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PART I

Synthesis and New Materials for Thin Films

ORGANO-SOLUBLE, SEGMENTED RIGID-ROD POLYIMIDES: SYNTHESIS AND PROPERTIES

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ABSTRACT

Several segmented, rigid-rod polyimides have been prepared that are soluble in organic solvents in their fully imidized form. The polymers were prepared from commercial dianhydrides and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB). Their intrinsic viscosities ranged from 1.0 to 4.9 dL/g. Tough, colorless films could be cast from m-cresol solutions at 100°C. The polymers had glass transition temperatures (Tgs) above 275°C and displayed outstanding thermal and thermo-oxidative stability. Fibers were prepared from the 3,3',4,4'-tetracarboxybiphenyl dianhydride (BPDA) based polymers that had moduli of 130 GPa and tensile strengths of 3.2 GPa. The thermal expansion coefficients and dielectric constants of thin films (20-25 μm) of the polymers were as low as -2.40×10^{-6} and 2.5, respectively.

INTRODUCTION

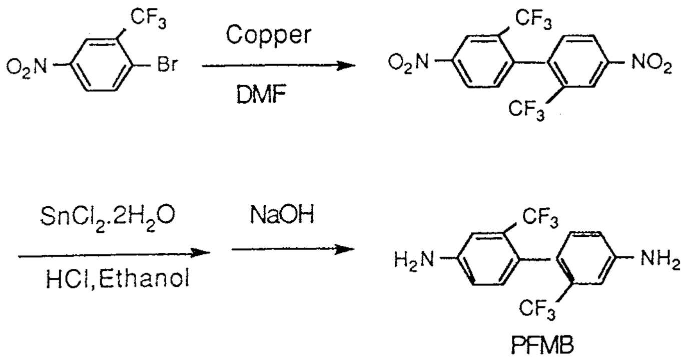
This research was part of an ongoing program aimed at the synthesis of soluble, rigid-rod or segmented rigid-rod polyimides[1-3]. Such polymers are sought for use as high modulus fibers and reinforcing components in molecular composites[4]. It is also anticipated that the polyimides that contain rigid-rod segments will prove useful as composite resins and in microelectronic applications.

The approach described in this paper involved the polymerization of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB). The incorporation of this moiety in aromatic polyamides has been shown to dramatically affect their properties[5]. The substituents in the 2- and 2'-positions of the aromatic rings force them into a noncoplanar conformation, which decreases the polymers' crystallinity and enhances their solubility. The twisted conformation also interrupts the conjugation along the backbone and, thus, reduces or eliminates absorption of visible radiation. It was postulated that similar effects would be observed in polyimide systems. In fact, it was felt that the all-para-linked, rigid segments would enhance the polymers' mechanical properties, in particular the moduli. The high chain rigidity was expected to result in very low thermal expansion coefficients[6]. The perfluoromethyl groups were also expected to enhance other desirable properties such as thermal stability while decreasing water absorption and permittivity.

RESULTS AND DISCUSSION

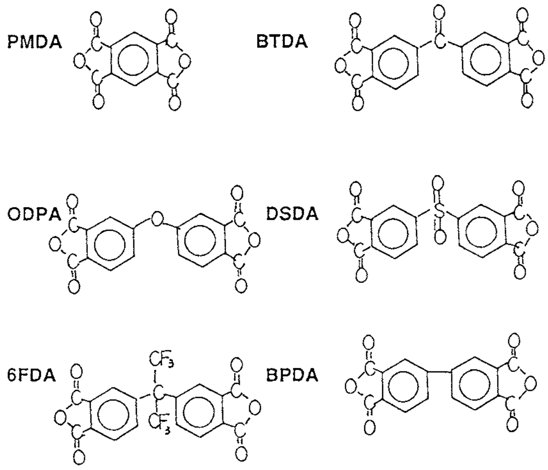
Monomer Synthesis

The TFMD was synthesized from 2-bromo-5-nitrobenzotrifluoride by the described procedure[6].



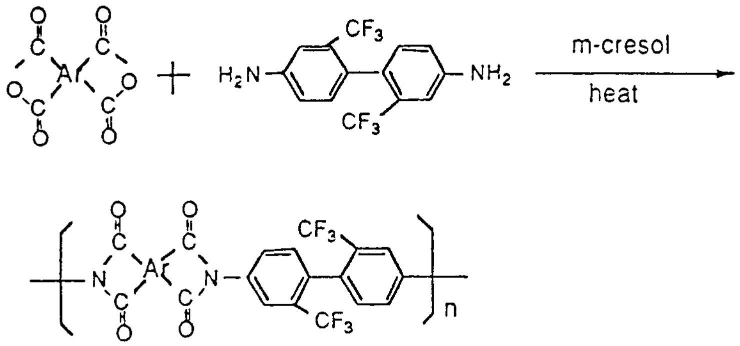
The following dianhydrides were purchased from commercial sources and were heated at 150 to 180°C under reduced pressure overnight prior to use.

Dianhydrides Used in Polymerization



Polymerizations

The polymerizations of TFMB with the dianhydrides were carried out in refluxing m-cresol containing isoquinoline (2%, w/v) with a solids concentration of 10% (w/v). Under these conditions the intermediate poly(amic acids) spontaneously cyclized to the corresponding polyimides. The water of imidization that was generated was removed by distillation.



With the exception of the polymer prepared from PMDA, all of the polymers remained in solution throughout the polymerization. When the viscous solutions of the polymers prepared from BTDA, 6FDA, and BPDA were cooled below 80°C, they set to an opaque gel-like structure. This phenomenon was reversible as the clear, free-flowing solutions could be regenerated by heating to 80 to 100°C. The gellation phenomenon could be delayed or prevented by diluting the reaction mixtures with m-cresol. All of the polymers were isolated by precipitation in methanol.

In an attempt to obtain a more rigid polyimide, an alternating copolymer was prepared from BPDA and pyromellitic dianhydride (PMDA). Thus, BPDA was treated with a 2:1 molar excess of TFMB to afford a soluble oligomer (7), which was polymerized with an equivalent amount of PMDA. In comparing copolymer 8 with the homopolymer prepared from BTDA, one can see that the length of the rigid segment between the biphenyl moieties has been increased. Thus, the copolymer contains longer rigid-rod segments.

Polymer Properties

The polymers' solubility in solvents other than m-cresol depended on their structure (Table 1). Their intrinsic viscosities in m-cresol at 30°C varied from 1.0 to 4.9. Tough, colorless films could be cast from m-cresol solutions at 100°C. The UV-visible spectra of these films showed 85-90% transmittance above 400 nm.

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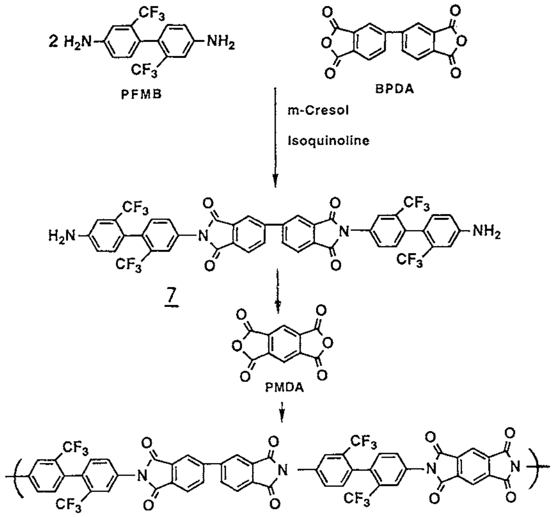

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Table 1. Polyimide Properties

Polyimide	Dianhydride Used	$[\eta]^a$ (dL/g)	Tg^b (°C)	TGA^c (°C)	$Solvents^d$
1	PMDA	INS	ND	555	INS
2	BTDA	1.6	ND	550	MC
3	ODPA	1.1	275	570	MC,NMP,TCE
4	DSDA	1.0	320	540	MC, NMP
5	6FDA	1.9	320	530	MC,NMP,TCE
6	BPDA	4.9	ND	600	MC
8	BPDA/PMDA	3.0	ND	600	MC

a. Intrinsic viscosity determined in *m*-cresol at 30°C.
b. Mid-point of change in slope on DSC thermogram obtained with a heating rate of 20°C/min.
c. Temperature at which a 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10°C/min.
d. INS=insoluble; MC-*m*-cresol; NMP=N-methylpyrrolidone; TCE=*sym*-tetrachloroethane.

The polymers prepared from ODPA, DSDA and 6FDA displayed glass transition temperatures (Tgs) of 275°C, 320°C, and 320°C, respectively (Table 1). The Tgs of the other polymers could not be detected by Differential Scanning Calorimetry (DSC). The Thermal Gravimetric Analysis (TGA) thermograms of the polymers showed 5% weight losses between 530 and 600°C in air and between 515 and 600°C in nitrogen.

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Samples of the polymers prepared from ODPA and 6FDA were compression molded at 420°C and 2500 psi. The flexture moduli of these materials were 3.70 and 4.05 GPa, respectively. Their fracture energies (G_{IC}) were 0.68 and 0.89 kJ/m^2.

The thermal expansion coefficients (α) of unoriented thin films (20 μm) of the homopolymer (6) and the copolymer (8) prepared from BPDA were determined as a function of stress from 50 to 200°C (Figure 1). Extrapolation of the linear regression to zero stress gave an α of $5.43x10^{-6}$ for the homopolymer and an α of $-2.40x10^{-6}$ for the copolymer.

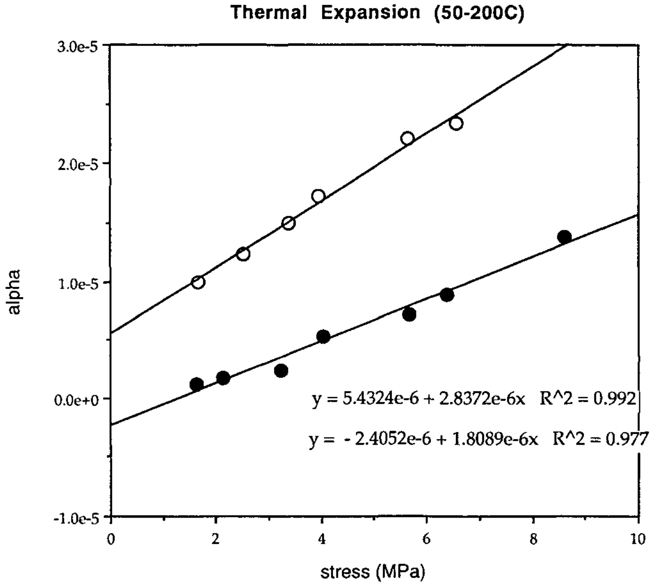

Figure 1. Thermal expansion coefficient (50% to 200°C) vs stress for thin (25 μm) films of polymer 6 (-O-) and copolymer 8 (-●-).

The dielectric constants of thin films (25 μm) of the homopolymer and copolymer, which were determined according to ASTM D-150, were 2.6 and 2.5, respectively. The dielectric constant temperature dependence at different frequencies was determined for a thin film of the homopolymer using DEA (Figures 2 and 3). The high permittivity observed in the first heating cycle was due to residual solvent. The subsequent cooling cycles and second heating cycles were almost identical. The permittivities below 200°C were almost constant.

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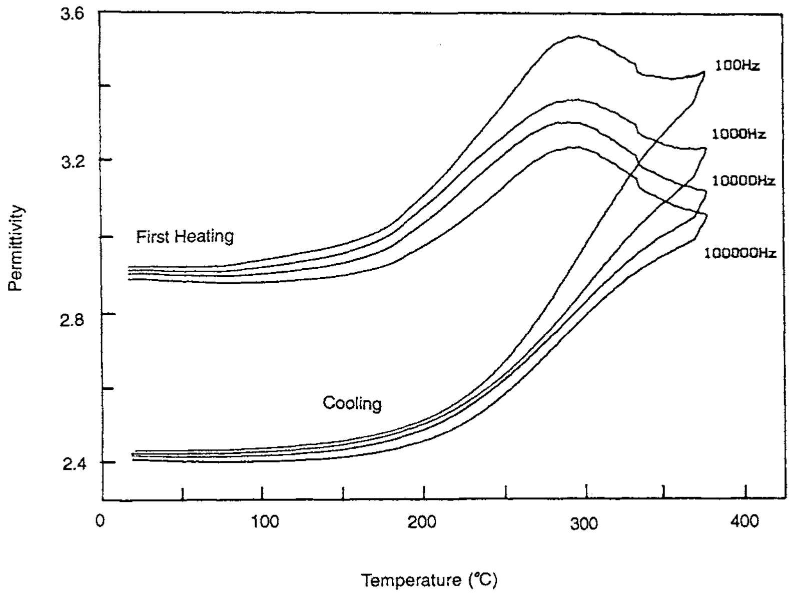

Figure 2. Permittivity at different frequencies vs temperature for a thin (25 μm) film of polymer 6.

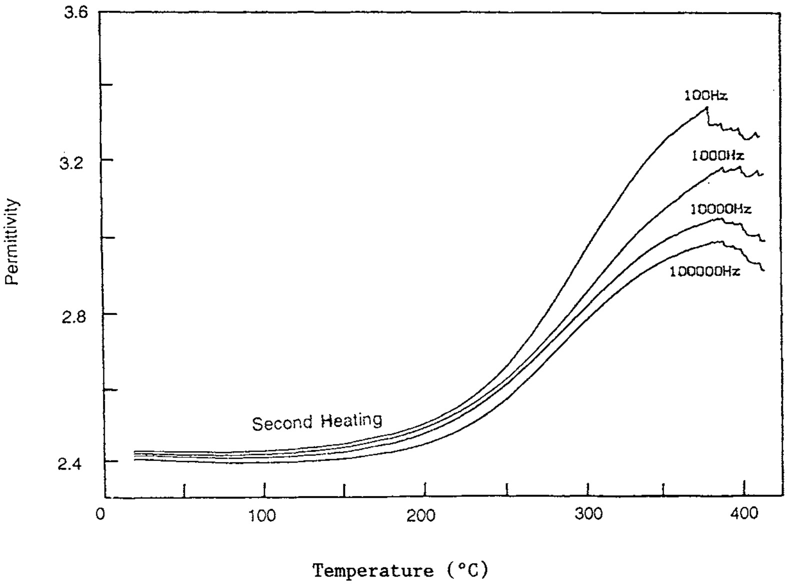

Figure 3. Permittivity at different frequencies vs temperature for a thin (25 μm) film of polymer 6.

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Liquid-Crystalline Phenomena

The gel-like structures of the polymers in m-cresol were examined microscopically through a cross-polarizer. The gel of the polymer prepared from 6FDA contained liquid-crystalline spherulites. This behavior was exibited previously by gels of a rigid-rod polyimide[7]. The gels of the polymers prepared from BTDA and BPDA were highly birefringent, but did not possess any apparent textures. When the BPDA-based gel was annealed at 90°C, it developed a Schlieren texture typical of a nematic-like phase.

Fiber Spinning Study

A study was carried out to determine the conditions necessary for the preparation of fibers of the polyimide based on BPDA. Fibers were successfully spun from hot m-cresol solutions of the polymer. These fibers were subsequently drawn at elevated temperatures. The tensile strength and tensile moduli of the fibers were 3.2 GPa and 130 GPa, respectively[8].

Acknowledgment

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