

MOLECULAR STRUCTURE OF MAIN-CHAIN TYPE OF L.C. POLYIMIDE HAVING TERPHENYLBISIMIDE AS MESOGEN

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ABSTRACT

The series of aromatic-aliphatic polyimide P-XTPE (η_{inh} : 0.58~1.20 dLg⁻¹) were prepared by the polycondensation under high pressure of the salt monomers derived from diaminoalkane (the number of methylene units X=8~12) and diethyl 4,4"-terphenyltetracarboxylate. P-8TPE exhibited enantiotropic Nematic phase, whereas all the other polyimides did monotropic one. Moreover P-9TPE and P-11TPE exhibited Smectic phase on cooling and the crystal-to-crystal transition on heating. All transition temperatures except for crystal-crystal transition exhibited odd-even effect with the number of methylene unit. Molecular structures of their crystal and liquid crystal were investigated using solid-state ¹³C NMR measurement and so on.

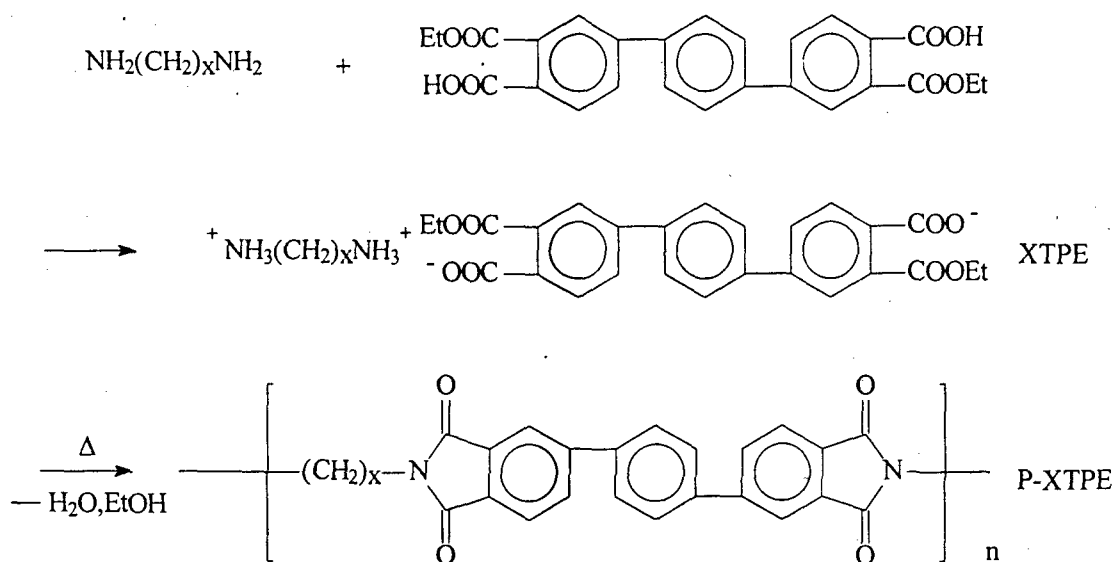
INTRODUCTION

Aromatic polyimides are super-engineering plastics which exhibit excellent mechanical and thermal properties. They 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 polyimides backbones. Aromatic imide ring has been suggested as an excellent mesogen for thermotropic liquid crystalline poly(imide-ester)s³ and poly(imide-carbonate)s⁴. However, no study has been reported on the real thermotropic liquid crystalline polymer whose mesogen was composed of only aromatic imide rings. These are very interesting to study because of their simple structure and easy analysis. We studied the properties of aliphatic-aromatic polyimides synthesized by high pressure polycondensation of their nylon-type salt monomers derived from aliphatic diamines and aromatic tetracarboxylic acids, such as 4,4' - oxydiphthalic acid⁵, pyromellitic acid⁶ and 4,4' - biphenyltetracarboxylic acid⁶. It was found that only the polyimide obtained from 4,4"-terphenyltetracarboxylic acid⁷ showed liquid crystallinity. This paper reports the first simple thermotropic liquid crystalline polyimide synthesized by

high pressure polycondensation and its molecular structure.

RESULTS AND DISCUSSION

New thermotropic liquid crystalline polyimides ($\eta_{inh} = 0.58\sim 1.20 \text{ dLg}^{-1}$) having aliphatic methylene chains and imide ring were prepared by polycondensation under high pressure of salt monomers derived from aliphatic diamines (number of methylene units, $X=8\sim 12$) and diethyl 4,4''-terphenyltetracarboxylate. The high-pressure polycondensation of the salt monomers was carried out by using a piston-cylinder-type hot-pressing apparatus with use of a teflon capsule as a reaction vessel. The polymerization was carried out under 260 MPa at 250°C for 5 h and linear polyimides were obtained readily as yellowish white pellets. On the other hand, polyimides formed under atmospheric pressure had higher inherent viscosities than under high pressure, or were insoluble in any solvent. IR spectra of these polyimides are the same shape as P-XTPE and show the formation of the imide group strongly. This result may show that the polymerization under atmospheric pressure was easy to bring cross-linking such as intermolecular imidiation due to super-activate molecular motion.



The eight-numbered polyimide showed enantiotropic mesophase behavior (Figure 1), whereas all the other polyimides were monotropic as observed from the DSC thermogram. From the DSC and X-ray measurements, distinct odd-even effects were observed where the mesophase structure and properties vary remarkably with a change in the number of carbon atoms of the flexible spacer. The even-numbered

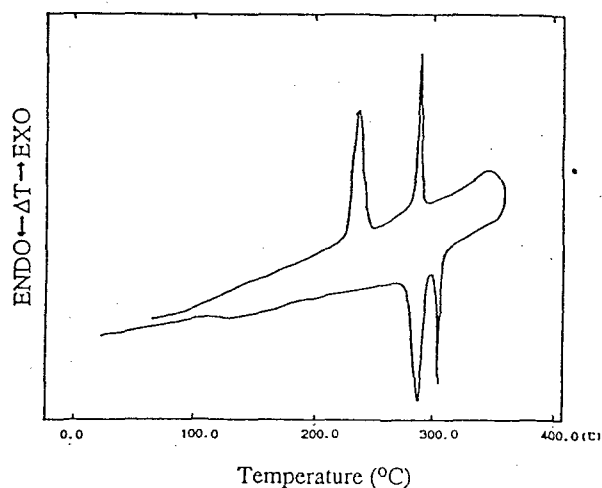


Fig.1 DSC Curves for P-8TPE

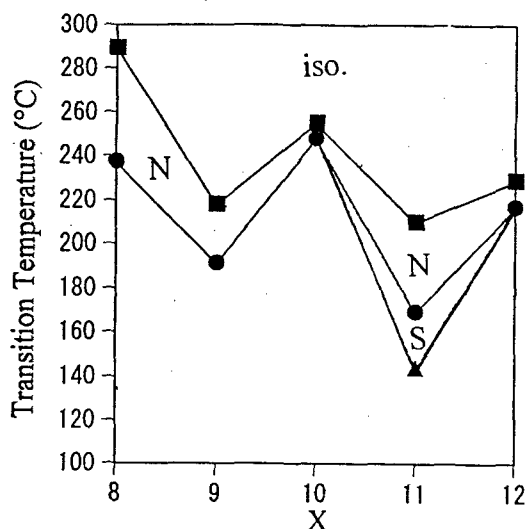
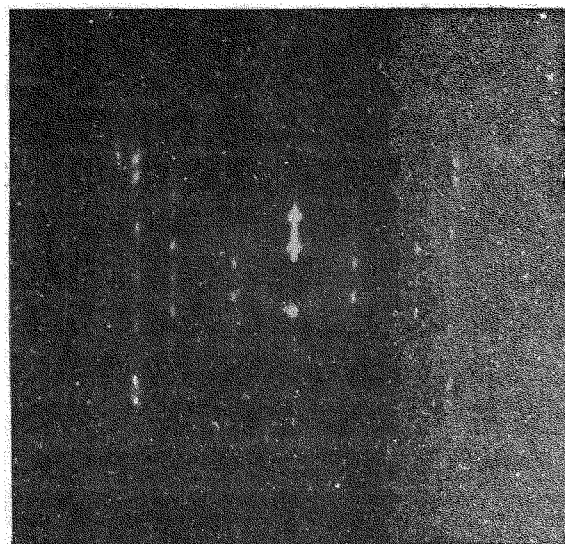
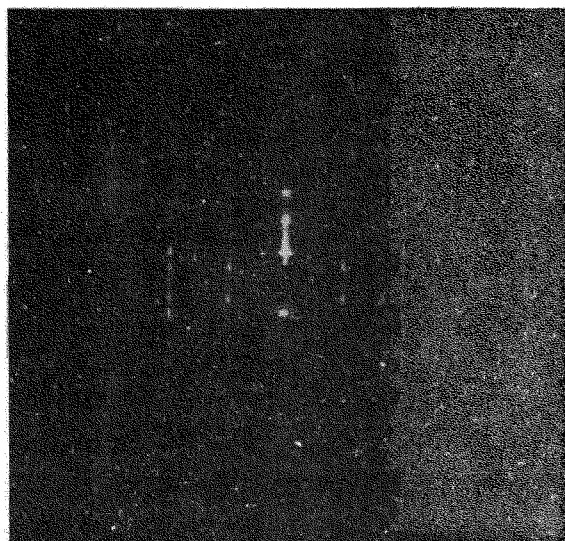


Fig.2 Dependence of Transition Temperatures on Number of Methylene Units on cooling

polyimides exhibited a Nematic phase seen from the observation of schlieren and inversion-wall textures on cross-polarizing microscope. On the other hand, odd-numbered polyimides exhibited not only Nematic but also Smectic phase. The Smectic phase was seen from the wide-angle X-ray diffraction patterns which exhibited an inner sharp reflection, so-called layer reflection, and an outer broad split reflection. Both the melting temperature on cooling (Figure 2) and the isotropization temperature exhibited an odd-even effect with a change in the number of methylene units.

Figure 3 shows wide angle X-ray diffraction patterns of P-11TPE taken at 150°C (crystal 1) and 205°C (crystal 2). A total of about 50 diffraction spots was observed in each picture. Since these pictures showed different crystal pattern, it is indicated that a crystal-to-crystal transition exist between 150°C and 205°C. Further, P-11TPE exhibited another crystal-to-crystal transition just before melting on heating. P-9TPE also exhibited a crystal-to-crystal transition on heating. Since all the crystal-to-crystal transitions are irreversible thermally, X-ray diffraction pattern of each crystal can be taken at room temperature.

Molecular structure of P-11TPE is investigated by solid-state high resolution ^{13}C NMR measurement (Figure 4). The spectrum of the liquid crystalline glass is similar with that of crystal 1. Therefore the molecular conformation of liquid crystal is same with that of crystal 1. On the other hand, the spectrum of crystal 2 is different from others. It can be said that the molecular conformation of crystal 2 is different from crystal 1.



205°C

Fig.3 WAXD patterns of P-11TPE

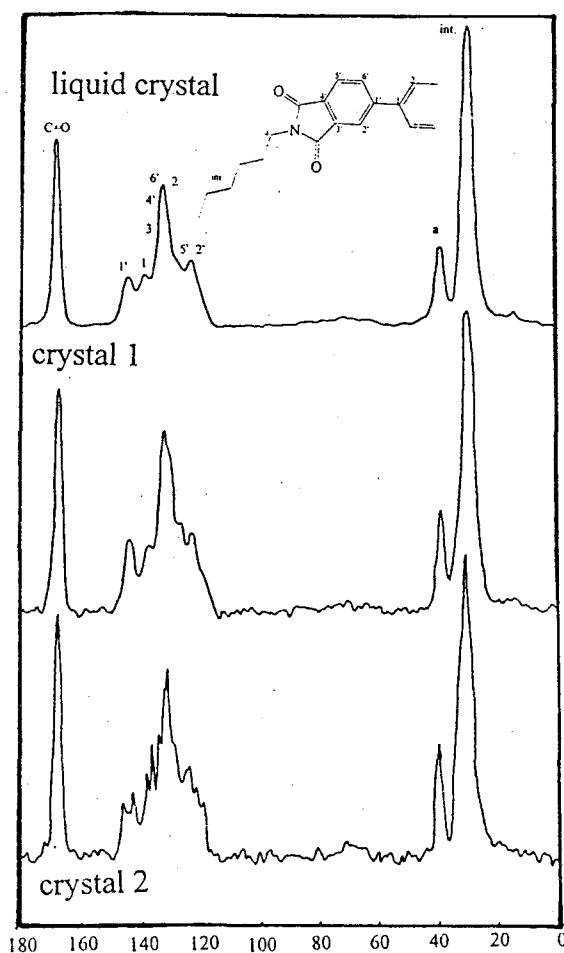


Fig. 4 Solid State ^{13}C NMR Spectra of P-11TPE

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