Polymer Bulletin 27, 257–260 (1991)

Polymer Bulletin

Liquid crystalline polyesters with two-dimensional mesogenic units

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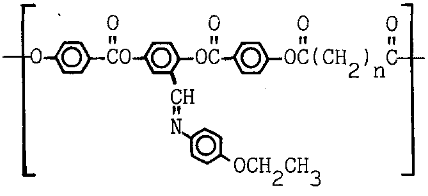
Dedicated to Prof. Dragutin Fleš on the occasion of his 70th birthday

Summary

A series of thermotropic, liquid crystalline (LC) polyesters was prepared in which the mesogenic group contained an unusually large, polarizable pendant group in an attempt to increase intermolecular interactions so as to impart a more isotropic character to the mechanical properties of the solid polymer. The series included repeating units containing main chain, polymethylene flexible spacers of increasing lengths. All of the polymers formed stable nematic LC phases and had relatively low melting temperatures, but recrystallization from the melt was very slow in each case.

Introduction

Many new types of mesogenic structures are being evaluated as repeating units in main chain, liquid crystalline polymers, LCPs, especially structures with complex geometries (1,2). One objective of these evaluations is to impart a more isotropic or three-dimensional behavior to the mechanical properties of either molded LCP materials, which generally have poor lateral strength, or extruded LCP fibers, which generally fibrillate very easily. The present study is concerned with the synthesis and properties of a series of main chain, thermotropic polyesters, I, based on branched mesogenic units, which may impart a substantial two-dimensional molecular geometry to the polymer as shown below (3) and possibly, therefore, a three-dimensional degree of interchain interaction:



; n = 4, 6, 8

I

Results and discussion

The polyesters in this series (Ia, Ib, Ic) were prepared by the reaction of a substituted hydroquinone monomer, 2,5-dihydroxybenzylidene-4-phenetidine (II), with a diacid chloride monomer selected from

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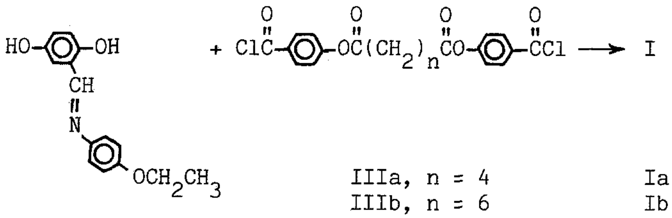
*To whom offprint requests should be sent a series of α,ω-bis(4-chloroformylphenyloxycarbonyl)alkanes, III, containing either 4 (IIIa), 6 (IIIb) or 8 (IIIc) methylene groups, as shown below:



II

IIIa, n = 4 Ia
IIIb, n = 6 Ib
IIIc, n = 8 Ic

Monomer II was prepared in high yield by the reaction of 2,5-dihydroxybenzaldehyde with 4-phenetidine. The monomers of Series III were prepared by the procedure of Bilibin and coworkers (4). The results of the spectroscopic analyses and elemental analyses of the Series III monomers were in good agreement with the expected structures. The reactions of II with each of the three monomers of Series III were carried out in 1,1,2,2-tetrachloroethane at 0°C to obtain the series of polymers, Ia,b,c, and the molecular weights and thermal properties of the polymers obtained are given in the table.

The characterization of the liquid crystalline properties of this series of new LC polymers was carried out by differential scanning calorimetry, DSC, and by use of a hot stage on a polarized light microscope. Heating and cooling rates of 40°/min, which are high for the DSC method, were set after observation of possible decomposition of the polymers at temperatures slightly higher than 200°C. The results obtained by this method for the melting, T_m, and isotropization, T_i, transitions for the polymers of Series I are collected in Table 1. As seen in the data in this table, each polymer was subjected to two heating cycles and an intermediate cooling cycle.

TABLE
Molecular weights and thermal transitions of Series III polymers

Polymer	$\overline{M}_n$	$\overline{M}_w$	T_m,[a] °C	DSC Cycle	T_i,[a] °C
Ia	4800	8400	77-105(92)	1st heating	210-237(221)
				1st cooling	204-225(212)
				2nd heating	200-237(221)
Ib	4600	8100	71-100(92)	1st heating	210-230(219)
				1st cooling	200-220(214)
				2nd heating	208-230(217)
Ic	2900	5200	80-100(85)	1st heating	157-190(172)
				1st cooling	160-174(165)
				2nd heating	157-190(172)
				2nd cooling	162-177(167)

[a] Transition temperatures were taken as the peak values of the endotherms in the DSC thermograms and are given in brackets.

For Polymer Ia no crystallization exotherm was observed in the DSC cooling thermogram, but the isotropization and deisotropization processes were reproducible in multiple heating and cooling cycles. The isotropization transition in the second heating cycle of this polymer had a temperature range somewhat broader than that in the first heating cycle, but there was little difference in the peak value. Similarly, no recrystallization process was observed for Polymer Ib, and furthermore, no melting endotherm was observed in the second heating cycle even for a sample that was annealed for 24 hours at a temperature 15°C below the first cycle melting transition. Nevertheless, the isotropization-deisotropization transitions were also highly reproducible in the multiple heating-cooling cycles of Polymers Ib and Ic, even though the melting transitions were not. All three polymers showed typical nematic textures by polarized light microscopy above the first heating cycle T_m.

Experimental

Monomer II was synthesized by the reaction of 2,5-dihydroxybenzaldehyde and 4-phenetidine as described below. 4-Phenetidine, 8 ml, was dissolved in 15 ml dry methanol. Into this solution was added 4 g of the 2,5-dihydroxybenzaldehyde in 15 ml dry methanol. The reaction was kept under nitrogen and at room temperature, and a yellow precipitate was slowly formed, from which 6 g of the monomer (81% yield) was obtained; M.P. 142°C. Analysis of the monomer by mass spectroscopy gave the expected molecular weight of 257. Elemental analysis: Calcd., C: 70.04, H: 5.84, N: 5.45; Found, C: 70.00, H: 5.80, N: 5.34. The proton NMR spectrum of the monomer in deuterated acetone contained a triplet at 1.29-1.46 for 3 H of the CH_3 in CH_3CH_2O-, a quartet at 3.95-4.21 for 2 H of the CH_2 in CH_3CH_2O-, a multiplet at 6.81 to 7.42 for 7 H of the benzene rings, a singlet at 8.74 for 1 H of the CH=N. Two singlets at 7.88 and 12.5 for the two OH groups both disappeared after D_2O treatment.

The series of monomers, IIIa-c, was prepared by the procedure reported by Bilibin (4), and each was characterized by mass spectroscopy, ^1H NMR spectroscopy and melting point measurements. The results were in good agreement with those reported in the literature (4,5). The elemental analyses of these monomers were as follows:

	Calcd.		Obsvd.	
Monomer	C	H	C	H
IIa	56.71	3.81	56.59	3.80
IIb	58.55	4.47	58.41	4.37
IIIc	60.14	5.05	60.25	5.09

Acknowledgment

The support of this study by the State Education Commission of China and by the National Natural Science Foundation of China is highly appreciated.

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Accepted September 5, 1991 C