Synthesis and Properties of Liquid Crystalline Polyesters with Banana-Shaped Mesogens

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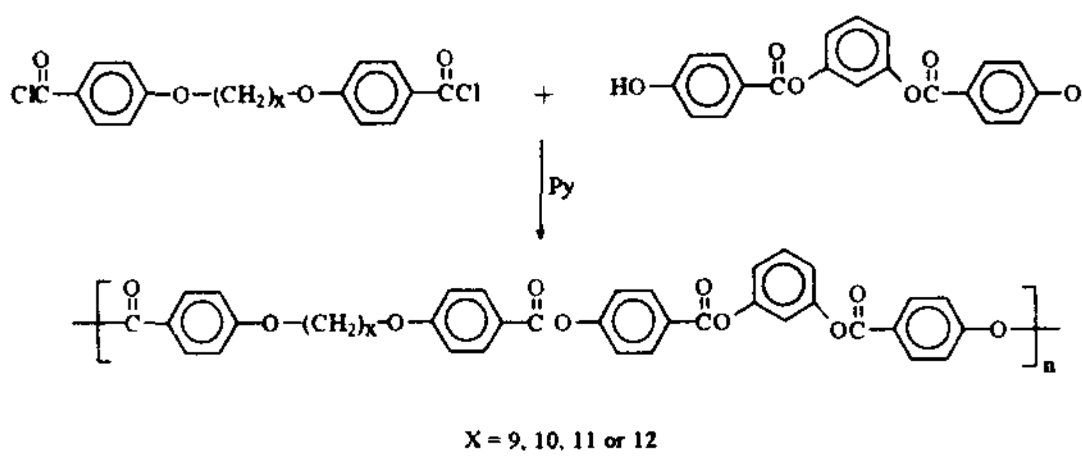
Abstract

A series of LC polyesters containing banana-shaped mesogen and flexible spacer were synthesized. Their structures were identified by FT/IR- and NMR-spectrometry. Thermal and mesomorphic properties were investigated by using DSC and polarizing microsope. Structure of mesophase was investigated by using x-ray diffractimetry.

1. Introduction

Since Meyer et al. [1] discovered ferroelectricity in tilted smectic phases of chiral molecules, chirality has been a most attractive subject in the research field of liquid crystals [2-6]. When any structural factors can reduce the overall symmetry of the mesophase, the chirality of mesophase could appear even in LC molecules without chemical chirality. In 1996, Niori et al. [7] observed the first obvious example of ferroelectricity in a smectic phase formed by non-chiral banana-shaped molecules. Link et al. [4] found spontaneous formation of macroscopic chiral domains in a fluid smectic phase derived from non-chiral molecules with bent cores. In 1997, at a conference in Berlin [8], the banana phases were tentatively named with the code letters B_1 to B_7 according to the order of discovery, which should not be mixed up with the notation of B for a smectic mesophase of rod-like molecules. Over the last few years, a considerable number of studies have been made on the relationship between the structure and properties for the compounds composed of bent cores such as banana-shaped molecules [9-21]. On the other hand, little attention has been given to polymeric materials containing banana-shaped mesogenic moiety [22].

In this study, we report the synthesis of aromatic polyesters consisting of banana-shaped mesogen and characterization of their mesophase, as well as the effect of structural variation of central core in the mesogenic unit. The polymers have been synthesized according to the polycondensation reaction shown in Scheme 1.



Scheme 1. Synthesis of LC Polyesters.

2. Experimental

IR and NMR spectra were obtained by a Jasco 300E FT/IR and Brucker DPX 200 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by differential scanning calorimeter (duPont TA 910 DSC) and polarizing optical microscope (Zeiss, Jenapol). DSC measurements were performed in a N_2 atmosphere. The DSC heating and cooling rates were of 20 °C/min. Optical textures were observed by the polarizing microscope equipped with a camera and a thermo-controller (Mettler FP82HT). X-ray analysis was performed in transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder

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which was sealed with a window of 7 μm thick Kapton films on both sides. The sample was heated with cartridge heaters and its temperature monitored by a thermocouple placed close to the sample. Subtracting the scattering from the Kapton gave a background scattering correction.

3. Results and Discussion

A series of new polyesters containing banana-shaped mesogen and flexible spacer were synthesized by polyesterification. The structures of polyesters were identified by FT-IR and NMR spectroscopy. The polymers were soluble in a mixture of chloroform and trifluoroacetic acid (98:2 v/v). The values of inherent viscosities were in the range of 0.43-0.72 dL/g. Polymers showed two melting transitions. The solid-to-solid transition occurred at 142-162°C, and the melting was observed at 193-224°C depending on the structure. By x-ray measurement, all polymers are semicrystalline. When 1,3-phenylene unit in the central core is modified with another aromatic unit, these polyesters can form the mesophase.

4. Acknowledgements

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5. References

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