Synthesis of Novel Organic Materials Using Crown Ether

Tetsuya Kogiso,* Kouhei Tomita,* Mitsuhiro Yamada,* and Shin-ichi Inoue*§

Functional Material Laboratory, Department of Applied Chemistry, Aichi Institute of Technology, 1247 Yachigusa, Yakusa, Toyota, Aichi 470-0392, Japan

INTRODUCTION

Polyimides (PIs), which have reliable high-performance stability, chemical resistance, dielectric properties, and good mechanical strength, have been widely used in aerospace, auto and electronic industries since they were developed in the 1960s. Numerous attempts have been made to introduce high performance properties into polymeric materials. For example, various imide-containing elastic polymers (IEPs) have been developed as high-performance polymers that can be applied in microelectronics and in specialty coatings. We previously reported a new approach for obtaining IEPs via elastic and high-molecular-weight polyurea and pyromellitic dianhydride[1, 2], and recently reported producing silica hybrid composites using water glass as a raw material. Many studies have also been carried out on polyimides to obtain a new class of imide-containing polymeric materials. The various techniques can be classified into two fundamental types, those produced by chemical and physical methods. A number of studies of the chemical method have been carried out already, but physical method remains largely unexplored.
We are interested in rotaxane or catenane structures[3] (Figure 1). This study uses crown ether as a raw material for producing PIs with rotaxane structure. Accordingly, preparation of a new functional polymer material is expected.

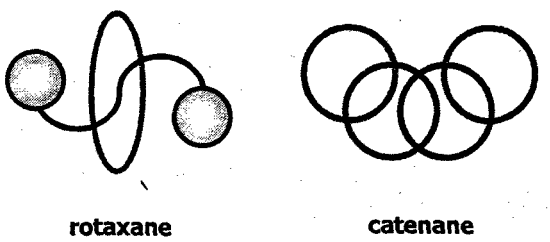


Figure 1. Rotaxane and catenane structures.

EXPERIMENTAL SECTION

Materials

4,4 -diphenylmethanediamine (MDA, Nachalai Tesque Inc.), pyromellitic dianhydride (PMDA, Kishida Reagents Chem.) and 18-crown 6-ether (18C6, Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. *N*-methyl-2-pyrroridone (NMP, Nachalai Tesque, Inc.) was kept over a 3Å molecular sieve.

Measurements

FT-IR spectra were recorded on a JASCO FT/IR-5300 with ATR-500/M. ^{1}H and ^{13}C NMR spectra were performed on a UNITY *plus*-300 varian NMR spectrometer at room temperature. Tensile properties were investigated using Orientec RTC-1225A with model-U-4310 at room temperature. Thermal gravimetric analysis (TGA) measurements were performed on a TA Instruments Hi-Res Modulated TGA 2900 Thermogravimetric analyzer at heating rate of 5 °C/min under N_2. Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument DSC-2910 at a heating rate of 10 °C/min under N_2.

Preparation of Polyimide-crown

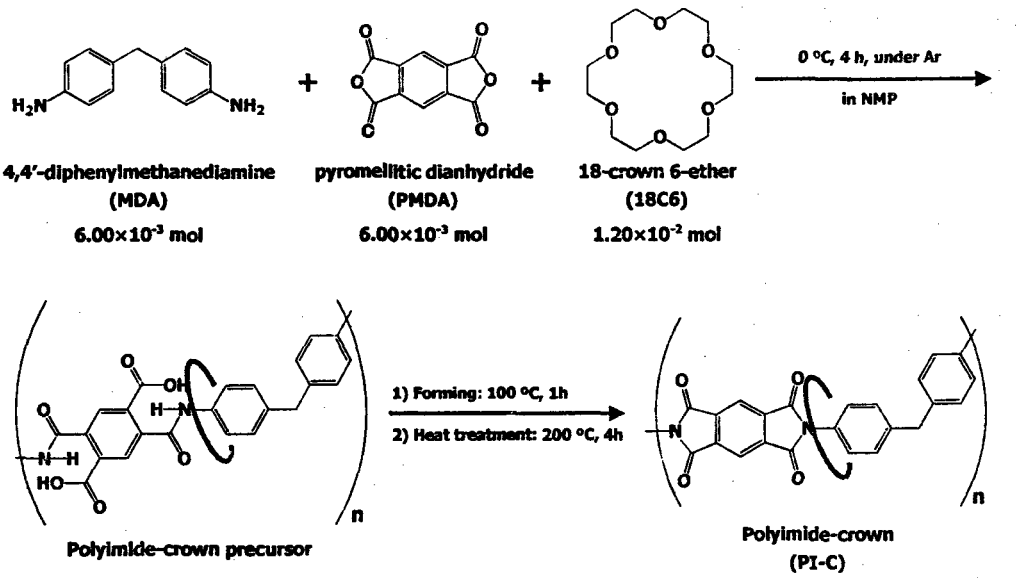
Scheme 1 shows the preparative procedure for making the polyimide-crown (PI-C) composite. The PI-C was prepared by the reaction of PMDA with MDA containing 18C6 in NMP. MDA (1.2 g, 0.0060 mol) was dissolved in NMP (20mL) at room temperature (25±2 °C) for 1 hour under Argon, and then 18C6 (3.2 g, 0.012 mol) was added. The mixture was stirred for 1 hour under Argon at room temperature. PMDA (1.3 g, 0.0060 mol) was added to obtaining solution and stirred at 0 °C for 4 hours under Argon.
The reaction mixture (5 g) was treated in a centrifugal casting machine at 100 °C for 1hour. Furthermore, the resulting film was treated at 200 °C for 4 hours *in vacuo* (2~3 mmHg).

RESULTS AND DISCUSSION

Characterization of Polyimide-crown

18C6 which did not form a rotaxane structure was extracted with a solvent. The characteristic IR absorption bands of the imide group appear at 3040 and 2897 ($\upsilon_{C\text{-}H}$), 1777 and 1696 ($\upsilon_{C=O}$), 1510 ($\upsilon_{C=C,\ aroma}$) 1354 ($\upsilon_{C\text{-}N}$), 1194 ($\delta_{C\text{-}H,\ aroma}$) and 718 cm^{-1} ($\delta_{C=O}$), and the ether group appear at 2870 ($\upsilon_{C\text{-}H}$) and 1094 cm^{-1} ($\upsilon_{C\text{-}O\text{-}C}$).
The introducing rate was calculated by change of material weight before and after the reaction and ^{1}H NMR measurement of unreacted 18C6. The introducing rate of 18C6 to the resulting film was about 6 %.

Scheme 1. Synthesis of Polyimide-crown



Thermal gravimetric Analyses

A study on thermal degradation was carried out using TGA. Figure 2 shows the TGA curve under N_2 for PI-C precursor. The first step change appeared with the removal of the water. The second step change (weight-loss at 110 °C) occurred with the removal of NMP as a solvent. The third step change (weight-loss at 270 °C) arose from decomposition of 18C6. The forth step change (weight-loss at 370 °C) arose from decomposition of PI. As compared with PI, thermal stability of PI-C was almost the same.

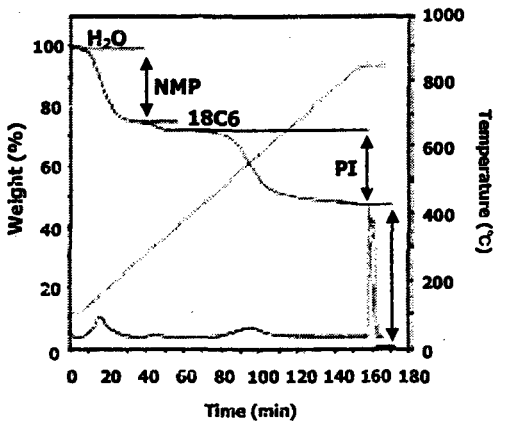


Figure 2. TGA curves of Polyimide-crown precursor under N_2 at 5 °C/min.

Acknowledgment

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References and Notes

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* Department of Applied Chemistry, Aichi Institute of Technology

§ Corresponding author. E-mail: sh-inoue@aitech.ac.jp