

Extended Chain Polymers I. Synthesis of Lyotropic Liquid Crystalline Copoly (Azomethine-Amide)

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There is currently a considerable interest in the synthetic chemistry of liquid crystalline polymers. Up to date, various types of polymer molecules exhibiting lyotropic and thermotropic mesophases have been investigated¹.

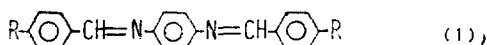
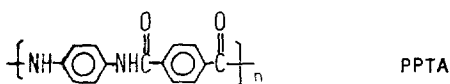
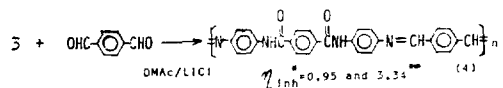
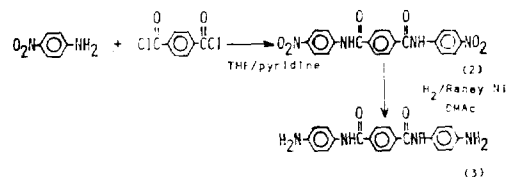
Among the polymers that exhibit lyotropic mesophases, para-aromatic polyamide, especially poly(p-phenyleneterephthalamide) (PPTA) has been investigated in greatest detail. PPTA forms nematic mesophase above a critical concentration in sulfuric acid. The most unique aspect about the spinning of the PPTA mesophase is the exceptionally high strength and stiffness characteristic of the as-spun fiber, commercially known as Kevlar^{®2}. On the other hand, para-aromatic azomethine compounds such as 1 is a well-known mesogen in the synthesis of low molecular weight liquid crystal³. Para-aromatic azomethine bond is characterized to be more rigid than the para-aromatic amide bond. Moreover, special prop-

erties such as fluorescence, syn-anti isomerization and π -electron delocalization are inherent to this para-aromatic azomethine bond⁴.

Following these considerations, we were encouraged to prepare strictly alternating copoly (azomethine-amide) (4) as a promising liquid crystalline polymer.

The preparation of 4,4'-diaminoterephthalanilide (3) is described elsewhere⁵. Polycondensation of 3 with terephthalaldehyde was carried out in DMAc/LiCl under dry nitrogen bleeding. After 5 hours' stirring at 9–10°C, 4 was obtained as a yellow precipitate.

The transmission IR spectra of 3 and 4 are



* measured at a concentration of 0.5g/dl in 98% H₂SO₄

** after the thermal post-polymerization which was carried out at 300°C under dry nitrogen bleeding

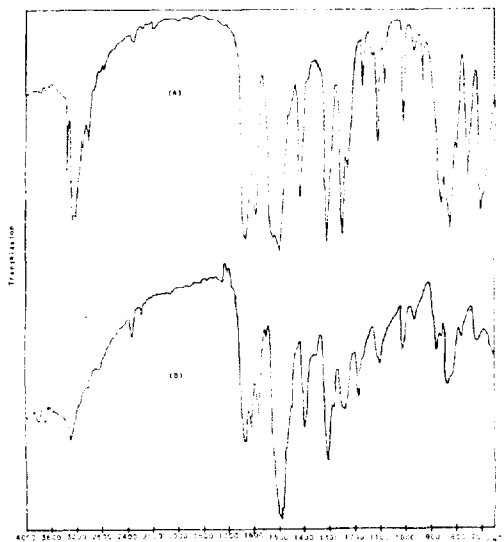


Fig. 1. IR spectra of (A) : monomer(3), (B) : polymer(4).

shown in Fig.1. Disappearance of the characteristic frequencies of the primary amino group (free, bands at 3,400–3,300cm⁻¹) and the appearance of the band at 1,605cm⁻¹ which is due to aromatic azomethine bond stretching are in good agreement with the structure of 4. As-obtained precipitate(4) was proved to be highly crystalline by the X-ray diffraction, which is shown in Fig.2. High thermal stability of 4 is shown in Fig.3, which was expected reasonably from the molecular structure of the repeating unit. In addition, 4 showed typical behavior of azomethine (Schiff-base) functionality, changing its color to red when exposed to acids.

4 was insoluble in most of common organic solvents, but it was dissolved in concentrated sulfuric acid with strong pearlescence when the solution was sheared. Partial phase diagram of 4($\eta_{inh}=0.95$) in 100% sulfuric acid is shown in Fig.4. According to the Flory's theory of rigid rod polymer³, the axial ratio of 4 is appreciated to be higher than 100, which is sufficiently high for the polymer(4) to

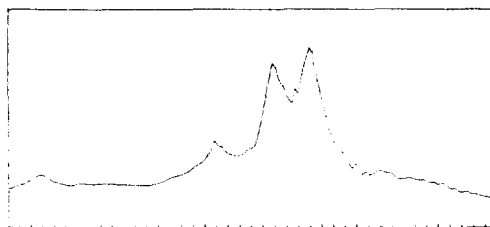


Fig. 2. X-ray diffraction pattern of polymer(4).

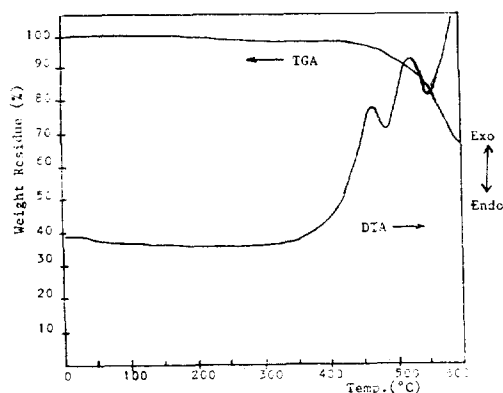


Fig. 3. DTA and TGA of polymer(4).

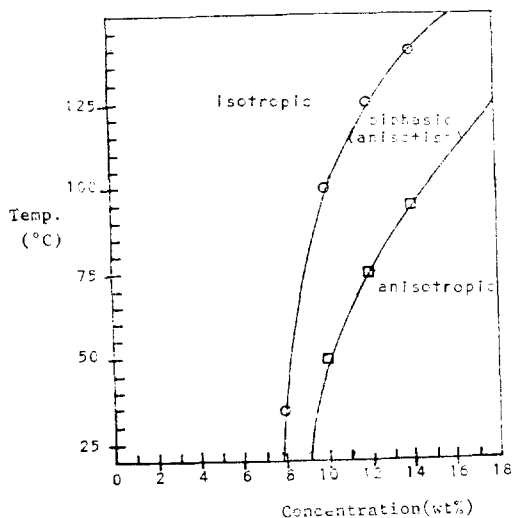


Fig. 4. Partial phase diagram* of polymer(4) in 100% sulfuric acid.

* Transition points from the crystal solvate to anisotropic single phase were not determined due to their poor reproducibility.

be classified as a "extended chain polymer".

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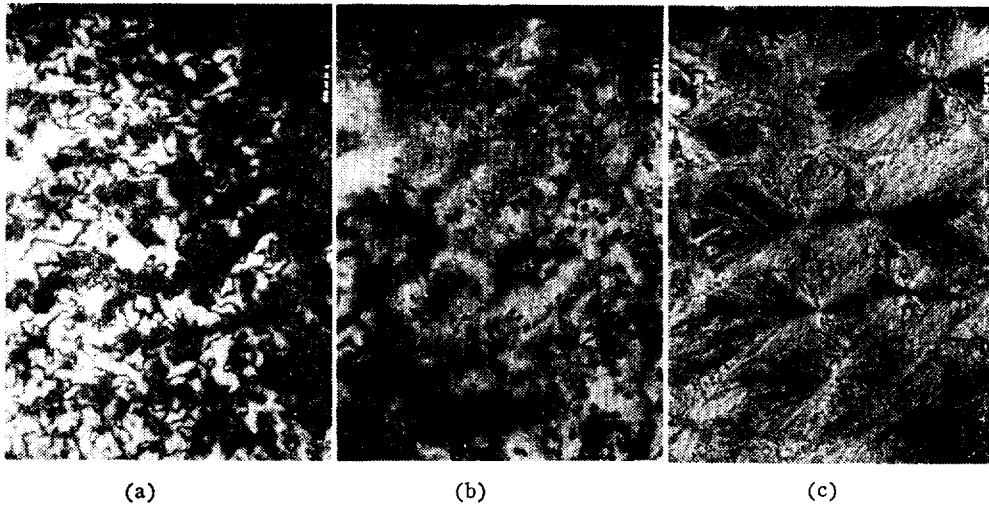


Fig. 5. Mesomorphic structures of 4 in 100% sulfuric acid under cross-nicol.

- a) Thread-like texture
- b) Formation of isotropic area when the anisotropic sample was heated
- c) Crystallization from the anisotropic mesophase

Textures of mesophase including the thread-like nematic one are shown in Fig.5 together with the photograph that exhibits crystallization from the lyotropic mesophase.

Further studies on the physical property, conformational characteristic and the phase behavior of this novel liquid crystalline polymer is in progress.

References

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