Alternate Poly(amide-imide)s Based on 1,4- and 1,3-Bis(4-trimellitimidom) benzene and Their Mixtures

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Abstract: Several series of alternate poly(amide-imide)s [P(A-alt-I)s] were synthesized by aromatic dicarboxylic acid (I-p or I-m), which was prepared by the condensation of p-phenylenediamine (or m-phenylenediamine), trimellitic anhydride, and various aromatic diamines by means of direct polycondensation. A diimide-diacid (I-p) with a p-phenylene group was used to synthesize P(A-alt-I)s III, and P(A-alt-I)s IV were synthesized by a diimide-diacid (I-m) prepared from m-phenylenediamine. Another series of P(A-alt-I)s V was synthesized from both I-p and I-m (1/1 mole) with various diamines. Polymers of series III have low inherent viscosities and limited solubility, but polymers of series IV have high degrees of polymerization. Series V copolycondensated from I-p and I-m has improved solubility and degrees of polymerization relative to series III. The degree of crystallinity was found to be III > V > IV. Glass transition temperatures for most of series III were not observed below 400 °C, and those of series IV and V were in the range of 238–325 °C and 262–328 °C, respectively. The 10% weight loss temperatures in nitrogen or in air of these three series are all in the range of 482–582 °C. Because series V has limited solubility for casting into films from DMAc solutions, two diamines were selected to synthesize series VI by changing the I-p/I-m ratio. Solubility was improved when the content of I-p in diimide-diacid was less than 15%, and the degree of crystallinity reduced as the content of I-p in diimide-diacid decreased. Polymers containing a few I-p showed an increase in the initial modulus.

Keywords: Poly(amide-imide)s, p-Phenylenediamine, m-Phenylenediamine, Trimellitic anhydride.

Introduction

Aromatic polyimides and polyamides have high thermal stability and unique combination of other properties, and are of use in high-temperature resistant high-strength/high-modulus fibers and engineering resins [1-7]. Drawbacks of these polymers are their insolubility and intractability, which cause difficulties in both synthesis and processing. This problem is circumvented in polyimides, especially in thin film formation, through processing of the soluble poly(amic acid) precursors. The processability of a polymer can be improved by the lowering of its softening point and glass transition temperature. Solubility can be increased by the incorporation of flexibilizing groups and bulky units in the polymer backbone [8-14], and crystallinity can be adjusted by varying the regular moieties or reducing rigid moieties [15-20]. For example, by using 3,4'-oxydianiline instead of partial magnitude p-phenylenediamine we can synthesize soluble Kevlar. Another method synthesizes copolymers such as alternate poly(amide-imide)s [P(A-alt-I)s] and poly(ester-amide)s, which are more tractable than polyimides [21-23].

In this research, P(A-alt-I)s containing p-phenylenediamine (p-PDA) or (m-phenylenediamine (m-PDA), which are useful diamines for synthesizing important aramids, were synthesized.

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J. Polym. Res. is covered in ISI (CD, D, MS, Q, RC, S), CA, EI, and Polymer Contents.
from I-p and/or I-m and various diamines. Because diimide-diacid prepared from p-PDA was insoluble and was difficult to polymerize, another series was synthesized by mixing p-PDA/m-PDA in various ratios. The method involves using p-PDA (or m-PDA) and TMA to prepare an imide ring-preformed dicarboxylic acid I-p (or I-m), which (or mixture of I-p and I-m) is then reacted by direct polycondensation with another aromatic diamine to form P(A-alt-I). Synthesis and properties of polymers were investigated.

**Experimental**

1. Materials

Aromatic diamines: p-Phenylenediamine (from Wako) and m-phenylenediamine (IIa; from TCI) were vacuum-distilled before use. All other diamines such as 2,4-toluylenediamine (IIb; from TCI), 4,4'-oxydianiline (IIc; from TCI), 3,4'-oxydianiline (IId; from Chriskev), 4,4'-methylene diamine (IIe; from TCI), 4,4'-thiodianiline (IIe; from TCI), 4,4'-phenylenedi oxydianiline (IIf; from TCI) were used as received. The diamines 4,4'-isopropylidenediyldiamine (IIg; from TCI), 4,4'-[sulfonylbis-(1,4-phenyleneoxy)]dianiline (IIh; from TCI) and 4,4'-[sulfonylbis-(1,4-phenyleneoxy)]dianiline (IIi; from TCI) were obtained from Chriskev Corp. and used without further purification. Trimellitic anhydride (TMA, from Wako) and triphenyl phosphite (TPP, from TCI) were used without further purification. Commercially available calcium chloride (CaCl₂) was dried under a vacuum at 150 °C for 6 hours. N-Methyl-2-pyrrolidone (NMP, from Fluka), N,N-dimethylformamide (DMF, from Fluka) and pyridine (Py, from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2. Synthesis of diimide-dicarboxylic acids

Previous reports [24-28] from our laboratory described how diimide-dicarboxylic acids were synthesized from TMA with various aromatic diamines. A typical example for the preparation of diimide-dicarboxylic acid is as follows: a mixture of TMA (120 mmole, 23.04 g) and m-phenylenediamine (IIa) (60 mmole, 6.48 g) was dissolved in 120 mL of dry DMAC and stirred till the solution became clear. Toluene (20 mL) was then added, and the mixture was heated to 140 °C until water (about 2.1 mL) was distilled off. Heating continued to distill off the residual toluene. After cooling, the precipitate of I-m was isolated by recrystallization from N,N-dimethylformamide (DMF), and was dried to produce 29.3 g of I-m (yield: 99%); m.p. 412-413 °C. Anal. Calcd for C₂₃H₁₂N₂O₈ (456.37): C, 63.16%; H, 2.65%; N, 6.14%. Found: C, 62.65%; H, 2.93%; N, 6.23%.

Another diimide-dicarboxylic acid I-p was synthesized in a similar manner: m.p. 473-474 °C. Anal. Calcd for C₂₃H₁₂N₂O₈ (456.37): C, 63.16%; H, 2.65%; N, 6.14%. Found: C, 62.63%; H, 2.99%; N, 6.26%.

3. Synthesis of poly(amide-imide)

An example for the preparation of polymer IVb is as follows. A mixture of 0.183 g (1.5 mmole) of 2,4-tolylenediamine (IIb), 0.684 g (1.5 mmole) of diimide-diacid I-m, 0.46 g of calcium chloride, 1.5 mL of pyridine, 1.0 mL of triphenyl phosphite and 7.0 mL of NMP were heated while being stirred at 100 °C for 3 hours. At the end of reaction, the polymer solution was trickled into stirred methanol, giving rise to a stringy precipitate, which was washed thoroughly with hot water and methanol, collected by filtration and dried. The product obtained was 0.86 g (yield: 99%). The inherent viscosity of the polymer solution was 1.19 dL/g at 30 °C, measured at a concentration of 0.5 g/dL in N,N-dimethylacetamide (DMAC) containing 5 wt% LiCl. Other poly(amide-imide)s were synthesized in an analogous manner.

4. Measurements

Inherent viscosities of all polymers were determined at 30 °C and 0.5 g/dL concentration using a Cannon-Fenske viscometer. Solubilities were determined at 1% (w/w) concentration. Wide-angle X-ray diffraction patterns were obtained on a Rigaku Geiger D-Max IIIa X-ray diffractometer, using Ni-filtered CuKα radiation (40 kV, 15 mA) with powder or film specimens of about 0.05 mm in thickness. An Instron Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the sample. A gage of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and the average of at least five individual determinations is reported. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen (30 cm³/min) at a heating rate of 20 °C/min. The samples were heated to 400 °C, then quenched from the elevated temperature to room temperature in the air to yield amorphous samples so that Tg of polymers could be