First Observation of a Thermotropic Liquid Crystal in a Simple Polyimide Derived from 1,11-Diaminoundecane and 4,4″-Terphenyltetracarboxylic Acid

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Received April 24, 1995
Revised Manuscript Received June 26, 1995

Aromatic polyimides are well-known as some of the most useful superengineering plastics because of their high thermal stability, good chemical resistance, and excellent mechanical properties and are used widely in aerospace, electronics, and other industries.[1,2] Recently, the study of liquid crystalline polyimides was initiated where an ester connecting group was introduced into the polyimide backbones.[3–6] Kricheldorf et al., Chen et al., and Sato et al. have suggested that an aromatic imide ring may be an excellent mesogen through the studies on thermotropic liquid crystalline poly(imide–ester)s[3–13] and poly(imide–carbonate)s.[14–16] Some thermotropic properties of poly(ether–imide)s have also been reported by Asanuma et al.[17] However, there is no report so far on the thermotropic liquid crystals for the simple polyimides which consist of imide rings and polymethylene spacers.

During the course of the studies on the properties of aliphatic–aromatic polyimides synthesized by the high-pressure polycondensation of the nylon-salt-type monomers derived from aliphatic diamines and aromatic tetracarboxylic acids such as 4,4′-oxydiphthalic acid,[18] pyromellitic acid,[19,20] and 4,4′-biphenyltetracarboxylic acid,[21] we have found that the polyimide obtained from 1,11-diaminoundecane and 4,4″-terphenyltetracarboxylic acid showed an enantiotropic liquid crystalline phase. The present paper reports the first example of a thermotropic liquid crystal which formed from this type of simple polyimide.

The polyimide P-11TPE used here was synthesized according to Scheme 1. Each procedure is described in detail below.

The 1:1 salt monomer 11TPE composed of 1,11-diaminoundecane and diethyl 4,4″-terphenyltetracarboxylate was prepared as follows. A mixture of 3.703 g (10 mmol) of 4,4″-terphenyltetracarboxylic dianhydride in 500 mL of ethanol was heated at 100 °C for 10 h, affording the diethyl 4,4″-terphenyltetracarboxylate solution. To this solution was added a solution of 1.863 g (10 mmol) of 1,11-diaminoundecane in 300 mL of ethanol dropwise with stirring at 60 °C. After the solution was stirred at room temperature for 3 h, the precipitate formed was collected by filtration and dried under vacuum at 80 °C. The yield of the salt monomer was 5.668 g (87%). Mp: 155 and 164 °C (by DTA at a heating rate of 10 °C min^{-1}). IR (KBr, cm^{-1}): 1717 (ester C=O), 1571 (overlapped NH_3^+ and carboxylate C=O). Elem anal. Calcd for $C_{37}H_{48}N_2O_8$: C, 68.50; H, 7.46; N, 4.32. Found: C, 67.92; H, 7.18; N, 4.25.

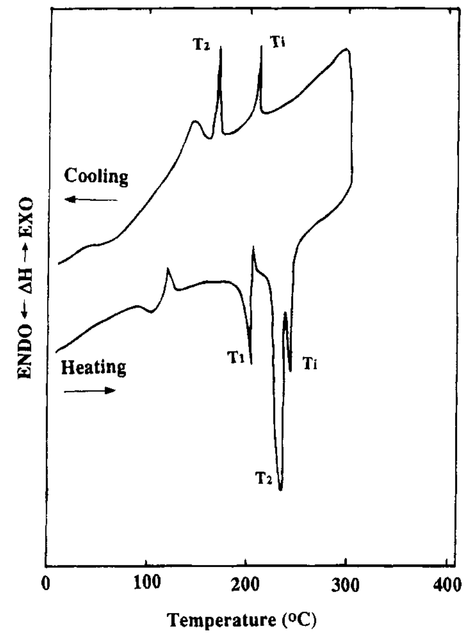
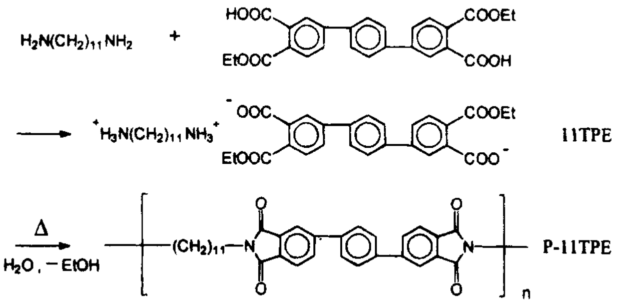


Figure 1. DSC thermograms of P-11TPE observed at a heating or cooling rate of 10 °C min^{-1}.

Scheme 1



The high-pressure thermal polycondensation of salt monomer 11TPE was carried out as follows. A 0.5-g portion of 11TPE was placed into a Teflon capsule (15-mm inside diameter), and then the capsule was loaded into the cylinder. The piston–cylinder was then set inside a furnace, and pressure was applied at room temperature. The polymerization was then conducted at 250 °C under 260 MPa of pressure for 5 h. After the polymerization, the temperature was lowered to room temperature, followed by the release of the pressure to 1 atm. The polymer, in the form of a flat cylindrical pellet (15-mm diameter and about 3-mm thickness), was removed from the capsule. The pellet was then dried at room temperature under vacuum at 80 °C for 20 h to completely remove the water and ethanol produced during the polymerization. The inherent viscosity of polyimide P-11TPE was 0.66 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} in concentrated sulfuric acid at 30 °C. IR (KBr, cm^{-1}): 1773 and 1719 (imide C=O), 1380 (C–N), 743 (imide ring). Elem anal. Calcd for $C_{33}H_{32}N_2O_4$: C, 76.13; H, 6.20; N, 5.38. Found: C, 76.30; H, 6.15; N, 5.23.

The DSC thermograms of P-11TPE as observed by a Perkin-Elmer DSC-II calorimeter are shown in Figure 1. Upon heating to the isotropic melt, three distinct endothermic peaks can be observed at 200 °C (T_1), 228 °C (T_2), and 240 °C (T_i), the enthalpies being 3.8, 13.6, and 1.2 kJ mol^{-1} of repeat unit, respectively. Some other transitions, corresponding to the glass transition and crystallization, are observed at 89 and 117 °C, respectively, but these disappear by annealing at 160 °C and hence are not significant for the argument. The

DSC transition at T_1 can be attributed to the crystal–crystal transition from the X-ray analyses mentioned below. The middle transition at T_2 corresponds to the crystal to liquid crystal transition since the specimen gains the fluidity showing the high birefringence. T_i is the isotropization temperature of the liquid crystal. Upon cooling, the polyimide exhibits three corresponding transitions at 210, 169, and 144 °C, the enthalpies of which are 1.2, 1.4, and 3.5 kJ mol^{-1} of repeat unit, respectively. Thus, P-11TPE forms the enantiotropic liquid crystal from 228 to 240 °C on heating and from 210 to 169 °C on cooling.

Parts A–C of Figure 2 show the X-ray patterns taken with a Rigaku–Denki X-ray diffractometer for the oriented specimens which were annealed at characteristic temperatures of 160 (below T_1), 205 (between T_1 and T_2), and 235 °C (between T_2 and T_i), respectively. Here the oriented specimen was prepared by drawing a fiber from the isotropic melt, and the fiber axis that corresponds to the polymer chain axis is placed in the vertical direction. The narrow distribution of reflections points to the high degree of orientation in the fiber.

The X-ray diffraction pattern of Figure 2A taken for the specimen annealed at 160 °C is highly ordered; the amorphous halo is nearly absent, and significant peaks are measurable up to $2\theta = 30°$, with about 50 peaks clearly detected. The unit cell of the crystal is orthorhombic with $a = 12.48$ Å, $b = 4.56$ Å, and $c = 47.4$ Å. The c repeat distance is consistent with twice the repeat length of the polymer, and the unit cell volume, $V = 2697$ Å^3, requires four repeat units per unit cell; the derived density is then 1.28 g mL^{-1}, which is only slightly higher than the observed value of 1.25 g mL^{-1}.

When the specimen is heated to the temperatures between T_1 and T_2, the positions and relative intensities of most reflections change, but the well-ordered crystalline pattern is still observed. Although the crystal structure was not determined because of the coexistence of two or more crystalline phases, it is obvious that the DSC T_1 transition corresponds to the crystal–crystal transition.

Figure 2C shows the X-ray diffraction pattern for the liquid crystalline phase. Comparing with the X-ray pattern of part A or B of Figure 2, one can find that most sharp reflections disappear and that only two major reflections remain. One is the inner sharp reflection with a spacing of 23.6 Å and the other the outer broad reflection with a spacing of around 4.5 Å. These features can be attributed to the smectic mesophase.

The optical microscopy obviously indicated the fluidity of the liquid crystal, but no well-defined texture showing the smectic phase was attained even after the prolonged annealing. This may be caused by the high viscosity of the mesophase because of the high molecular weight of the specimen. Some ambiguity thus remains with respect to the identification of the smectic type, but the DSC and X-ray data are enough to conclude that the present simple polyimide as a first example can form a thermotropic liquid crystal.

The study of the liquid crystallinity of the polyimides, derived from the salt monomers composed of other aliphatic diamines and diethyl terphenyltetracarboxylate, is continuing. The details will be published in a succeeding paper.

Acknowledgment. The authors gratefully acknowledge the support for this work by a Grant-in-Aid for Scientific Research B from the Ministry of Education,

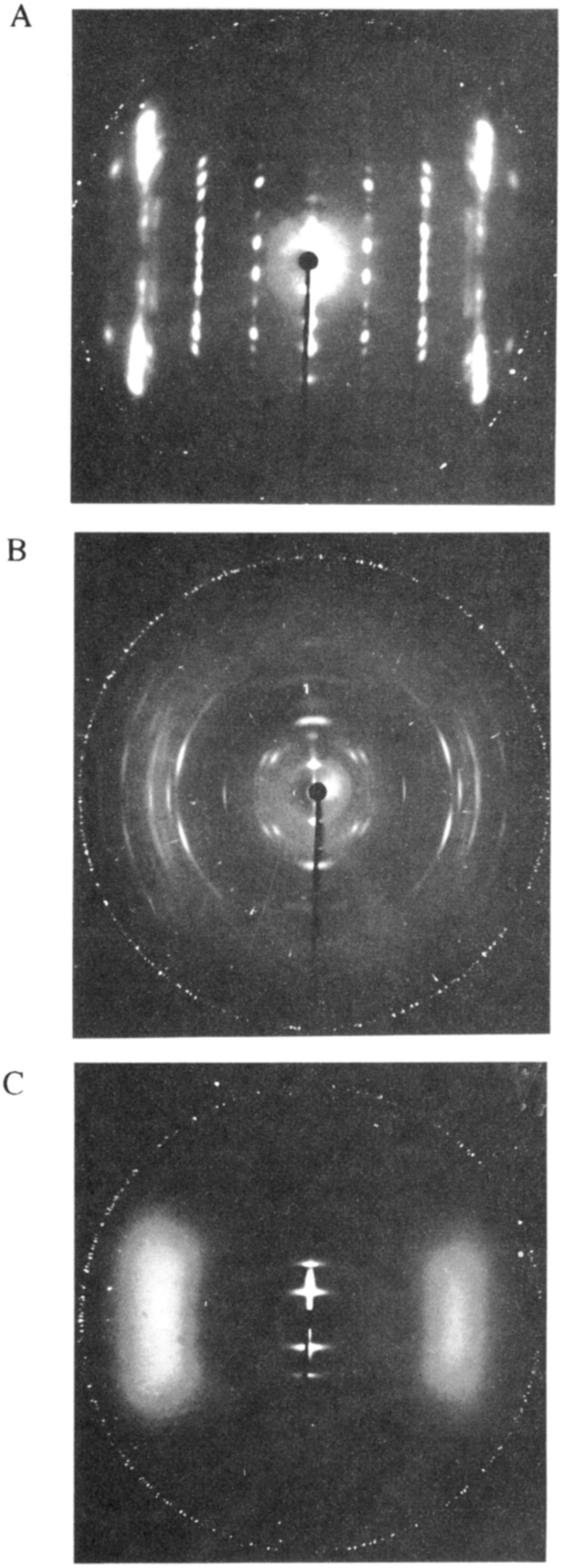


Figure 2. X-ray diffraction patterns for the fibrous P-11TPE specimens that were annealed (A) at 160 °C, (B) at 205 °C, and (C) at 235 °C and subsequently quenched to room temperature.

Science, and Culture of Japan (No. 05453142). We also are indebted to Hitachi Chemical Co., Japan, for the generous gift of 4,4″-terphenyltetracarboxylic dianhydride and to Mr. Yoshihiro Kumagai for helpful advice on the preparation of this new polyimide.

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MA950557C