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Soluble High-Temperature Polyterephthalamides

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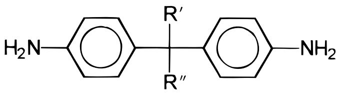
Introduction. Aramids represent a class of high-temperature polymers usually formed by the reaction of aromatic diamines and aromatic diacylchlorides. The high-temperature properties of these polymers make them useful as high-strength, high-modulus fibers, high-performance plastics, and adhesives. There is much interest in such new high-temperature materials for aerospace and microelectronics applications where materials must be able to withstand harsh manufacturing/operating conditions. However, many of the favorable high-temperature properties of aramids also cause difficulties in their processing due to their low solubility in appropriate organic solvents. Polyterephthalamides, in particular, have been reported to be especially insoluble, except in undesirable solvents such as concentrated sulfuric acid or amide solvents containing added inorganic salts.[1] There have been considerable efforts to synthesize organic-soluble aramids, by the introduction of bulky substituents along the polymer chain[2], the introduction of solubilizing linkages,[3] and the use of *N*-alkylation or *N*-arylation of the amide group (see review with references).[4]

Missing from the vast number of aramid materials that have been studied were all para polyterephthalamides derived from terephthalic acid and diamines with the following general structure:



where RN and RO are alkyl, perfluoroalkyl, or aryl groups. We found that when terephthaloyl chloride was reacted with various diamines with the general structure shown above, in solvents such as *N*-methylpyrrolidinone (NMP), in the presence of pyridine, high-molecular-weight polymers were formed. These polymers were isolated by precipitation into methanol and, surprisingly, could be redissolved in NMP and processed into thin films or fibers from solution.

Experimental Section. 1. Materials. Terephthaloyl chloride (Aldrich) was sublimed prior to use. 2,2′-Bis(4-aminophenyl)hexafluoropropane (**Ia**), 2,2′-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**Ic**). and 4,4′-(9-fluorenylidene)dianiline (**Id**), all from Chriskev Chemical, were sublimed twice before use. 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoromethane (**Ib**) was prepared according to a literature procedure.[5] All other materials were commercially available and used as received unless otherwise noted.

2. Characterization. NMR spectra were recorded on an IBM WP 250 spectrometer operating at 250.1 MHz (^{1}H). Polymer films for thermal analysis were cast from NMP at concentrations between 15 and 30% solids. Glass transition temperatures, taken as the midpoint of the change in slope of the base line, were measured on a DuPont DSC 1090 instrument at a heating rate of 10 °C/min. Thermal gravimetric analyses (TGA) on the polymer samples were conducted on a Perkin Elmer model TGA-7 at a heating rate of 10 °C/min or isothermally at 400 °C in a nitrogen atmosphere. Intrinsic viscosity measurements were determined by using a Cannon-Ubbelohde dilution viscometer in NMP at 30 °C. Refractive index values were obtained on 2−3 μm thick samples spun-coated onto quartz wafers which were then cured to 350 °C. Measurements were made on a Metricon Prism Coupler (PC-2000) which is an optical waveguide technique providing both in-plane and out-of-plane refractive indices.

3. Polymerization. A typical polymerization procedure is as follows. A 50 mL three-neck flask equipped with a nitrogen inlet and a mechanical stirrer was charged with 3.11 g (9.3 mmol) of 2,2-bis(aminophenyl)-hexafluoropropane (**Ia**), 2.1 g of pyridine, and 15 mL of NMP. The solution was stirred until the diamine dissolved and then cooled to 0 °C. To this solution, 1.89 g (9.3 mmol) of terephthaloyl chloride was added and washed in with 15 mL of NMP. The solution was allowed to warm to room temperature and was stirred for 12 h. The formation of a high-molecular-weight polymer was evident by the dramatically increased solution viscosity. The polymer was precipitated into 500 mL of a vigorously stirred methanol/water (1:1) solution and then filtered. The precipitated polymer was washed several times with methanol and then water and vacuum-dried to constant weight. The polymer (**IIa**) was isolated as 4.23 g (98%) of a white powder and had a intrinsic viscosity of 0.43 dL/g, measured in NMP at 30 °C. The yields were essentially quantitative for all of the polymerizations.

Results and Discussion. The polymerizations were carried out by reacting stoichiometric amounts of diamine with terephthaloyl chloride in the presence of pyridine. These exothermic polymerization reactions were performed at 0 °C at a concentration of 15% solids in NMP. The reactions were allowed to slowly warm to room temperature and stirring was continued for 12 h, resulting in the formation of high-molecular-weight polymers in all cases. There was no trace of NMP or pyridine salts in the final polymer after washing and drying was complete, as determined by NMR.

We were surprised initially that the polymers were soluble in polar aprotic solvents such as NMP, dimethyl sulfoxide, and dimethylacetamide because most all para polyterephthalamides, which do not contain large bulky substituents, fail to redissolve in such solvents after isolation from their initial polymerization solutions.[1] The inclusion of small flexible linkages, such as aryl ether linkages, do not lead to soluble polyamides. Our attempts to make aramids using 4,4′-oxydianiline and 3,3′-bis(trifluoromethyl)-4,4′-diaminobiphenyl gave polymers that precipitated from solution and would not redissolve in organic solvents. Attempts to dissolve the polymers in solvents containing inorganic salts were not performed because we desire to have final materials with low ionic impurities. We were able to successfully incorporate substituted methylene linkages into the

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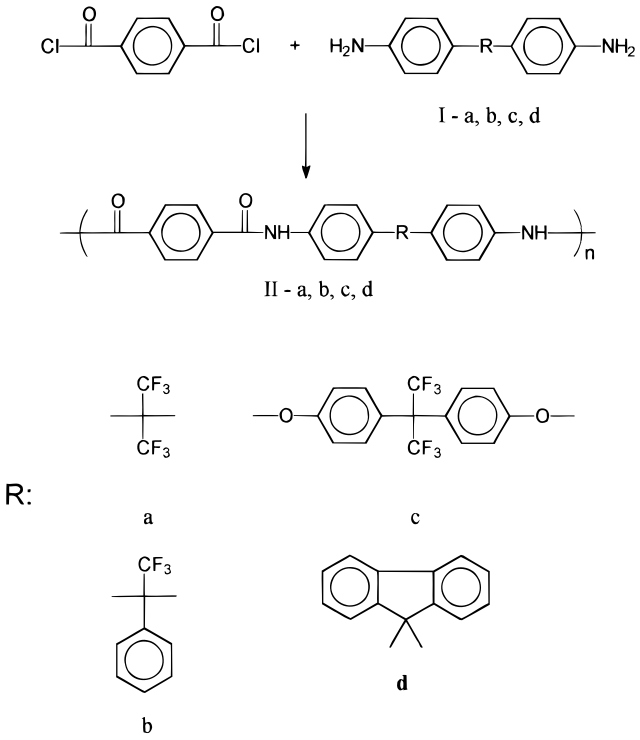

Figure 1. Synthesis and structures of polyterephthalamides.

Table 1. Characterization Data for Polyterephthalamides

sample entry	$[\eta_{\mathrm{int}}]^a$ (dL/g)	T_g − DSC (°C)	isothermal wt loss at 400 °C (%/h)	T_d − 5% wt loss (°C)
IIa	0.41	323	1.8	460
IIb	0.40	332	1.7	460
IIc	0.48	238	2.9	478
IId	0.47	415	1.5	476

[a] Measured in NMP at 30 °C.

polymer chains, resulting in a number of soluble polyterephthalamides (Figure 1).

The polymers were dissolved in NMP and films were cast and heated slowly to 350 °C to effect solvent removal. Polymers **IIa**, **IIb**, and **IId** gave excellent, transparent, tough, fingernail creasable films. The films had very good adhesion to glass and attained a good degree of solvent resistance after thermal annealing at 350 °C. The polymers did not redissolve, even in boiling solvents, after being cast into films. Polymer **IIc** also gave tough films, but these films turned opaque upon heating for reasons not yet understood.

Physical characterization data for the polymers are shown in Table 1. The intrinsic viscosities of the polymers were measured (NMP at 30 °C) and are consistent with values obtained for high-molecular-weight, non-rodlike, aromatic condensation polymers. The substituted methylene linkages provide kinks in the backbone of the polymer which lead to smaller hydrodynamic volumes when compared to rigid-rod type systems. These kinks lead to the lower intrinsic viscosity values and increased solubility of these polymers. However, gel permeation chromatography and light scattering in appropriate solvents (NMP) were not available to confirm this. The polymers were clearly high-molecular-weight as evidenced by their easily discernable T_g values and their excellent film-forming properties. The polymers had glass transition temperatures (T_g) between 238 and 415 °C, and the transitions were easily seen by DSC. The high T_g for polymer **IId** is consistent with other high-temperature polymers that contain the fluorene unit in the polymer backbone. We saw no evidence of crystallinity in any of the thermograms. All of the polymers exhibited good thermal stability as measured by the temperature at which a 5% weight loss occurs, with all of the polymers being stable to greater than 450 °C in N_2. The refractive indices for polymer **IId** were measured by prism-coupling techniques at 632.8 nm and found to have an in-plane refractive index, n_{TE}, of 1.69 and an out-of-plane refractive index, n_{TM}, of 1.68, showing that this polyamide is only slightly anisotropic ($\Delta n = 0.01$). The refractive index value is in the same range as observed for other aromatic high-temperature polymers, typically between 1.70 and 1.50.

Summary. A new series of all para polyterephthalamides has been prepared. These polymers exhibited the unexpected ability to redissolve in polar aprotic solvents, and they also showed high thermal stability. Thin films of the polymers have been made, and all of the polymers yielded tough, fingernail creasable films. Several of the polymer films are transparent and colorless. Further studies on the utility of these polymers as high-temperature thermoplastics and adhesives are currently underway.

References and Notes

(1) Preston, J. In *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley Interscience: New York, 1988; Vol. 11, p 398.
(2) Imai, Y. *High Perform. Polym.* **1995**, *7*, 337.
(3) Gaudiana, R. A.; Minns, R. A.; Rogers, H. G.; Sinta, R.; Kalyanaraman, P.; McGowan, C. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1249.
(4) Harruna, I. I.; Bota, K. B. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 1, p 396.
(5) Hedrick, J. L.; Charlier, R.; DiPietro, R. A.; Jayaraman, S.; McGrath, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 2867.

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