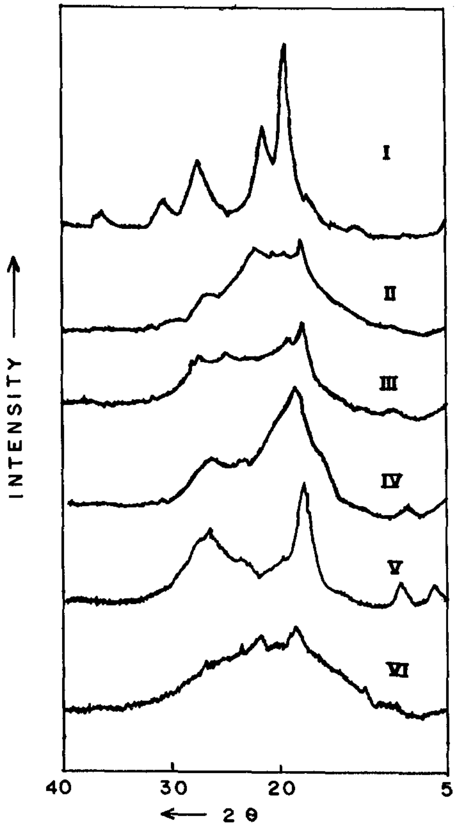


Fig. 1 XRD CURVES OF POLY-IMIDES I-VI

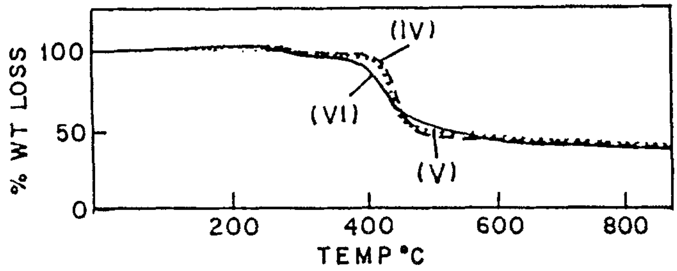


Fig. 2 TGA CURVES OF POLYIMIDES (IV, V, VI) IN NITROGEN

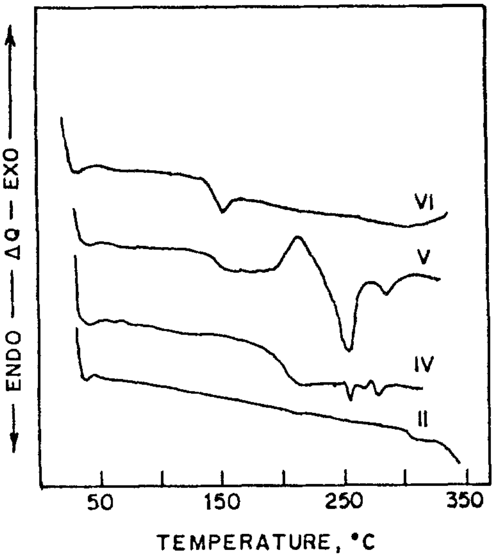


Fig. 3. DSC CURVES OF POLYIMIDES (II, IV, V AND VI)

AT A HEATING RATE OF 20°C/min

at a heating rate of 10 ^{o}C / min. All polyimides showed a similar pattern of decomposition without any weight loss below 335 ^{o}C . TGA curves of representative polyimides are given in Fig. 2. Thermal characteristics, such as, initial decomposition temperature (IDT), T_{10}, T_{30}, T_{50}, and T_{Max}, i.e., temperatures at 10 %, 30 %, 50 % and maximum decomposition are incorporated in Table 3. T_{Max} was determined from the DTG curves.

The glass transition temperatures (Tg) of some polyimides were determined on Mettler DSC 30 S (Fig.3)

Table 3
Thermal Characteristics of Polyimides (I - VI) in Nitrogen.[a]

Polyimides ->	I	II	III	IV	V	VI
Tg	-	302	-	201	150	148
IDT	371	360	349	347	340	335
T_{10}	461	459	432	452	396	384
T_{30}	600	477	460	473	448	428
T_{50}		509	478	500	506	485
T_{Max}		490	473	483	460	423

[a] All temperatures in °C.
IDT - Initial decomposition temperature.
T_{10}, T_{30}, T_{50}, and T_{Max} are temperatures corresponding to 10 %, 30 %, 50 %, and maximum decomposition, respectively.

and the values are incorporated in Table 3. The Tg values were high for polyimides containing short aliphatic spacers. The polyimides derived from PMDA exhibited higher Tg values than those derived from BTDA. The DSC curve of Copolyimide V shows probable existence of cold crystallization.

CONCLUSIONS

Strictly alternating copolyimides of two different dianhydrides separated by aliphatic spacers can be prepared by the reaction of imide containing diisocyanates with different dianhydrides. Thermal and other physical properties of these copolyimides are intermediate between the two sets of homopolyimides. These polyimides have good solubility in many polar solvents and have good thermal stability.

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