

NOTES

Preparation and Properties of Disiloxane-Containing Polyamides from 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and Aromatic Dicarboxylic Acids

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A considerable number of disiloxane-containing condensation polymers such as polyamides, polyimides, and heterocyclic polymers has been reported,¹⁻⁹ some of which showed good thermal stability and enhanced solubility in organic solvents. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (BATS), which is a commercially available diamine monomer, was already utilized for the preparation of polyimides^{2,3,6,9} and aliphatic polyamides.^{7,8} The BATS-based polypyromellitimide had a melting temperature of 210°C,⁹ while the polyamides obtained from aliphatic C₃–C₈ dicarboxylic acids had low melting temperatures around 60–120°C.⁷ However, to our knowledge, the aliphatic-aromatic polyamides derived from BATS and aromatic dicarboxylic acids have not been reported to date. The purpose of this study is to elucidate the effect of tetramethyldisiloxane linkage on the properties of the disiloxane-containing aliphatic-aromatic polyamides.

EXPERIMENTAL

Materials

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (BATS), supplied by Chisso Corp., was purified by distillation over calcium hydride; bp 120°C/4.5 Torr. Isophthaloyl chloride (**1a**) and terephthaloyl chloride (**1b**) were obtained commercially and purified by vacuum distillation before use. 4,4'-Oxydi(benzoyl chloride) (**1c**) was prepared conventionally by reaction of 4,4'-oxydi(benzoic acid) with thionyl chloride. Triethylamine and all the solvents used were purified by distillation.

Polymerization

Polymer 2a. To a solution of 2.485 g (10.0 mmol) of BATS and 3.0 ml of triethylamine in 26 ml of chloroform were added 2.030 g (10.0 mmol) of solid IPC all at once with stirring at 0°C. Then the solution was stirred at room temperature for 3 h under nitrogen. The resulting viscous solution was poured into 500 ml of hexane. The precipitated polymer was col-

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lected and dried. The polymer was purified by dissolution in 20 ml of dimethylformamide (DMF), followed by precipitation with 500 ml of water. The product was then dried at 90°C for 24 h under vacuum. The yield was 3.46 g (91%). The inherent viscosity of the polymer in *N*-methyl-2-pyrrolidone (NMP) was 0.60 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. The IR spectrum (film) exhibited absorptions at 3350 cm⁻¹ (N-H), 2900 cm⁻¹ (CH₂), 1650 cm⁻¹ (C=O), 1270 cm⁻¹ (Si-CH₃), and 1050 cm⁻¹ (Si-O-Si). *Anal.* Calcd for (C₁₈H₃₀N₂O₃Si₂)_n: C, 57.10%; H, 7.98%; N, 7.40%. Found: C, 57.41%; H, 7.69%; N, 7.30%.

Polymers **2b** and **2c** were prepared by a similar procedure to that described above.

Measurements

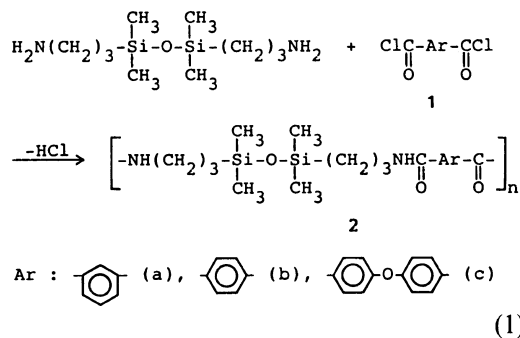
IR spectra were recorded on a JASCO FT/IR-5000 Fourier transform spectrophotometer. Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-30M, DSC-41M, TGA-30M, respectively. Wide angle X-ray diffraction patterns were obtained for films on a Rigakudenki XG X-ray diffraction apparatus using nickel-filtered Cu-K α radiation (30 kV, 50 mA). Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of a gel permeation chromatography (GPC) on the basis of polystyrene calibration on a JASCO HPLC BIP-1 apparatus (column, Shodex GPC AD-80M/S polystyrene gel; eluent, DMF containing 0.01 mol l⁻¹ of lithium bromide). Tensile properties were obtained with a Toyo Baldwin Tensilon UTM-III at a strain rate of 20% cm⁻¹.

RESULTS AND DISCUSSION

Polymer Preparation

The conventional low-temperature solution polycondensation method¹⁰ was used in the

preparation of disiloxane-containing aliphatic-aromatic polyamides **2a–2c** starting from BATS and aromatic diacid chlorides **1a–1c** (eq 1). The polymerization was carried out at room temperature in an organic solvent with the use of triethylamine as an acid acceptor.



The effect of reaction medium was first examined on the polycondensation of BATS with **1a**, and the results are summarized in Table I. The polymerizations in all the solvents used proceeded readily in homogeneous solution. Among them, chlorinated hydrocarbons such as dichloromethane and chloroform was found to be effective for the preparation of polymer **2a** with reasonably high inherent viscosity of over 0.5 dl g⁻¹, compared with NMP, a typical amide-type solvent. Other polymers **2b** and **2c** having inherent viscosities of 0.3–0.4 dl g⁻¹ were also obtained by the polymerizations in chloroform (Table I). A GPC study indicated that polymer **2a** with inherent viscosity of 0.60 dl g⁻¹ corresponded to \bar{M}_w and \bar{M}_n values of 190000 and 106000, respectively, relative to standard polystyrene, and the \bar{M}_w/\bar{M}_n ratio was 1.8.

The structures of the polymers thus obtained were confirmed to be the proposed disiloxane-containing polyamides by means of IR spectroscopy and elemental analysis.

Polymer Characterization

The X-ray diffraction study indicated that all the polymers were amorphous. These disiloxane-containing polyamides dissolved readily in a variety of solvents such as DMF,

Table I. Preparation of polyamides from BATS and aromatic dicarboxylic acid chlorides^a

Diacid chloride	Reaction medium	Polymer		
		Code	Yield %	η_{inh}^b dl g ⁻¹
1a	Dichloromethane	2a	84	0.51
1a	Chloroform	2a	91	0.60
1a	<i>N</i> -Methyl-2-pyrrolidone	2a	78	0.26
1b	Chloroform	2b	90	0.42
1c	Chloroform	2c	95	0.32

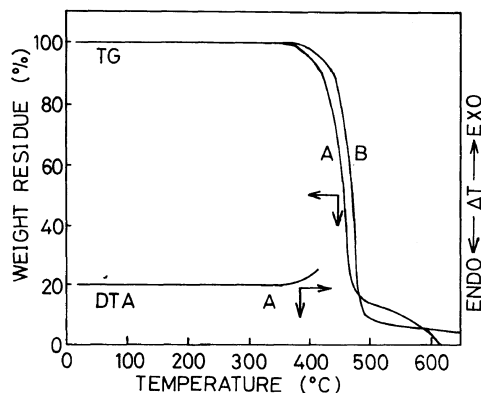
^a Polymerization was carried out with 10 mmol of each monomer and 21 mmol of triethylamine in 26 ml of the solvent at 20°C for 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

NMP, dimethyl sulfoxide, pyridine, tetrahydrofuran, *m*-cresol, and chloroform at room temperature, and even in hot ethanol. They are practically insoluble in hexane. Since aliphatic-aromatic polyamides derived from aliphatic diamines and aromatic diacids dissolved only in acidic media such as *m*-cresol and trifluoroacetic acid,¹¹ the enhanced solubility characteristics of the disiloxane-based polyamides are probably attributable to the amorphous nature of these polymers due to the existing tetramethyldisiloxane linkage which disturbs the close packing of the polymers.

A colorless, transparent and flexible film of polymer **2a** could be obtained by hot pressing or by casting from the DMF solution. The cast film had a tensile strength of 14 MPa, an elongation at break of 23%, and a tensile modulus of 1.1 GPa.

The thermal behavior of the polymers was evaluated by means of DTA, DSC, and TG. Figure 1 shows the DTA and TG curves of polymer **2a**, and thermal properties are summarized in Table II. None of the polyamides decomposed below 320°C in air, and the 10% weight loss occurred between 420°C and 440°C in air and nitrogen. These decomposition temperatures are somewhat higher than

**Figure 1.** DTA and TG curves of polymer **2a** at a heating rate of 10°C min⁻¹ in air (A) and in nitrogen (B).**Table II.** Thermal behavior data of polyamides

Polymer	Glass transition temperature ^a °C	Decomposition temperature ^b	
		In air °C	In nitrogen °C
2a	82	420	440
2b	90	400	435
2c	91	425	440

^a Determined by DSC at a heating rate of 20°C min⁻¹ in nitrogen.

^b Temperature at which 10% weight loss was recorded by TG at a heating rate of 10°C min⁻¹.

those of the polyamides derived from BATS and aliphatic diacids, as well as wholly aliphatic polyamides.⁷

The glass transition temperatures (T_g) are between 82 and 91°C irrespective of the nature of the aromatic moiety introduced in the polymer backbone. Since the polyisophthalamides and polyterephthalamides containing C₆-C₈ methylene chains have T_g 's between 105 and 125°C,¹¹ the T_g 's of the disiloxane-containing aliphatic-aromatic polyamides are quite reasonable, and are about 60°C higher than those of the polyamides based on BATS and aliphatic diacids, which are below 20°C.⁷ It is of interest that the T_g 's of the polyamides obtained here are about 10–15°C higher than

those of the polyimides derived from BATS and both 3,3',4,4'-biphenyltetracarboxylic and 3,3',4,4'-benzophenonetetracarboxylic dianhydrides.⁹ This may be explained by the presence of hydrogen bonding in the polyamides.

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