

## ***Liquid Crystal Polymers***

### **Thermotropic Polyketones: A New Class of Main-Chain Liquid Crystalline Polymers**

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#### SUMMARY

The first examples of thermotropic liquid crystalline (LC) polyketones have been synthesized by the Friedel-Crafts acylation of biphenyl, fluorene and terphenyl with  $\alpha,\omega$ -dicarboxylic acid alkanes in a phosphorous pentoxide/methanesulfonic acid (PMMA) condensing agent. Polyketones prepared from biphenyl and fluorene exhibit good solubility as well as low thermal transition temperatures due to the copolymeric nature of these polymers. Both molecular weight and the inherent copolymer composition appear to influence the mesophase behavior in these polymers. Optical polarization microscopy has revealed smectic textures for all the polyketones exhibiting LC behavior.

#### INTRODUCTION

In our search for new classes of main-chain and side-chain thermotropic liquid crystalline (LC) polymers, we have focused on the examination of the interconnecting unit between the mesogen and the spacer or between the side-chain mesogen and the polymer backbone. These studies have led to several new classes of LC polymers; polyethers (1-6), polythioethers (7), aromatic poly(ether sulfone)s (8), poly(vinyl ether)s and poly(propenyl ether)s (9). Much of this effort has stemmed from a review of low molar mass liquid crystal literature with note taken as to the functionalities utilized to connect mesogens to flexible spacers. Besides ester and ether bonds, the keto linkage also seems to be prevalent in that body of literature (10-13). It is the goal of this paper to present our preliminary information on the synthesis and characterization of the first examples, according to our knowledge, of thermotropic main-chain LC polyketones.

#### EXPERIMENTAL

##### A. Materials

Biphenyl, terphenyl, fluorene, sebacic acid, 1,10-decanedicarboxylic acid, and phosphorous pentoxide were obtained from Aldrich. Methanesulfonic acid was obtained from Lancaster Synthesis. The phosphorus pentoxide / methanesulfonic acid condensing agent (PPMA) was prepared in a weight ratio of 1:10 as described in the literature (14). Reagents were used as received.

## B. Techniques

<sup>1</sup>H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Spectra were recorded from either D<sub>2</sub>SO<sub>4</sub> solutions at 100°C or in CDCl<sub>3</sub> solutions at room temperature both with TMS as internal standard. IR spectra were recorded from CHCl<sub>3</sub> cast films on KBr plates or KBr pellets on a Perkin-Elmer Model 1320 infrared spectrophotometer. Thermal transitions were determined with the aid of a Perkin-Elmer DSC-4 differential scanning calorimeter. Glass transition (T<sub>g</sub>) was determined at the inflection of the transition. All mesomorphic transitions, T<sub>1</sub>, T<sub>2</sub>, etc. and anisotropic-isotropic (T<sub>i</sub>) transition temperatures were read at the maximum of the endothermic or exothermic peaks. Heating and cooling rates were 10°/min, with indium used as a calibration standard. After the first heating scan, the sample was "annealed" at about 10°C above the isotropization temperature for 5 minutes. Under these initializing conditions, beginning with the second heating and cooling scans, all DSC scans gave perfectly reproducible data. The transitions reported in Table I were read during the second, or subsequent, heating and cooling scans. A Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP52 hot stage was used to observe the thermal transitions and to analyze the anisotropic textures (15). Gel permeation chromatography (GPC) analyses were carried out with a Perkin-Elmer Series 10 LC equipped with a LC-100 column oven, LC 600 autosampler and Sigma 15 data station. The measurements were made using the UV detector, THF as solvent (1 ml/min, 40°C), and a set of PL-gel columns of 10<sup>2</sup>, 5 x 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup> and 10<sup>5</sup> Å, and a calibration plot constructed with polystyrene standards (Supelco).

## C. Synthesis of the Polyketones

Polyketones were prepared at 60°C using PPMA as the condensing agent and solvent. All reactions become homogenous within 5 minutes of addition to PPMA. IR and NMR spectroscopy was utilized to determine chain end nature. An example of a polymerization follows. To 15 ml of PPMA, 0.8850g (5.5 mmol) of biphenyl was added and the suspension was heated to 60°C. At this temperature, 0.9232g (4.6 mmol) of sebacic acid was added with vigorous stirring. Reaction proceeded homogeneously thereafter and was continued for 3 to 4 hours. Polymer was collected by pouring the solution into rapidly stirred cold water. This suspension was stirred for one to six hours to hydrolyze anhydrides of methanesulfonic acid or other mixed anhydrides. The crude polymer was collected by filtration and purified by reprecipitation into acetone from 1-methyl-2-pyrrolidone (NMP) solutions. Further purification consisted of two acetone reprecipitations from NMP solutions. IR spectroscopy confirmed the absence of carboxylic acid termination.

## RESULTS AND DISCUSSION

Recently, Ueda and Kano have reported the first preparation of polyketones from diaryl compounds and dicarboxylic acids using a phosphorus pentoxide / methanesulfonic acid condensing agent (PPMA) (16). This agent was first prepared by Eaton, et. al., as a replacement for polyphosphoric acid (PPA) using either methanesulfonic acid or trifluoromethanesulfonic acid as the matrix solvent (15,17). One system prepared by Ueda and Kano utilized biphenyl with either sebacic acid or 1,12-dodecanedicarboxylic acid. This system would meet the requirements suggested by deGennes for

the preparation of main-chain LC polymers (18): mesogenic units separated by flexible spacers. No thermal studies, however, were reported for any of the systems prepared.

TABLE I

## SYNTHESIS AND CHARACTERIZATION OF THE LIQUID CRYSTALLINE POLYKETONES

| No.            | R <sup>b</sup> | -(CH <sub>2</sub> ) <sub>n</sub> - | YIELD (%) | $\bar{M}_n$ | $\bar{M}_w$<br>(GPC) | $\bar{M}_w/\bar{M}_n$ | THERMAL TRANSITIONS (°C) <sup>a</sup> |                  |                |                |                |                |                |                |                |                |
|----------------|----------------|------------------------------------|-----------|-------------|----------------------|-----------------------|---------------------------------------|------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                |                |                                    |           |             |                      |                       | HEATING                               |                  |                |                |                | COOLING        |                |                |                |                |
|                |                |                                    |           |             |                      |                       | T <sub>g</sub>                        | T <sub>1</sub>   | T <sub>2</sub> | T <sub>3</sub> | T <sub>4</sub> | T <sub>i</sub> | T <sub>1</sub> | T <sub>2</sub> | T <sub>3</sub> | T <sub>i</sub> |
| 1              | B              | 8                                  | 93        | ----        | ----                 | ---                   | 83                                    | 147              | 165            | 183            | ---            | 214            | 134            | 144            | 164            | 197            |
| 2              | B              | 8                                  | 41        | 2450        | 4230                 | 1.7                   | 33                                    | 126              | 167            | ---            | ---            | 171            | ---            | ---            | ---            | 129            |
| 3              | B              | 8                                  | 47        | 4120        | 8100                 | 2.0                   | 46                                    | 118              | 135            | 144            | ---            | 160            | ---            | ---            | ---            | 112            |
| 4              | B              | 10                                 | 50        | 3240        | 19700                | 60.9                  | 35                                    | 118              | 134            | 144            | ---            | 157            | ---            | ---            | ---            | 108            |
| 5 <sup>c</sup> | B              | 10                                 | 94        | ----        | ----                 | ---                   | 49                                    | 121              | ---            | ---            | ---            | 157            | ---            | ---            | ---            | ---            |
| 6              | F              | 8                                  | 78        | 1030        | 2460                 | 2.4                   | 44                                    | 103              | 119            | 130            | 137            | 146            | ---            | ---            | ---            | 108            |
| 7              | F              | 10                                 | 75        | 1680        | 7120                 | 4.2                   | 46                                    | 93               | 113            | 125            | 133            | 137            | ---            | ---            | ---            | 105            |
| 8              | T              | 10                                 | --        | ----        | ----                 | ---                   | --                                    | 162 <sup>d</sup> | ---            | ---            | ---            | ---            | ---            | ---            | ---            | ---            |

a) T<sub>g</sub>, GLASS TRANSITION; T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub>, MESOMORPHIC TRANSITIONS; T<sub>i</sub>, ANISOTROPIC-ISOTROPIC TRANSITION.

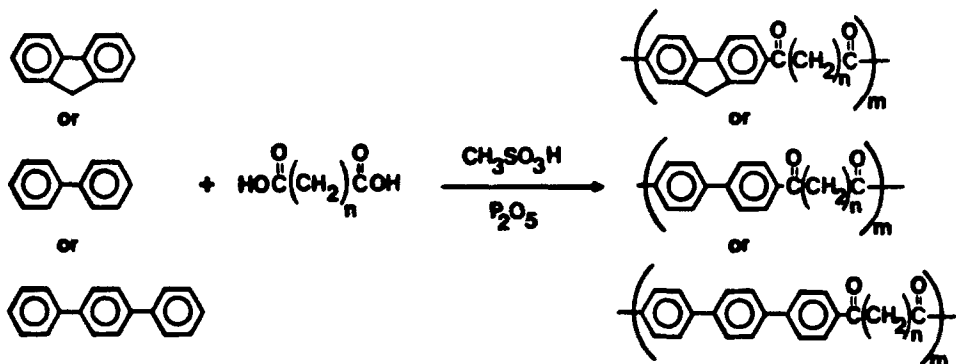
b) B, BIPHENYL; F, FLUORENE; T, TERPHENYL.

c) CARBOXYLIC ACID CHAIN ENDS AS DETERMINED BY IR.

d) T<sub>dec.</sub> = 200°C.

Behavior of LC polyketones might be anticipated from the behavior of low molar mass LC ketones. In general, the keto linkage has given rise to more ordered mesophases than comparative n-alkoxy derivatives at the expense of low thermal transition temperatures and solubility (10-13). Since we are interested in the influence of the mesogen-flexible spacer linkage in main-chain LC polymers, we have prepared polyketones from biphenyl, fluorene and terphenyl in combination with sebacic acid and 1,10-decanedicarboxylic acid. The reaction methodology for the preparation of these polyketones is given in Scheme 1.

The results of the synthesis and characterization of the LC polyketones are given in Table I. The solubility of the prepared polymers varies not only with the molecular weight, but also with the repeat structure, specifically the mesogenic unit. For polyketones prepared from biphenyl, solubility is good in solvents like THF and CHCl<sub>3</sub> at room temperature for number-average molecular weights up to approximately 4500. Fluorene based polyketones maintain a similar solubility up to only  $\bar{M}_n = 2500$ . For higher molecular weight polymers, hot 1-methyl-2-pyrrolidone and, eventually, concentrated sulfuric acid are required for clean



Scheme 1: Synthetic avenue used in the preparation of thermotropic liquid crystalline polyketones.

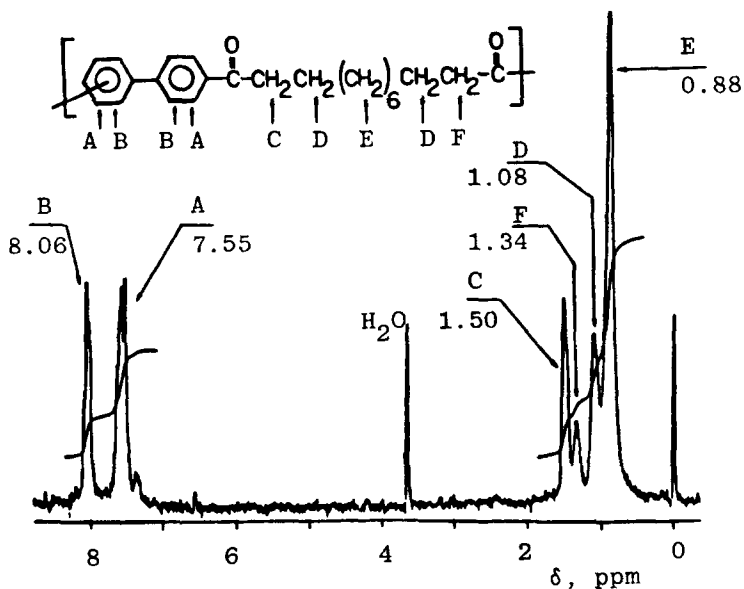


Figure 1: 200 MHz  $^1\text{H-NMR}$  ( $\text{D}_2\text{SO}_4$ , TMS,  $100^\circ\text{C}$ ) of a polyketone based on biphenyl (No. 4, Table I).

solutions. Polymers prepared from terphenyl, only one listed in Table 1, always produced gels during reactions and remained insoluble and infusible making work-up difficult.

Some of this behavior may be explained by the structures of the resulting polymers. In their preparations of polyketones by this methodology, Ueda and Kano observed ortho and para substitution in the

prepared polymers and indicated a strong monomer effect in the proportion of ortho to para isomers observed. Therefore, we have examined the chemical structure of polymers prepared from biphenyl by 200 MHz  $^1\text{H-NMR}$ . An example of a 200 MHz  $^1\text{H-NMR}$  ( $\text{D}_2\text{SO}_4$ ,  $100^\circ\text{C}$ , TMS) spectrum for a polymer prepared from biphenyl and 1,10-decanedicarboxylic acid is shown in Figure 1. As indicated no clear AA'BB' pattern is observed for a para substituted phenyl ring. In addition, signals are observed for  $-\text{CO}-\text{CH}_2-$  in the ortho (1.34 ppm, F) and para (1.50 ppm, C) configurations. It should be noted that these signals appear further upfield than might be expected, because the spectrum was recorded in deuterated sulfuric acid. From this spectrum, by measuring the integration corresponding to each signal, the content of ortho substitution is about 29 mol%.

The effect of ortho versus para substitution in preparation of the polyketones based on fluorene would be smaller due to an enhanced reactivity in the para position of the phenyl ring. With terphenyl, however, some degree of substitution might occur on the center ring leading to branching and crosslinking. We currently do not have information to support this conjecture, however, this would possibly explain the insolubility and infusibility of terphenyl containing polymers. The mixture of structural isomers in these polymers necessitates their consideration as copolymers, since a 4,4'-disubstituted biphenyl is mesogenic and a 4,2'-disubstituted biphenyl is not. This classification not only explains their solubility behavior, but also influences their thermal behavior.

The thermal phase behavior of these polymers has been characterized by differential scanning calorimetry (DSC) and optical polarization microscopy. Although X-ray diffraction data is not currently available to us, biphenyl and fluorene based polyketones appear to be amorphous. An example of a DSC thermogram is shown in Figure 2 for the biphenyl - sebacic acid system (No. 3, Table I). Upon heating, several small overlapping endothermic transitions are observed followed by a large isotropization endotherm. Only one transition, however, is observed on cooling. A higher molecular weight polymer (No. 1, Table I, Figure 3) of the same system exhibits completely different thermal behavior. Four transitions are observed both on heating and cooling. Presently, we do not have sufficient information to elucidate this behavior, but both molecular weight and the inherent copolymer composition seem to be important variables.

Fluorene based polyketones exhibit a similar thermal behavior to biphenyl containing low molecular weight oligomers. A DSC thermogram is shown in Figure 4 for a fluorene - sebacic acid polyketone (No. 6, Table I). Again several transitions are observed on heating with only one transition observed on cooling. Polymer prepared from terphenyl decomposed at  $200^\circ\text{C}$ .

The mesomorphic behavior of these polymers appears to be smectic as determined by optical polarization microscopy. Typically, bâtonnet structures are observed both on heating and cooling for fluorene and biphenyl containing polymers. Lower temperature phases in both biphenyl and fluorene polyketones exhibit more defined textures. An example of textures observed in these polymers are shown in Figure 5 for a fluorene - 1,10-decanedicarboxylic acid polymer (No. 7, Table I).

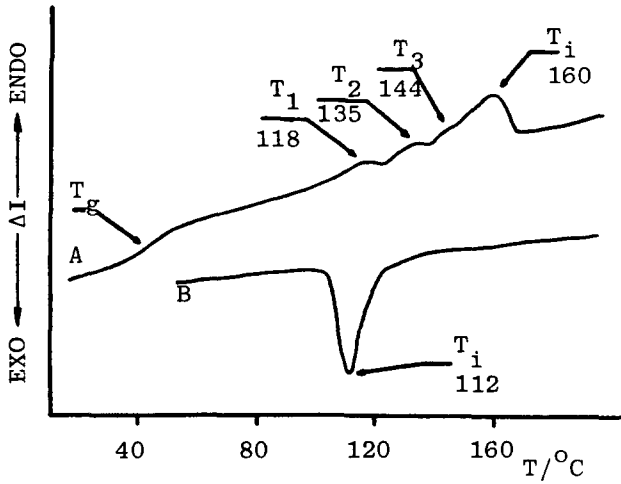


Figure 2: DSC thermograms for a polyketone based on biphenyl (No. 3, Table I): A) heating, B) cooling.

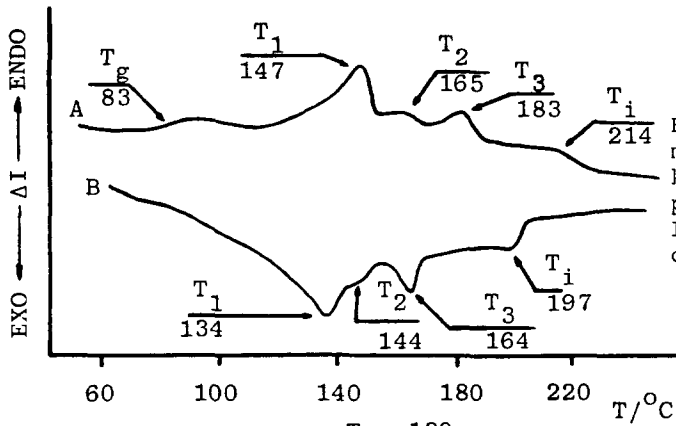


Figure 3: DSC thermograms for a polyketone based on biphenyl (No. 1, Table I): A) heating, B) cooling.

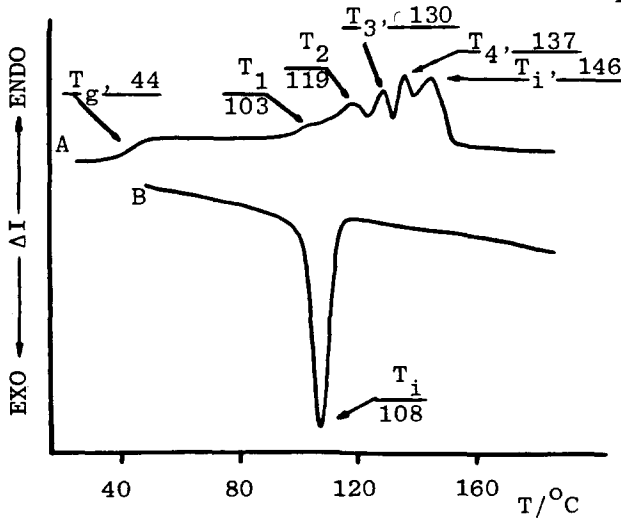


Figure 4: DSC thermograms for a polyketone based on fluorene (No. 6, Table I): A) heating, B) cooling.



Figure 5: Optical polarization micrograph for a polyketone based on fluorene and 1,10-decanedicarboxylic acid (No. 7, Table I); smectic bâtonnets at 135°C (heating cycle, 80x).

In conclusion, we have demonstrated that polyketones prepared from rod-like monomers such as fluorene and biphenyl with  $\alpha,\omega$ -dicarboxylic acid alkanes display mesomorphic behavior. According to our knowledge, these polymers represent the first examples of LC polyketones. In addition, the copolymeric nature of the polymerization leads to polymers having good solubility at low molecular weights. The copolymer composition and molecular weight seem to have a great influence on the mesomorphic properties of this system. Further studies are in progress to elucidate these trends.

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