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Liquid crystalline polyesters by staged-addition polycondensation

A. Delvin and C. K. Ober

Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, NY 14853, USA

SUMMARY

A series of model liquid crystalline (LC) polyesters have been prepared by low temperature solution polycondensation using staged addition methods. The model thermotropic polyesters were composed of aliphatic spacers and mesogenic groups made from substituted terephthalic acid and methyl hydroquinone. Both the mesogenic groups and the spacers were placed in the main chain. Attractive properties of these polymers include solubility in many organic solvents such as THF and DMSO with softening temperatures below 150°C. Some of these polymers show no melting transitions, and depending on the terephthalate group substituent, either smectic or nematic phases are formed. Results from GPC analysis show good solubility of polymers in THF with M_W lower than 10,000 compared to polystyrene standards. The synthesis and characterization of these LC polyesters are reported here.

INTRODUCTION

Ever since the recognition of liquid crystallinity in polymers approximately a decade ago, the number and types of new polymers with liquid crystalline behavior has increased rapidly. Recently a number of entirely aromatic LC polyesters have been commercialized. Fundamental studies of such polymers are difficult because of their high melting temperatures and limited solubility. Another class of polymers, composed of both spacers and mesogenic groups in the main chain, has been used to investigate the properties of main chain LC polyesters in general. They have lower melting points, but often retain the poor solubility characteristics of the rigid rod polymers (1,2).

We have been interested in using the latter class of polymers to investigate the rheological and physical properties of LC polyesters and to correlate their behavior with both molecular weight and distribution. In this regard, we have developed a family of LC polyesters by a straightforward synthetic route with improved solubility in solvents such as THF and DMSO. At the same time, these polymers have low transition temperatures and can therefore be readily studied in the melt.

The polymers were prepared using a staged-addition solution polycondensation reaction, outlined in Figure 1. Briefly, the mesogenic group was built up in the first stage by adding 2 parts of a substituted terephthalic acid to one part of substituted hydroquinone. In a second stage, to the product of the first stage, was added one part diol to introduce the spacer and to complete the polymerization. In this way, a mesogenic structure was built up to produce what is in effect a random copolymer. This copolymer has several possible mesogenic groups with different substituent arrangements. The thermal properties, and molecular weights of these polymers are described in the present communication. Preliminary WAXD studies of these new LC polymers are described elsewhere (3).

EXPERIMENTAL

1. *Synthesis of LC Polymers*

All chemicals were purchased from Aldrich; methyl hydroquinone (99%), nitroterephthalic acid (99%) and all diols were used as received. Bromoterephthalic acid (96%) was recrystallized with an 80/20 vol-% distilled water/ethanol solution. Pyridine was distilled and stored with desiccant. Solvents were used as received, and all glassware was oven dried.

Methylterephthalic acid could not be purchased commercially and so was synthesized by oxidation of 2,4-dimethylbenzoic acid with potassium permanganate and distilled water (4). Conversion of the starting material was followed by thin layer chromotography (TLC). Manganese oxide was filtered off and the filtrate was mixed with 1 N HCl to precipitate the product. The product was then removed from the acid solution by filtration and recrystallized in acetic acid. Finally, the precipitate was washed with deionized water and dried under vacuum at 60°C.

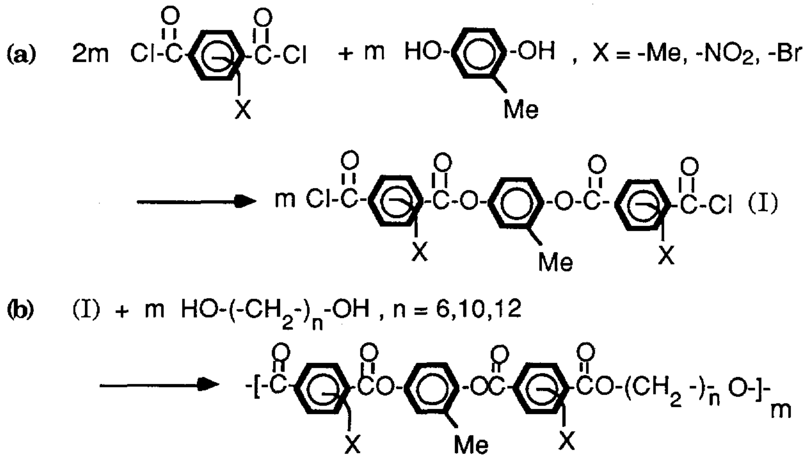
The substituted diacids (eg. bromoterephthalic acid, 0.0132 mol) were first converted to their acid chlorides by refluxing with thionyl chloride and 4-5 drops of DMF as catalyst. After two hours, the unreacted thionyl chloride was distilled off. Each polymerization step was carried out in the same reaction flask as the remaining diacid chloride. After distillation, in a typical polymerization, 0.82 g (0.59×10^{-3} mol) of methyl hydroquinone was dissolved in a graduated funnel with 20 ml methylene chloride and 25 ml pyridine. The solution was slowly dripped into the reaction flask and stirred over night under N_2 atmosphere.

Finally, polymerization was initiated by addition of 0.78 g (6.59×10^{-3} mol) hexamethylene diol that had been dissolved in pyridine and methylene chloride. This solution was dripped slowly into the reaction vessel over two hours; the reaction was then stirred for 24 hours under nitrogen atmosphere. The resulting polymer was washed in 1 N HCl, precipitated in methanol, extracted in a Soxhlet extractor with methanol and vacuum dried.

2. *Physical Characterization*

^{1}H-NMR was carried out on a Varian XL-200. All DSC traces were made using a Perkin Elmer DSC-2C differential scanning calorimeter. Inherent viscositities were measured with a Cannon-Ubbelhode viscometer in either DMF or 15% phenol in chloroform at 24°C. Molecular weights were determined using a Waters 804E GPC calibrated with monodisperse polystyrene standards through Ultrastyragel™ columns with 500, 10^3, 10^4, and 10^6Å pore sizes.

Figure 1 - Schematic of Polymer Synthesis



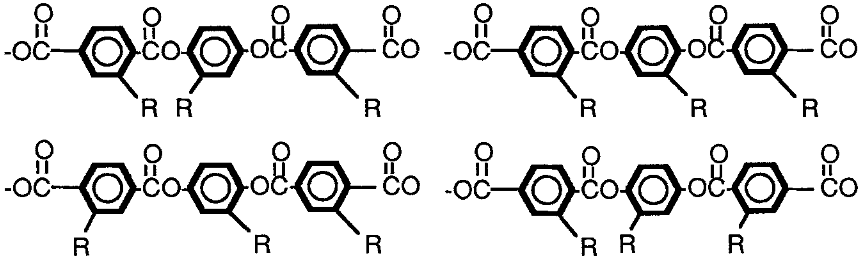
RESULTS AND DISCUSSION

The LC polyesters reported here were prepared by a staged-addition route instead of synthesizing specific monomers prior to polymerization. In the case of semiflexible LC polymers, the mesogenic structure is typically prepared, purified and isolated as a new monomer. The mesogenic group is then reacted with a spacer. Alternatively, the spacer is capped with components of the mesogenic group to form a symmetrical monomer, and then copolymerized with the missing mesogenic component.

We have instead reacted the components of the mesogenic group to produce an acid chloride capped intermediate, and then, without purification, reacted the intermediate with the spacer diol to form the polymer. Staged addition has been used previously to prepare block copolymers by solution polycondensation, and here we are forming random LC copolymers with alternating spacer and mesogenic components. By using substituted aromatic components, we have prepared an LC copolymer composed of at least 4 different isomers of the mesogenic group as shown schematically in Figure 2. These isomers are also placed in the chain in an aregic fashion (5). Studies of these polymers by ^{1}H-

NMR indicated that the composition of the polymers was in the same 2:1:1 diacid:hydroquinone:diol ratio that was introduced in the starting reaction mixture.

Figure 2 - Possible Mesogenic Group Isomers



Shown in Table 1 are some of the properties measured for the LC polymers. The following designations were used for the polymer structures described in this report: the MP series contained methylterephthalic acid, the BP series contained bromoterephthalic, and the NP series contained nitroterephthalic acid. All polymers possessed a central methylhydroquinone unit. The numerical component of the name refers to the length of the polymethylene spacer. Listed in the table are the flow temperatures observed by optical microscopy as well as the temperature at the onset of clearing. Values of dilute solution viscosity measured in the specified solvents as well as the number

Table 1 - Properties of Soluble LC Polyesters

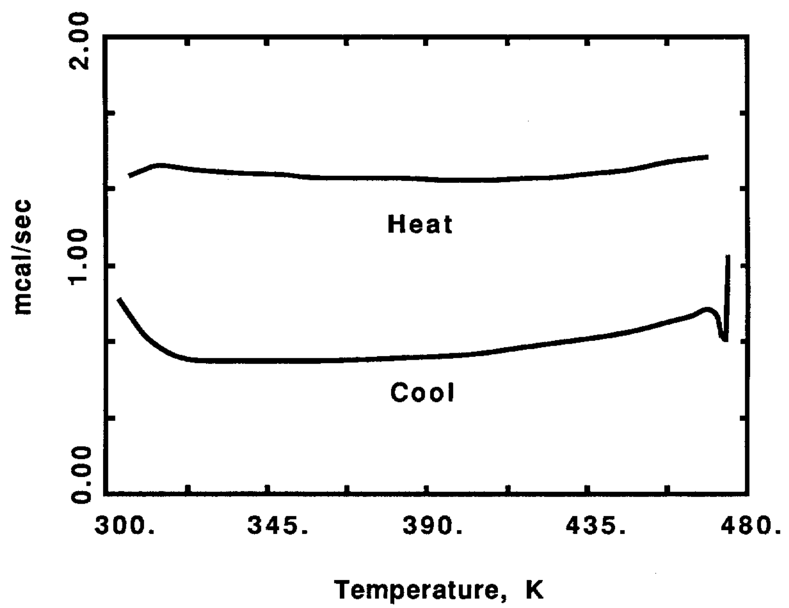
Polymer	T_f,°C	T_i,°C	[η], dl/g*	M_n	Solubility
MP6	167	210	0.50	4,120	DMF, THF, CH_2Cl_2
MP10	169	198	0.14	1,800	THF, $CHCl_3$, CH_2Cl_2
MP12	170	222	0.26	3,400	THF, DMSO, DMF, $CHCl_3$
NP10	204	230	0.44	--	DMF, DMSO
BP6	127	190	0.43	4,300	THF, $CHCl_3$, CH_2Cl_2
BP10	157	194	0.14	1,250	THF, $CHCl_3$, DMSO
BP12	168	187	0.42	3,900	THF, $CHCl_3$, DMSO

T_f = onset of flow, T_i = clearing ,
[η] = inherent viscosity, M_n = number average molecular weight;
*15 wt-%phenol in chloroform used as solvent.

average molecular weights determined by GPC are listed. Typical solvents for each polymer are also listed.

Thermal analysis shows that these polymers possessed little or no crystallinity, and are in fact "liquid crystalline glasses". DSC traces indicate that both melting and clearing transitions, if present, are extremely small or very broad. The DSC heating and cooling trace for BP6 shown in Figure 3 is typical for this class of polymers. Certainly in the case of the clearing transition, there was no DSC peak corresponding to the disappearance of the mesophase which could be observed by optical microscopy. The disappearance of the mesophase was observed to occur over a broad temperature range as exhibited by an extended biphasic region. Shown in Figure 4 is the appearance of the texture of polymer BP6 at the onset of the biphasic region. Softening temperatures of these polymers were in the range of 85 to 120°C. Glass transition temperatures occurred below the softening temperature, and in one case (BP6), T_g was measured as ca. 42°C.

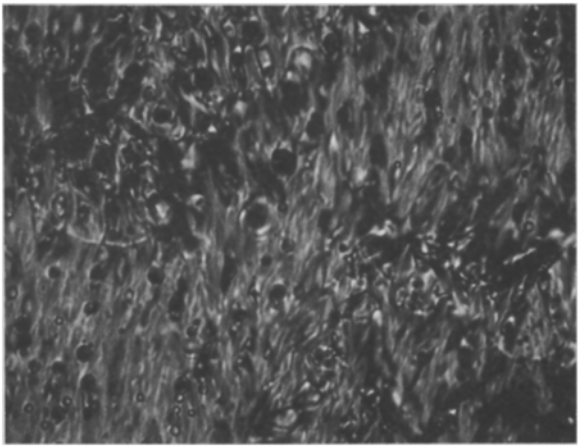
Figure 3 - Heating and Cooling Curves of BP6



Probably the most interesting property of these LC polymers is that they are readily soluble in many common organic solvents. To the best of our knowledge, these are among the first of a growing family of LC polymers to have solubility in organic solvents such as THF. In a prior report, LC polyethers which had similar solubilities were reported by Percec (6). Soluble LC polyesters with trifluoromethyl groups (7) and with central cyclohexyl components in the mesogenic group have also been reported (8).

The solubility of the LC polyesters described here has permitted us to record their GPC chromatograms. GPC data is reported along with other characteristics of these polymers in Table 1. Molecular weights were estimated using a polystyrene calibration curve. GPC traces showed that the molecular weight distribution, M_w/M_n, ranges from 2 to 3 for all samples. Based on polystyrene standards, the LC polymers with M_w up to 15,000 are completely soluble in THF. The polymers containing bromo and methyl substituents on the terephthalic residues were soluble in chlorinated solvents as well as THF. The nitro containing polymers were not soluble in THF, and were therefore not studied by GPC. Even though molecular weights could not be measured for all polymers by GPC, fibers and films could be pulled from these polymers indicating their high molecular weight. This is in marked contrast to other LC polyesters that we have prepared (9,10).

Figure 4 - Optical Photomicrograph of Polymer BP6 Showing Onset of Biphasic Behavior



Magnification:
128x

Temperature:
185°C

The liquid crystalline polyesters reported here are among the first to have observed solubility in common organic solvents. This improved solubility is believed to be based on the fact that these polyesters are composed of several isomeric forms of the same mesogenic group. The copolymerization has also led to reduced melting temperatures and essentially no crystallinity in the solid. At the same time, the range of mesophase stability was quite broad and biphasic behavior was observed.

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