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Thermotropic Functionalized Polyesters with Main-Chain Aromatic Ortho-Linked Units

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ABSTRACT: Three new series of soluble, low transition temperature, main-chain liquid crystalline polyesters and their six related LC model compounds were synthesized by a low-temperature solution method. These polyesters contain ortho-linked units or para-linked units with a bulky side group (phenylhydroquinone) and conjugated double bonds in the main-chain and can be cross-linked thermally and photochemically. The ortho-linked units used in this study were catechol, 4-methylcatechol, 4-nitrocatechol, 3,4-dihydroxybenzaldehyde, and 2,3-naphthalenediol. *p*-Oxycinnamoyloxy and *p*-phenylenediacryloyloxy groups introduced the reactive carbon–carbon double bonds in the main chains. All of them are thermotropic and formed nematic and/or smectic phases over broad ranges of temperatures in spite of high amounts of ortho-linked units in their structures. The synthesis of some of these polymers by transesterification in the melt at 275 °C produced insoluble polymers with a cross-linked structure.

I. Introduction

During the last decade liquid crystalline (LC) polymers have been developed and applied in electronics, in optoelectronics, and as new self-reinforced engineering materials.

LC polymers can be functionalized with reactive groups in order to modify their properties. By a cross-linking reaction between active groups LC elastomers of different structures can be formed. These permanent cross-linked networks have elastic properties and show thermodynamically stable and reversible LC phases.[1-4] Associated with these properties are the easy orientation of the LC phases by stretching the sample[1,3,5,6] and the alteration of its shape by external electric fields.[7] Cross-linking between active groups may also be used to prevent filbrillation which is one drawback to a broader commercial development of melt-processable LC polyesters.

The synthesis and study of functionalized main-chain thermotropic LC polyesters can be made difficult due to the low solubility and high-temperature transitions of these polymers.[8-11] These two characteristics can be conveniently modified by copolymerization with suitable comonomers: flexible units, kinks, and units which reduce the symmetry of the backbone. In particular, random copolymerization with asymmetric backbone entities and with entities with bulky side groups produces liquid crystalline polyesters with an asymmetric backbone and with a lack of a regular backbone sequence. These polymers have lower temperature transitions and greater solubility.[12-17a,b]

The solubility in common solvents and the low-temperature transitions of the functionalized main-chain LC polyesters described in this article were achieved by incorporating high proportions of sharply bent ortho-linked units or a para-linked unit with a bulky side group (phenylhydroquinone) in their chains.

The ortho-phenylene unit is a strongly angular nonmesogenic entity. However, it has been suggested that when this unit forms part of LC polymeric main chains, they are somehow excluded from the chains in such a way that the linearity of the chains is not drastically decreased.[16] In fact several wholly aromatic thermotropic LC copolyesters have been reported incorporating relatively high amounts of 1,2-dihydroxybenzene (catechol)[17a,b] (polymer I in Figure 1)[17a] as a comonomer in their structures. Only a low molecular weight LC compound with an aromatic ortho-linked unit as the rigid link between two mesogenic units has been described until now (compound I in Figure 1).[17c] This compound can be considered as the precursor of these LC polyesters with ortho-linked units.[17d]

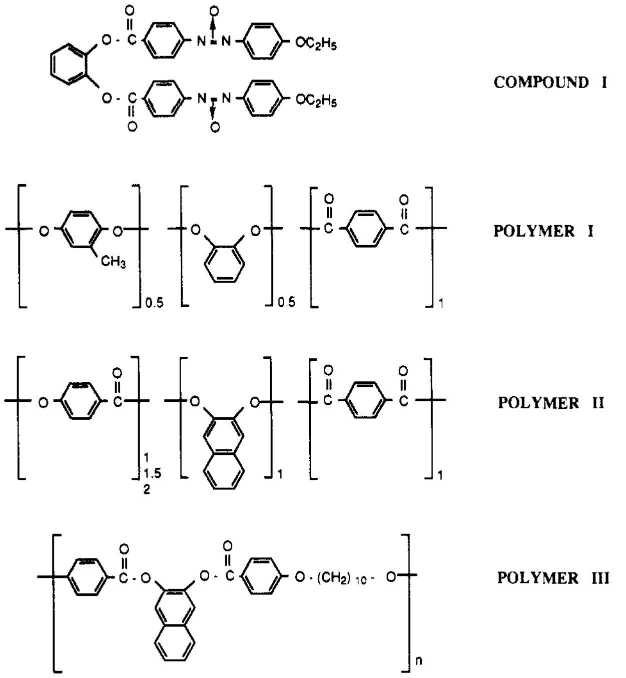

Figure 1. Compositions of previously reported LC esters with ortho-linked units.

2,3-Naphthylene is another ortho-linked sharply bent unit. It has been shown that the interlocking effect by the extruding 2,3-naphthylene unit can compensate for the destabilizing effect produced by this nonlinear unit, and LC polyesters incorporating high proportions of these units have been described (polymer II in Figure 1).[18] Also a thermotropic nematic main-chain semiflexible polyester incorporating 2,3-naphthalenediol as the central core of the mesogenic units has been reported[19] (polymer III in Figure 1).

p-Oxycinnamoyloxy and *p*-phenylenediacryloyloxy groups were used as a means of introducing a reactive function (carbon–carbon double bond) in the chemical structure of the LC polyesters described in this article.

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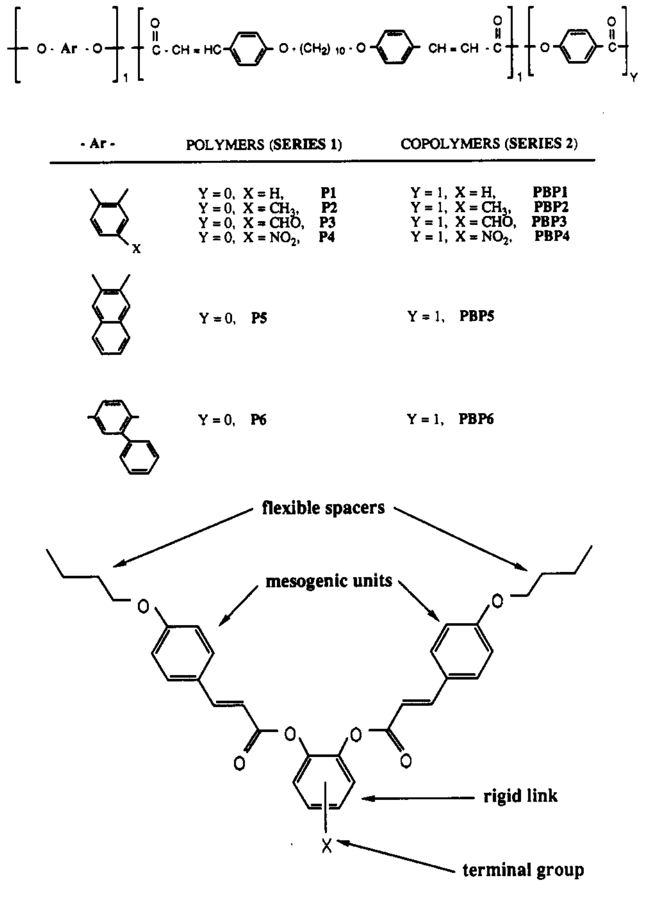


Figure 2. (a, top) Compositions of polymers of series 1 and 2. (b, bottom) Structure of the rigid units of polyesters P1–P5 (series 1).

Both groups have been used for the construction of cross-linkable LC polymers.[8,9,20]

The polyesters described in this paper are the following: Semiflexible polyesters P1–P5 (series 1) were synthesized with catechol, substituted catechols, and 2,3-naphthalenediol as the rigid links between the mesogenic units which are interconnected by decamethylene spacers (Figure 2a). The structure of the U-shaped rigid units of polyesters P1–P5 (series 1) is illustrated in Figure 2b. In addition, polymer P6 with phenylhydroquinone as the central core of the mesogenic units was synthesized.

It is known that copolymerization with *p*-hydroxybenzoic acid produces a considerable stabilization of the mesophase along with a notable decrease in the T_m and crystallinity of the copolymers.[21] Consequently and in an effort to obtain polymers with these characteristics, copolyesters of *p*-hydroxybenzoic acid, PBP1–PBP6 (series 2) (Figure 2), and wholly aromatic copolyesters of *p*-hydroxybenzoic acid and *p*-phenylenediacrylic diacid, PDA1–PDA6 (series 3), were synthesized (Figure 3).

The polymers were synthesized by condensation of carboxylic acids and phenols in dissolution at mild temperatures (Figure 4). Transesterification of carboxylic acids with the acetylated phenols at high temperatures (Figure 5) produced polymers with a cross-linked structure, P1c, P2c, P6c, PBP1c, PBP6c, and PDA1c.

Also, low molecular weight liquid crystalline model compounds M1–M6 with the same structure as that of the repeating mesogenic units of polymers P1–P6 were synthesized (Figure 6).

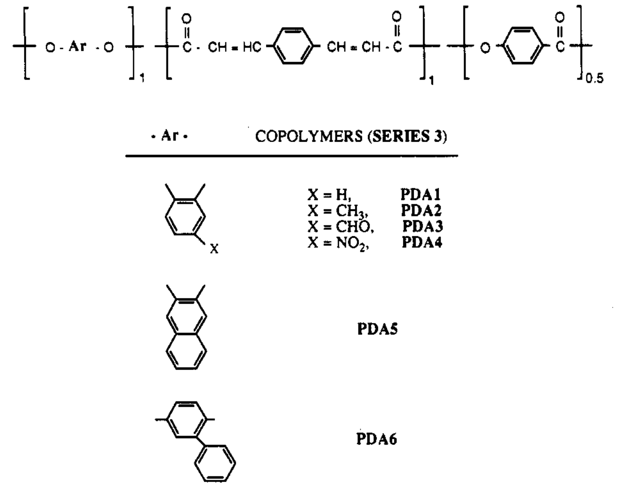


Figure 3. Compositions of polymers of series 3.

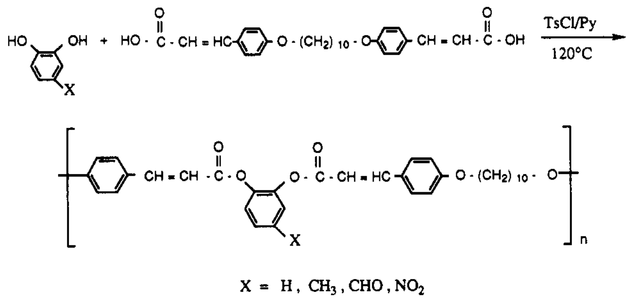


Figure 4. Synthesis of polymers P1–P4 (series 1).

Thermal properties and liquid crystallinity of the polymers and model compounds were studied by use of differential scanning calorimetry and hot-stage polarized microscopy. The solubility in common solvents and the thermal and photochemical cross-linking of the synthesized polymers were also studied.

II. Experimental Section

II.1. Materials. Catechol, 4-methylcatechol, 3,4-dihydroxybenzaldehyde, 4-nitrocatechol, 2,3-naphthalenediol, phenylhydroquinone, *p*-phenylenediacrylic diacid, and *p*-hydroxybenzoic acid were purchased from Aldrich.

p-Acetoxybenzoic acid (mp = 198 °C) and diacetates of catechol (mp = 64 °C), 4-methylcatechol (mp = 53 °C), and phenylhydroquinone (mp = 72 °C) were prepared by reacting *p*-hydroxybenzoic acid, catechol, 4-methylcatechol, and phenylhydroquinone with acetic anhydride at 100 °C, and the products were recrystallized from toluene, ethanol, and ethanol/water and distilled under a reduced pressure, respectively.

4-(Decycloxy)cinnamic acid and 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) were synthesized as described previously.[8]

II.2. Synthesis. Synthesis of Polymers. Polymers P1–P6 (series 1), PBP1–PBP6 (series 2), and PDA1–PDA6 (series 3) were synthesized by direct polyesterification of the acids with the phenols with tosyl chloride in pyridine by the method described by Higashi et al.[22] IR, UV, and elemental analysis data of the obtained polymers are given in Table I.

II.2.1. Synthesis of Polymers P1–P6. Since the synthetic procedure was the same for these polymers, only a representative example, for the preparation of polymer P1, is given. A pyridine solution (10 mL) of tosyl chloride (13 mmol) maintained at room temperature for 30 min was added to a solution of 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) (5 mmol) in pyridine (10 mL) and DMF (10 mL), and the mixture was maintained at room temperature for 10 min and then at 120 °C for 10 min. To this mixture was added dropwise a pyridine (10 mL) solution of catechol (5 mmol) at 120 °C for 20 min, and the whole mixture was maintained at 120 °C for 3 h. Isolation of the polymer was carried out by pouring the cold solution into 150 mL of acetone.

Table I
Elemental Analysis, IR, and UV Spectroscopy Data of Polymers

	%C		%H		IR (BrK), cm^{-1}			
polymer	found	calcd	found	calcd	ν(C=O)	ν(C=C)	ν(C-O)	UV (Cl$_3$CH): λ_{max}, nm
P1	75.15	75.53	6.05	6.71	1731	1630, 984	1289, 1172	305, 319
P2	75.20	75.79	6.33	6.90	1733	1630, 982	1257, 1173	304, 315
P3	73.55	73.92	5.98	6.38	1732, 1698	1631, 982	1258, 1174	307, 322
P4[a]	69.42	69.73	6.23	6.02	1737	1629, 981	1257, 1170	307, 320
P5	77.49	77.26	6.05	6.48	1733	1628, 982	1254, 1172	304, 315
P6	77.22	77.89	6.43	6.54	1731	1627	1255, 1166	306, 321
PBP1	74.03	74.53	6.43	6.10	1737, 1732	1629, 982	1256, 1158	304, 318
PBP2	74.12	74.76	6.31	6.27	1737, 1734	1629, 982	1256, 1172	304, 318
PBP3	73.53	73.24	5.11	5.85	1736, 1733, 1698	1628, 980	1255, 1159	305, 320
PBP4[b]	69.17	69.77	5.26	5.57	1737	1628, 982	1256, 1160	305, 320
PBP5	76.49	76.04	5.29	5.95	1735, 1732	1629, 982	1254, 1159	304, 318
PBP6	76.10	76.61	6.44	6.02	1734, 1731	1631	1257, 1156	306, 321
PDA1	73.02	73.29	4.27	4.00	1735, 1730	1632, 977	1239, 1165	306, 319
PDA2	73.14	73.76	4.05	4.40	1737, 1731	1632, 979	1257, 1135	304, 317
PDA3	72.02	72.05	3.21	3.71	1737, 1731, 1694	1632, 979	1251, 1132	305, 317
PDA4[c]	64.15	64.99	3.35	3.30	1738, 1735	1632, 979	1256, 1161	309, 324[d]
PDA5	75.87	76.11	4.32	4.01	1737, 1734	1632, 977	1243, 1163	309, 325[d]
PDA6	77.34	77.09	4.14	4.23	1735, 1730	1633, 978	1241, 1135	311, 330[d]

[a] %N: found = 2.01, calcd = 2.39. IR (cm^{-1}): 1527, 1348 (NO$_2$, st). [b] %N, Found = 1.52, Calcd = 1.98. IR (cm^{-1}): 1528, 1348 (NO$_2$, st). [c] %N, Found = 3.23, Calcd = 3.52. IR (cm^{-1}): 1529, 1349 (NO$_2$, st). [d] UV spectra of these polymers were obtained using *sym*-tetrachloroethane solutions.

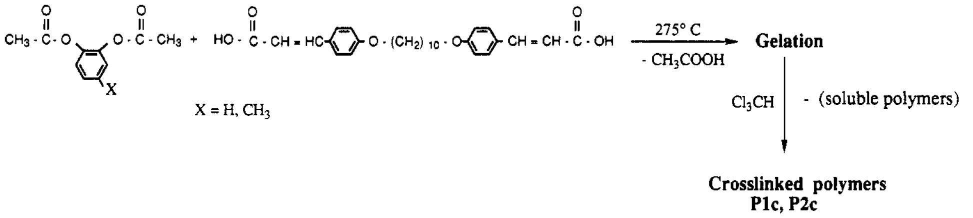


Figure 5. Synthesis of cross-linked polymers Plc and P2c.

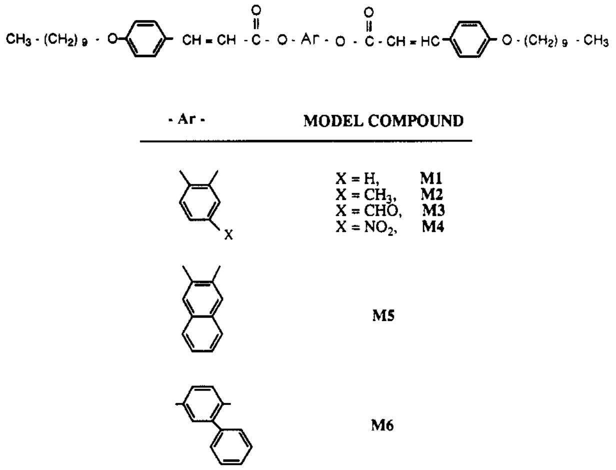


Figure 6. LC model compounds.

The precipitated polymer was filtered off, redissolved in chloroform and reprecipitated in acetone, extracted with acetone in a Soxhlet apparatus, and vacuum dried.

II.2.2. Synthesis of Polymers PBP1–PBP6. Since the synthetic procedure was the same for these polymers, only a representative example, for the preparation of polymer PBP1, is given. A pyridine (10 mL) solution of tosyl chloride (15 mmol) maintained at room temperature for 30 min was added dropwise for 20 min to a hot solution of 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) (4 mmol), catechol (4 mmol), and *p*-hydroxybenzoic acid (4 mmol) in pyridine (10 mL) and DMF (10 mL) preheated at 120 °C for 10 min. The whole mixture was maintained at 120 °C for 3 h. Isolation of the polymer was carried out by working up as described above.

II.2.3. Synthesis of Polymers PDA1–PDA6. Since the synthetic procedure was the same for these polymers, only a representative example, for the preparation of polymer PDA1, is given. A pyridine (10 mL) solution of tosyl chloride (13 mmol) maintained at room temperature for 30 min was added dropwise for 20 min to a hot solution of *p*-phenylenediacrylic diacid (4 mmol), catechol (4 mmol), and *p*-hydroxybenzoic acid (2 mmol) in pyridine (10 mL) and DMF (10 mL) preheated at 120 °C for 10 min; the whole mixture was maintained at 120 °C for 3 h. Isolation of the polymer was carried out as described above.

II.3. Synthesis of Model Compounds. Compounds M1–M6 were synthesized by direct esterification with tosyl chloride in pyridine. Compound M1: A pyridine solution (10 mL) of tosyl chloride (13 mmol) maintained at room temperature for 30 min was added to a solution of 4-(decyloxy)cinnamic acid (5 mmol) in pyridine (10 mL) and DMF (10 mL), and the mixture was maintained at 120 °C for 10 min. To this mixture was added dropwise a pyridine (10 mL) solution of catechol (2.5 mmol) at 120 °C for 20 min, and the whole mixture was maintained at 120 °C for 3 h. M1 was separated by pouring the cold solution into ice–HCl(concentrated), washed with water, and recrystallized in ethanol. Yield was 70%. The other model compounds M2–M6 were obtained by a similar procedure and with yields ranging from 65 to 80%. IR, UV, and elemental analysis data of these compounds are given in Table II.

II.4. Synthesis of Cross-Linked Polymers by Melt Transesterification. Polymers P1, P2, P6, PBP1, PBP6, and PDA1 were also obtained by high-temperature melt transesterification reaction of the carboxylic acids with the acetylated phenols. The high temperatures used for the synthesis of these polymers produced thermal cross-linking of the mixtures of the reaction. The cross-linked polymers isolated from these mixtures will be designated Plc, P2c, P6c, PBPlc, PBP6c, and PDAlc in order to differentiate them from the related un-cross-linked polymers P1, P2, P6, PBP1, PBP6, and PDA1.

As a very similar procedure was used to prepare all these cross-linked polymers, only a representative example, for the preparation of Plc, is given: 2.15 mmol of 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) and 2.15 mmol of the diacetate of catechol were introduced into a polycondensation tube, and dry nitrogen was bubbled at room temperature for 30 min. The tube was then placed into a salt bath preheated to 275 °C. After approximately 30 min of reaction the generation of acetic acid

Table II
Elemental Analysis, IR, and UV Spectroscopy Data of Model Compounds

	elem anal.				IR (BrK), cm^{-1}			
	%C		%H					
compd	found	calcd	found	calcd	ν(C=O)	ν(C=C)	ν(C-O)	UV (Cl_3CH): λ_{max}, nm
M1	77.05	77.38	8.77	8.56	1725	1626, 988	1290, 1170	305, 314
M2	77.59	77.55	8.03	8.68	1722	1627, 988	1290, 1172	306, 314
M3	75.87	76.02	8.30	8.22	1736, 1701	1628, 982	1276, 1177	306, 318
M4[a]	72.45	72.60	8.07	7.89	1736	1627, 973	1290, 1178	307, 319
M5	78.33	78.65	8.27	8.25	1729	1625, 966	1253, 1137	305, 315
M6	79.23	79.12	8.15	8.23	1729	1626, 972	1288, 1174	308, 321

[a] %N: found = 1.88, calcd = 1.92. IR (cm^{-1}): 1529, 1342 (NO_2, st).

Table III
General Properties and Transition Temperatures of Polyesters of Series 1

polymer	$\eta_{0.5}$,[a] dL/g	T_a,[b] °C	t_a,[c] h	T_g,[d] °C	T_{cr},[e] °C	$T_{k-k'}$,[f] °C	T_m, °C	LC[g] phase	ΔH_m,[h] kJ/mol	T_i, °C	ΔH_i,[h] kJ/mol	ΔS_i, kJ/mol
P1	0.20	A[i]		41	92		122	N	2.7	142	2.5	6.0
		B[j]		40				N		141	2.5	6.0
		90	12			107	120	N	18.7	141	2.7	6.5
		100	12				119	N	17.2	142	3.0	7.2
		110	24	49[k]	75		125	N	18.5	142	3.0	7.2
P2	0.18	A		32			65[l]	S		155	1.8	4.2
		B		31				S		154	2.0	4.7
P3	0.15	A		40				S + N		193	1.1	2.3
		B		41				S + N		193	1.1	2.3
		80	12	41			88	S + N	2.1	193	1.2	2.5
		85	12	40			90	S + N	2.0	193	1.1	2.3
P4	0.16	A		36				S		211	2.0	4.1
		B		35				S		213	2.1	4.1
		65	12	35			78	S	2.3	214	2.0	4.1
		70	12	36			80	S	2.1	214	1.9	4.0
P5	0.18	S		59	133			S + N		240	*m*	
		B		59				S + N		241	*m*	
		145	12	61		143	148	S + N	9.3	241	*m*	
		150	12	60			146	S + N	8.7	239	*m*	
P6	0.42	A		62	122	145	160	N	6.9	203	3.9	8.2
		B		62			160	N	0.4	196	3.9	8.3
		120	8	64		146	157	N	7.9	198	4.0	8.4
		140	12	65			156	N	7.5	199	4.0	8.4
		145	12	68[k]			160	N	7.7	200	4.0	8.4

[a] Solution viscosity numbers were measured on a 0.5 g/dL solution in chloroform at 35 °C. [b] Annealing temperature. [c] Annealing period. [d] The glass transition temperature was chosen at half-devitrification when judged by heat capacity increase at 10 °C/min. The samples were cooled at 10 °C/min before analysis to avoid hysteresis. [e] Temperature of recrystallization exotherm on heating runs of DSC analysis. [f] Temperature for crystal-to-crystal transition. [g] Liquid crystal phase; N stands for a nematic phase and S for a smectic phase. S + N stands, for polymer P3, smectic-to-nematic transition temperature = 165 °C and, for polymer P5, smectic-to-nematic transition temperature = 190 °C, both transition temperatures determined by visual observation with the polarizing microscope at the heating rate of 20 °C/min. [h] ΔH_m total enthalpy changes observed for crystal-to-crystal and crystal-to-mesophase transitions. ΔH_i enthalpy changes observed for mesophase-to-isotropic phase transitions. All the values of ΔH_m, ΔH_i, and ΔS_i are per repeating unit. [i] A = sample as polymerized. [j] B = Sample cooled from the isotropic phase at 10 K/min. [k] Sample annealed close to, but below, T_g. [l] T_m was not observed due to the amorphous nature of the polymer (flow temperature is given in place of T_m). Flow temperature was taken as the temperature at which the melt started to flow when heated on the hot stage of a polarizing microscope at 20 °C/min. [m] It was not precisely determined from DSC analysis because of small decomposition of the sample at temperatures >240 °C.

ceased, and the reaction mixture gelled as a consequence of the development of cross-linked structures. The reaction was stopped at the gel point, detected by a rapid increase in the viscosity of the reaction mixture indicated by the inability of bubbles to rise in the medium. The polymer was extracted from the hot polymerization tube, with the help of a spatula, as a transparent isotropic and elastic product. On cooling the product at room temperature it became rigid and tough and with the opalescent, metallic-like appearance characteristic of LC polymers. The obtained product was then extracted with chloroform in a Soxhlet apparatus and vacuum dried. Chloroform extracted soluble polymers from the sample at a rate of between 15 and 35% of the weight of the sample.

II.5. Films of polymers of series 1–3 were prepared by casting the polymer solution in chloroform onto glass plates and allowing the solvent to evaporate. The final removal of the solvent was done under vacuum. The film was then soaked in water for 30 min and then was lifted off from the glass plate and dried under vacuum for 24 h.

II.6. Photo-Cross-Linking Procedure. The films were photochemically cross-linked by exposing them to a low-pressure mercury lamp (16 W), kept at a distance of 10 cm from the films for 15, 30, 60, and 90 min. After irradiation the films were washed in chloroform for 10 min and dried under vacuum. IR spectra of the films before and after irradiation were recorded.

II.7. Infrared and UV Spectra. IR spectra were recorded on a Nicolet 205 spectrophotometer as mulls in Nujol or on KBr or as films prepared as described above. UV solution spectra were recorded in spectroscopic chloroform of *sym*-tetrachloroethane on a Hitachi V-3400 spectrophotometer.

II.8. Elemental analyses were performed on a Perkin-Elmer 240 analyzer.

II.9. Inherent viscosities of polymers were measured at 35 °C on solutions of 0.5 g/dL in chloroform or *o*-cresol.

II.10. Identification of the Mesophases. The optical texture and thermal behavior of the melts were examined on a heating stage Mettler FP-82 attached to a Meiji polarizing microscope.

II.11. Differential Scanning Calorimetry. DSC was performed on either a Perkin-Elmer DSC-2 or DSC-7 calorimeter calibrated following the standard procedure. The standard heating rate for thermal analysis was 10 °C/min. The samples were annealed isothermally by heating them above the temperature of isotropization and holding them for about 2 min and then cooling to the fixed annealing temperature T_a and keeping them for the fixed annealing time t_a. Then the samples were cooled again to below T_g.

The glass transition temperature, T_g, was taken as the temperature of half-devitrification of the sample when judged by heat capacity increase, at the given heating rate. The hysteresis at the glass transition was studied on amorphous samples, heating them to just above T_g and cooling at various chosen rates and then reheating for thermal analysis at 10 °C/min.

II.12. Thermogravimetric analysis was carried out with a Perkin-Elmer TGS-2.

III. Results and Discussion

III.1. Synthesis and General Properties. Direct polycondensations for polymers of series 1 were carried out at 120 °C in a mixture of pyridine–DMF using tosyl chloride as the condensation agent in accordance with the method described by Higashi et al.[22] Copolyesters of *p*-hydroxybenzoic acid, series 2 and 3, were obtained by a simpler process by adding the condensation agent to the mixture of dicarboxylic diacids, diphenols, and *p*-hydroxybenzoic acid without stepwise activation of the dicarboxylic diacids followed by alcoholysis with diphenols.[23]

All of the polycondensations proceeded homogeneously with the exception of the wholly aromatic copolyesters PDA5 and PDA6, which were insoluble in the reaction medium. Polymer PDA5 precipitated as a white powder a few minutes after the condensation agent was added, and the reaction mixture of polymer PDA6 gelled immediately after the condensation agent was added. The results of elemental analysis (Table I) are in good agreement with the calculated values, suggesting that the compositions of the polymers produced correspond to those of the monomer feed. The IR and UV spectra of the polymers were also consistent with the expected structures and compositions (Table I).

All the polymers, except for PDA5 and PDA6, were soluble in common organic solvents such as chloroform, methylene chloride, dioxane, DMF, and pyridine. Polymers PDA3 and PDA4 were not totally soluble in chloroform and methylene chloride, which gives an idea of the chemical heterogeneity of these copolyesters of *p*-hydroxybenzoic acid.

Considering the fact that the polymers did not precipitate out of the reaction medium as the polycondensation proceeded, the solution viscosity numbers of polymers containing ortho-linked units can be regarded as being rather low (about 0.20 dL/g). However, the solution viscosity numbers for polymers P6, PBP6, and PDA6 with an all-para-linked structure were moderately high.

Thermal and LC properties of the synthesized polymers are summarized in Tables III and IV. Most of the polymers have strong glass transitions, and their T_g's can be precisely determined from heating curves of DSC analysis (e.g., Figures 7, 8 (curve A), 9, 10a,b, and 11). The T_g's of the wholly aromatic copolyesters (series 3) are the highest, which can be attributed to the rigidity of their chains. Polymers of series 1 and 2 have lower T_g's, due to the relative flexibility of their chains introduced by means of the decamethylene spacer. For all the series of T_g's of the phenylhydroquinone-containing polymers P6, PBP6, and PDA6 (which will be referred to as 6's polymers) are consistently higher than those of the rest. These moderately high T_g's for these polymers can be ascribed to their higher molecular weights (higher solution viscosity numbers) and to structural factors such as restrictions on the internal chain motion imposed by the bulky side groups, pendant phenyl rings.

Table IV
General Properties and Transition Temperatures of Polyesters of Series 2 and 3

polymer	$\eta_{0.5}$,[a] dL/g	T_g,[b] °C	T_f,[c] °C	LC[d] phase	T_i,[e] °C
PBP1	0.24	46	95	N	285
PBP2	0.25	42	90	N	265
PBP3	0.19	46	100	N	>300[f]
PBP4	0.24	47	90	N	310
PBP5	0.22	59	95	N	>300[f]
PBP6	0.51	65	110	N	>300[f]
PDA1	0.19	100	165	N	>350
PDA2	0.14	90	150	N	>350
PDA3	0.20	99	170	N	>350
PDA4	0.21	102	175	N	>350
PDA5	0.23	130	230*	N	>350
PDA6	0.71	133	220	N	>350

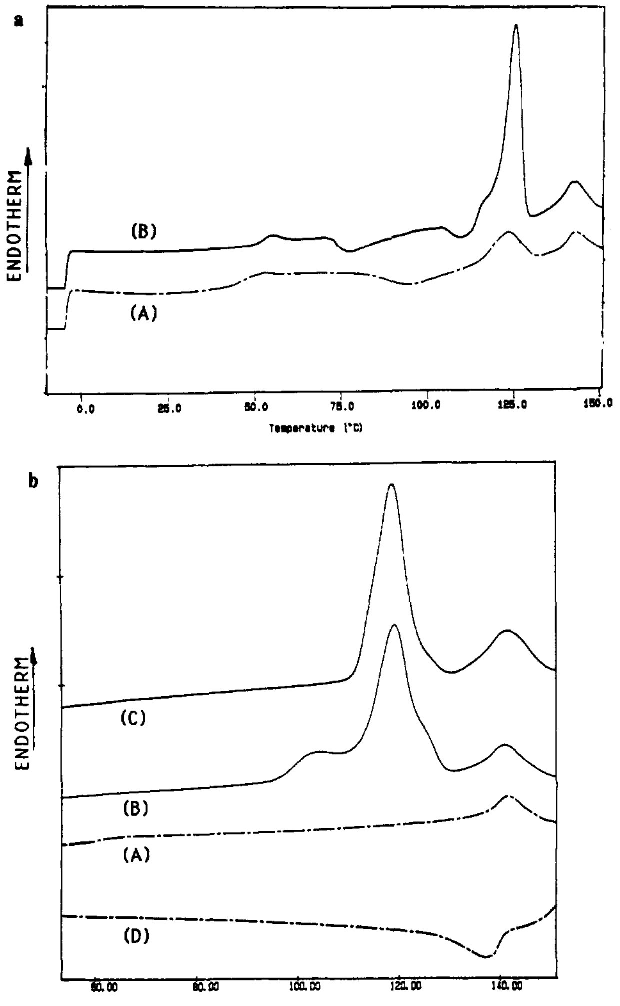
[a] Solution viscosity number were measured on a 0.5 g/dL solution in chloroform at 35 °C, except for polymers PDA3–PDA6, in which cases a 0.5 g/dL solution in *o*-cresol was used at 35 °C. [b] The glass transition temperature was chosen at half-devitrification when judged by heat capacity increase at 10 °C/min. The samples were cooled at 10 °C/min before analysis to avoid hysteresis. [c] Flow temperature was taken as the temperature at which the melt starts to flow naturally to form a fluid nematic phase. T_f's were determined by heating the samples between glass plates on the hot stage of a polarizing microscope at 20 °C/min. The asterisk indicates the polymer whose melt did not flow until after the cover was lightly pressed with the point of a spatula at 230 °C. [d] Liquid crystalline phase; N stands for a nematic phase. [e] For polymers of series 2 the isotropization temperature was taken as the temperature at which the formation of nematic drops from the isotropic melts was observed when they are cooled on the hot stage of a polarizing microscope at 20 °C/min. [f] It was not precisely determined because of small decomposition of the sample above 300 °C.

It can be proposed that the order that should follow the T_g's of the polymers containing ortho-linked units sould be 2's ≤ 1's < 3's < 4's < 5's, considering on the one hand the molar volume and polarity of the side groups and on the other hand the increase in the free volume produced by these side groups. However, not all the series consistently follow the order proposed.

In accordance with these results and keeping in mind that the dependence of T_g on the molecular weight cannot be neglected, it might be concluded that the observed trend in the T_g's of the present polymers is not only due to their structural character but also to the molecular weight of the polymers.

Copolyesters of series 2 and 3 seem to be essentially noncrystalline in character or extremely slow in crystallization. All the as-polymerized or annealed samples showed no melting endotherm on DSC analysis. The as-polymerized samples of polyesters of series 1 showed none or very weak melting endotherms and very weak crystallization exotherms on heating, and no crystallization exotherm was observed during slow cooling of the melts on DSC analysis. Also during the second heating scan in the DSC analysis these melting endotherms did not reappear, which implies that the rate of recrystallization from the melt is very slow.

For rigid-chain copolyesters of series 3, it seems that structural irregularity due to the random monomeric sequence, together with the random existence of irregular structures, would impede crystallization. However, it is known that for flexible polymers the crystallization process can be much more rapid than for rigid-chain polymers because the flexible chains can readily adjust their conformations into a growing crystalline structure.[24] For this reason it is surprising that samples of copolyesters of series 2 did not crystallize even after long periods of



TEMPERATURE (C) DSC

Figure 7. (a) DSC thermograms for polymer P1: sample (A) as-polymerized and (B) annealed at 110 °C for 24 h, heating rate 10 °C/min. (b) DSC thermograms for polymer P1: (A) second heating cycle, (B) annealed at 90 °C for 12 h, (C) annealed at 100 °C for 12 h, (D) cooling cycle, heating and cooling rate 10 °C/min.

annealing or after slow cooling of their melts. Furthermore also noteworthy is the unusual low tendency of the polyesters of series 1 to crystallize, in spite of their ordered sequence and relatively flexible chain. This suggests that the units used to build up the rigid segments of these polymers are particularly effective in promoting structural irregularity.

Due to the amorphous character of the polymers of series 2 and 3, their T_m's could not be determined; therefore, the flow temperature of these polymers is included in Table IV. Except for polymers with very viscous melts the flow temperatures were consistently about 50 °C higher than the T_g's of the polymers. The values of their T_f's were very low and typically 100 °C or below for semiflexible copolyesters of series 2 and below 200 °C for rigid-chain copolyesters of series 3.

The values of T_m's of sequentially ordered polyesters of series 1 were also very low. These low values of their T_m's can be ascribed to poor close packing of their chains caused either by the presence of bulky side groups, by positional isomerism of lateral substituents, or by the formation of bent structures due to the presence of ortho links. The combined effect of the last two factors would be particularly effective in preventing the extended close packing of the chains, which in turn would explain the very low values of the T_m's of polymers P2–P4.

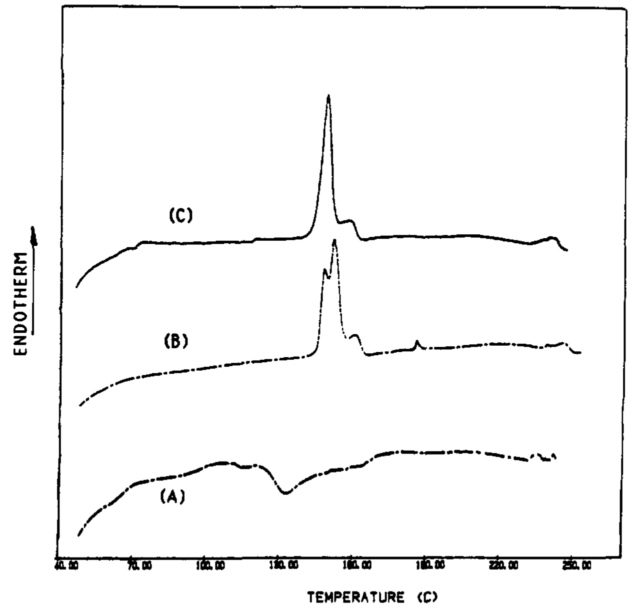


Figure 8. DSC thermograms for polymer P5: sample (A) as-polymerized, (B) annealed at 145 °C for 12 h, (C) annealed at 150 °C for 12 h, heating rate 10 °C/min.

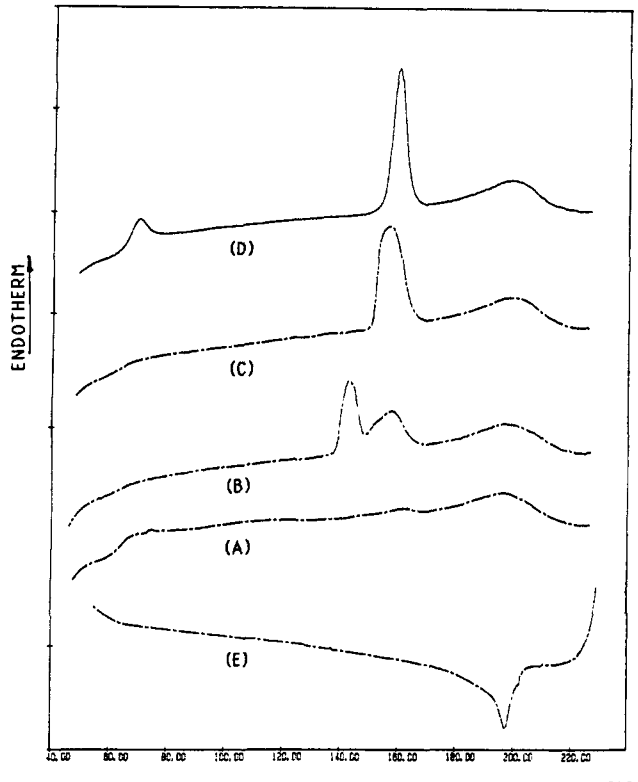


Figure 9. DSC thermograms for polymer P6: (A) second heating cycle, (B) annealed at 120 °C for 8 h, (C) annealed at 140 °C for 12 h, (D) annealed at 145 °C for 12 h and at 60 °C for 12 h, (E) cooling cycle, heating and cooling rate 10 °C/min.

III.2. Hysteresis in the T_g Region. Most of the samples of the synthesized amorphous polymers show endotherms at the glass transition region on the curves of DSC analysis (Figure 10a,b), when the samples were heated much more rapidly than they had previously been cooled. These endotherms are due to hysteresis of the heat capacity of mesophase glasses at the glass transition region. A qualitative study of these hysteresis peaks was carried out for an amorphous polymer PDA1.

Figure 11 shows the hysteresis study of polymer PDA1 in the mesophase glass transition region. The largest en-

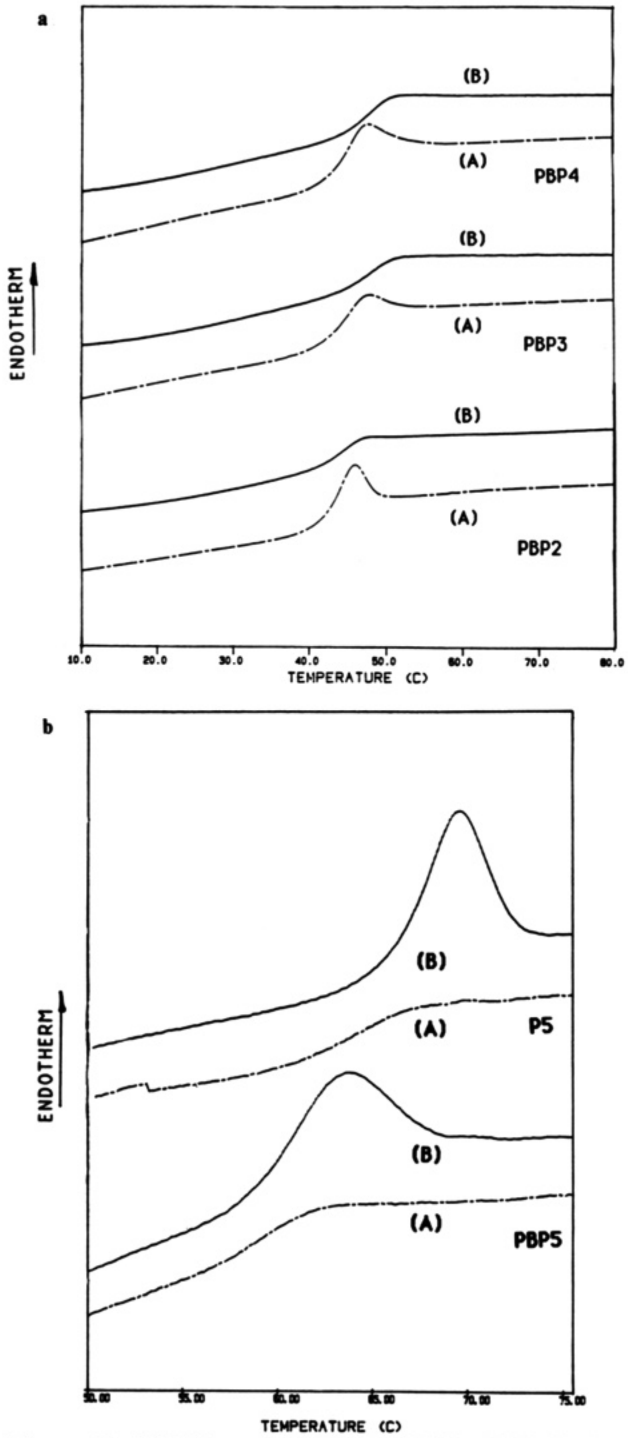


Figure 10. (a) DSC traces of polymers PBP2–PBP4 (series 2) in the T_g region: (A) as-polymerized samples and (B) quenched samples, heating rate 10 °C/min. (b) DSC traces of polymers PBP5 and P5 in the T_g region: (A) quenched samples and (B) samples cooled at −0.31 °C/min through T_g. Heating rate 10 °C/min.

dotherm peak is observed for the cooling rate 0.31 °C/min (curve A in Figure 11). As shown in Figure 11, the endotherm decreases as the cooling rate increases although the hysteresis peak does not disappear totally when the heating rate is equal to the prior cooling rate 10 °C/min. Moreover, even the quenched PDA1 shows a small hysteresis peak (curve E in Figure 11). Although a more detailed study is underway, this study of hysteresis may indicate that the freezing and unfreezing of motion of PDA1 at the glass transition temperature is asymmetric.[25]

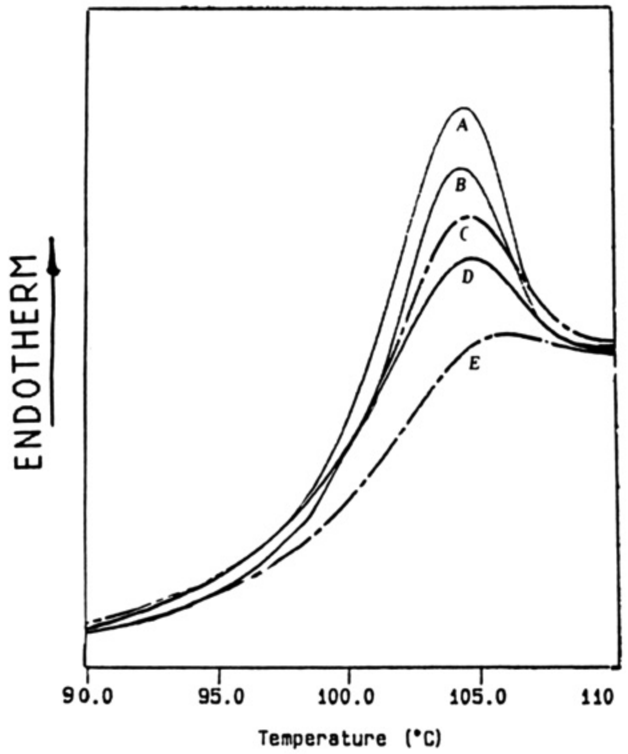


Figure 11. Hysteresis of PDA1 samples cooled at different cooling rates through T_g: (A) −0.31 °C/min, (B) −1.25 °C/min, (C) −5 °C/min, (D) −10 °C/min, and (E) quenched to liquid N_2. Heating rate 10 °C/min.

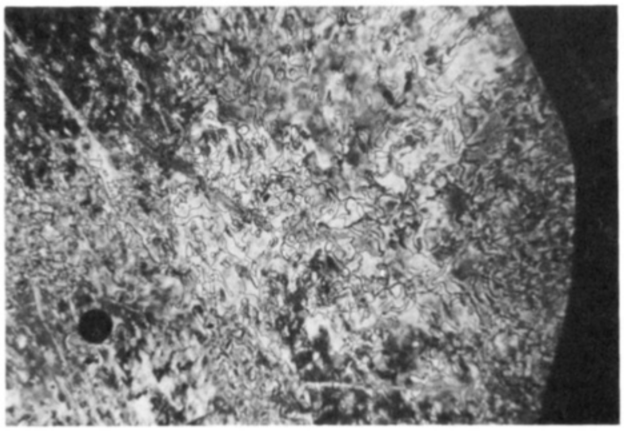


Figure 12. Polarized photomicrograph of nematic mesophase from P1 at 130 °C, showing a threaded texture (magnification ×100).

III.3. Thermal Treatment and Crystallization of Polymers.

As described before as-polymerized samples of the copolymers of series 2 and 3 showed no melting endotherms on DSC analysis. No crystallinity was observed for these polymers in the normal tridimensional sense by DSC criteria, even after prolonged annealing of their samples at various temperatures in the range from their T_g's to T_i's. However, some of the as-polymerized samples of the polymers of series 1 showed very weak melting endotherms, which implies that they have some semicrystalline character. Unfortunately, due to the fact that X-ray diffraction studies have not been carried out, their amorphous or semicrystalline nature cannot be further supported.

Polymers of series 1 did not show exotherms of crystallization on cooling the isotropic melt to temperatures well below their T_g's, implying that the mesophase-to-crystal transitions are supercooled below their T_g's.

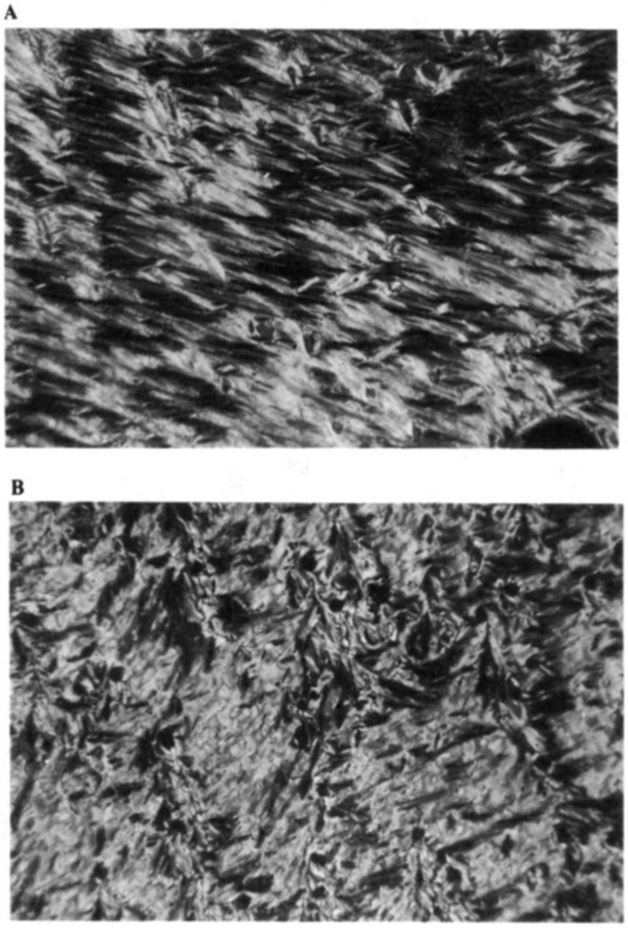


Figure 13. Representative optical polarization photomicrographs of smectic mesophases showing a broken fan-shaped type texture exhibited by P2 after 10 min of annealing at 150 °C cooling cycle (A) and P3 after 15 min at 155 °C cooling cycle (B) (magnification ×100).

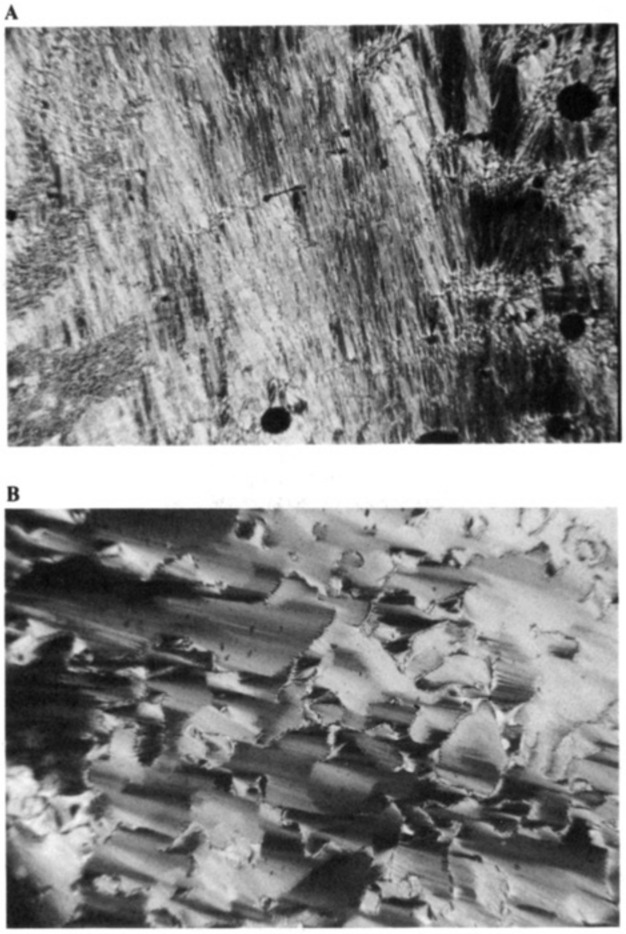


Figure 14. Polarized photomicrograph of smectic mesophases from P4 after 15 min at 175 °C (A) and P5 after 10 min at 170 °C cooling cycle (B) (magnification ×100).

However, samples of polymers P1, P5, and P6 showed weak recrystallization exotherms on subsequent heating runs on DSC analysis. When samples of these polymers were subjected to thermal treatment at the temperature of the minimum point of the exotherm, they showed well-defined melting endotherms. Figures 7–9 demonstrate how the DSC thermogram of polymers P1, P5, and P6 changes with annealing temperature and period. Samples of these polymers subjected to thermal treatment at the annealing temperatures and periods stated in Table III show that the endotherm area of the lowest melting endotherms (crystal-to-crystal transitions or premelting endotherms) decreased or even disappeared as the annealing temperature and period increased. However, the values of ΔH_m, the total heat transitions (crystal-to-crystal plus crystal-to-mesophase), remained quite constant, implying that a further increase of the annealing temperature or period did not produce an increase in the crystallinity of the polymers.

On the other hand, annealed samples of polymers P3 and P4 showed very weak melting endotherms. Increasing the annealing temperature or period did not bring a substantial increase in their area. Finally, samples of polymer P2 annealed at various temperatures between their T_g's and T_i's and for long periods of time showed no melting endotherms.

According to these results, it seems that ortho links are at least as effective at decreasing the ability of the polymers to crystallize as the para-linked unit with a bulky side group, phenylhydroquinone, is, or even more so. The combined effect of the presence of sharply angular structures together with the presence of lateral substituents makes the ordered tridimensional packing of the chains difficult. Moreover, the possibility of the random variation along the chain of the position of the substituent in ortho-linked units, monosubstituted catechols, further destroys the ability to crystallize of polymers P2–P4.

III.4. Liquid Crystalline Properties of Polymers. All the as-polymerized samples of the polymers of series 1–3 formed mesophases above their T_g's. However, the LC phases could not be identified as nematic or as smectic until fluid melt states were reached, at temperatures above their T_f's, typically about 50 °C above their T_g's. All these mesophases showed typical characteristics of liquid crystalline phases of high molecular weight compounds:[26] (a) Very small domains could be annealed to form bigger ones similar to those of the LC phases of low molecular weight compounds. (b) The transition mesophase-to-isotropic liquid took place over a relatively wide range of temperatures in which the mesophase coexists with the isotropic phase. This range of coexistence of phases was particularly broad for samples of random copolyesters of series 2, suggesting that they had a great chemical heterogeneity. (c) During slow cooling of the mesophases crystallization did not occur; therefore, the textures characteristic of the mesophases remained unchanged in the solid glasses at room temperature.

Polymers of series 1 formed smectic mesophases in melts except for polymers P1 and P6 which formed only nematic melts (Figure 12). As-polymerized samples of smec-

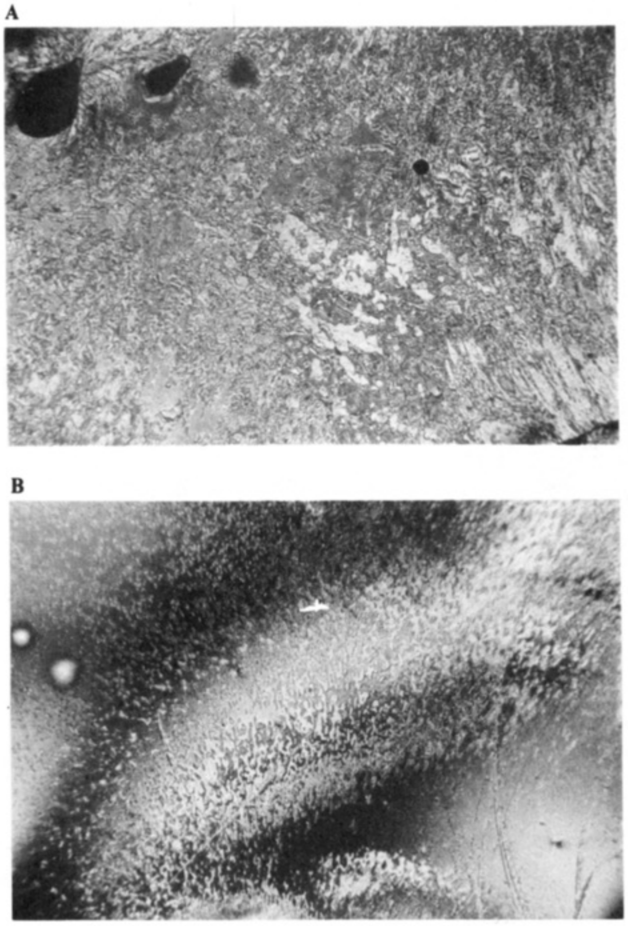


Figure 15. Representative optical polarization photomicrographs of quenched nematic mesophases from PDA2 at 250 °C, showing a polished marbled-type texture (A), and from PBP4 at 290 °C, showing a marbled homeotropic texture (B) (magnification ×100).

tic polymers P2–P5 formed, at temperatures between 30 and 50 °C above their T_g's, very viscous melts with very blurred smectic schlieren textures. Slow cooling of the isotropic melts of these polymers originated broken fan-shaped textures (Figures 13 and 14). These textures were transformed into blurred smectic schlieren textures by touching the cover glass of the preparation with the point of a spatula, but homeotropic textures could not be observed. Although the smectic-to-nematic transition for polymers P3 and P5 was not clearly detected by DSC analysis, it was determined by visual observation with the polarizing microscope at the heating rate of 20 °C/min. Also, on cooling the isotropic melts of these polymers on the hot stage of the polarizing microscope, typical transition bars at the nematic-to-smectic transition point could be observed.[27]

Figure 16. Schematic visualisation of the layered structure suggested for P2–P5 smectic mesophases. X = CH_3, CHO, NO_2, fused phenyl ring.

Table V
Transition Types, Temperatures, and Enthalpies of the Model Compounds Synthesized

compd	transition[a]	T, °C	ΔH, kJ/mol
M1	K–I	87.2	70.6
	I–S_A	80.4	6.2
	S_A–K	44.6	
M2	K–S_A	80.3	50.2
	S_A–I	97.5	7.3
M3	K–S_A	71.2	65.6
	S_A–I	129.5	7.7
M4	K–S_A	82.5	72.5
	S_A–I	153.3	9.7
M5	K–S_A	99.5	55.3
	S_A–I	164.2	10.1
M6	K–N	94.8	46.6
	N–I	128.9	2.2

[a] From DSC, second heating, 10 °C/min heating and cooling rate.

Polymers of series 1 showed relatively broad endotherms of isotropization in their DSC thermograms in both the heating and cooling cycle as shown in Figures 7 and 9. The isotropization temperature of P5 was determined by observation with the polarizing microscope because the endotherms of isotropization on DSC analysis could not be precisely identified (Figure 8). The isotropization transitions of the polymers of series 1 were observed with the polarizing microscope showing coexistence of the isotropic phase with characteristic nematic drops (for polymers P1, P3, P5, and P6) and with smectic bâtonnets (for polymers P2 and P4) over a relatively wide range of temperatures in both the heating and cooling runs. As can be seen in Figure 7 and from the ΔH_m data of Table III, a steady increase in ΔH_i was observed with increasing annealing temperature and time for polymer P1. The vicinity of T_m and T_i for this polymer suggests that the observed increase in ΔH_i is as a consequence not of the annealing of the mesophase but of the fusion of high melting point crystalline forms developed during the annealing process.

All the copolymers of series 2 and 3 formed melts at temperatures above their T_f's in which marbled, threaded, and schlieren textures typical of nematogens could be observed (Figure 15A,B). The isotropization temperatures for the copolymers of series 2 were determined by observation with the polarizing microscope because the endotherms of isotropization on DSC analysis were very broad and the peaks could not be precisely identified. The T_i's were very high and typically about 300 °C.

The values of T_i's of the copolymers of series 3 were not determined because of thermal decomposition of the samples before isotropization temperature was reached.

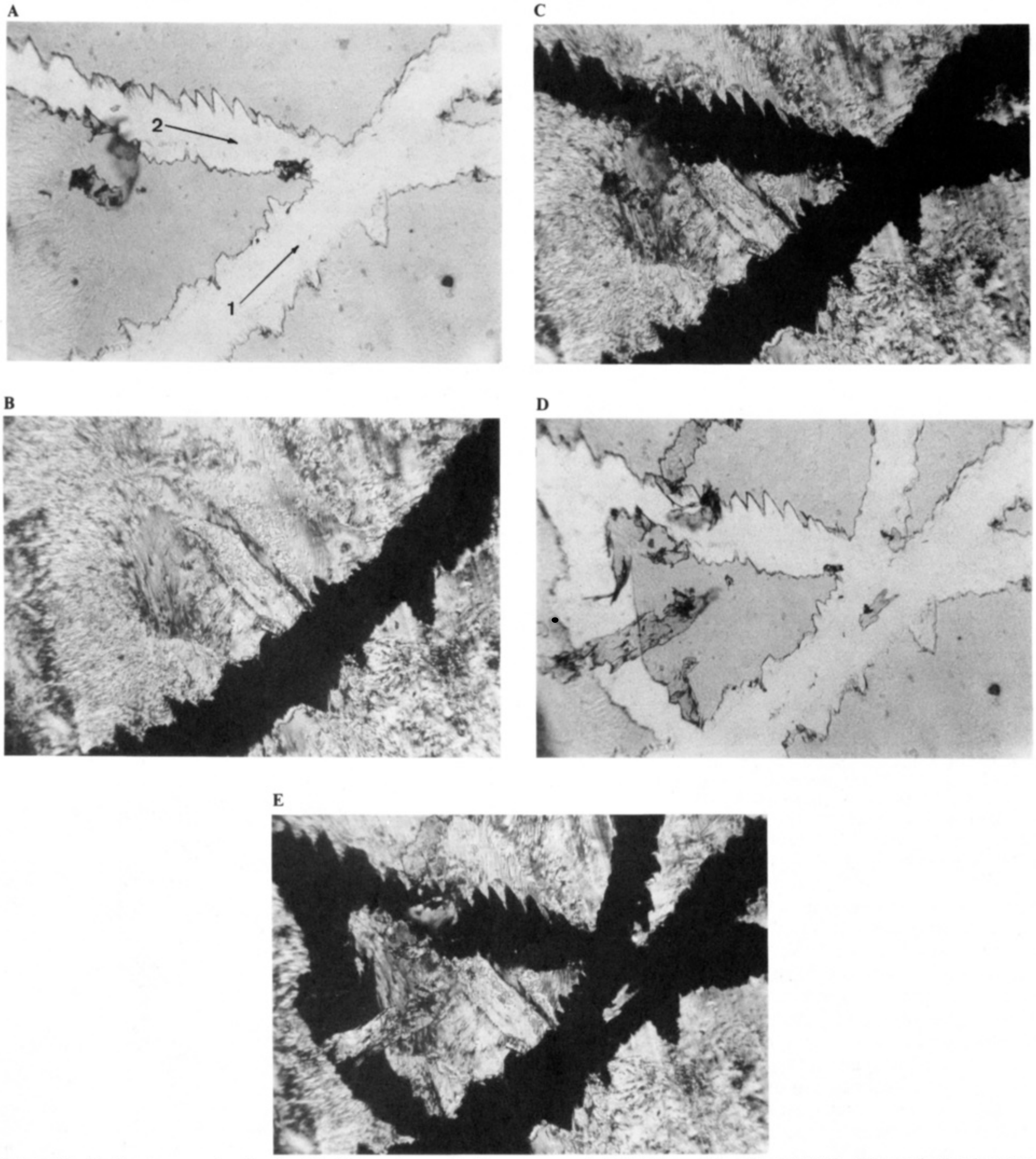


Figure 17. Photomicrographs showing the thermal cross-linking process of a PDA6 nematic melt at 300 °C. These photomicrographs were taken after the nematic melt was held in air at 300 °C: (A) time = 30 min, polarized light, (B) t = 10 min, crossed polarizers, (C) t = 30 min, crossed polarizers. The gel was twice broken at 300 °C with the point of a spatula, first after 10 min and then again after another 20 min at 300 °C in the directions of break lines 1→ and 2→, respectively. (D) and (E) t = 60 min, polarized light and crossed polarizers, respectively. At this point the melt has been converted into a nematic free-standing film (magnification ×100).

However, it was proven that their T_i's are higher than 350 °C by observing through the polarizing microscope the optical textures of their nematic melts at this temperature.

Copolymerization with p-hydroxybenzoic acid increases the rigid-rod character of the chains which causes a stabilization of the mesophase. However, the disorder of sequences produced by copolymerization decreases the degree of order of the mesophases and only nematic phases were found among these copolyesters. The high axial ratio of the p-phenylenediacryloyloxy group and the interlocking effect produced by the extruded ortho-linked units are factors which may account for the high T_i's of the copolyesters of series 3 in spite of the high proportion (40% moles) of sharply bent units in their chains.

III.5. Liquid Crystalline Properties of Model Compounds. As was the case with the homologous polymers, all the synthesized model compounds also had liquid crystalline properties. The S_A phase present in most of these model compounds was identified by the presence on heating of homeotropic textures with bunches of oily streaks without subjecting the sample to mechanical stress.[27] Only occasionally, fan-shaped textures could be observed on cooling due to the notorious tendency of these

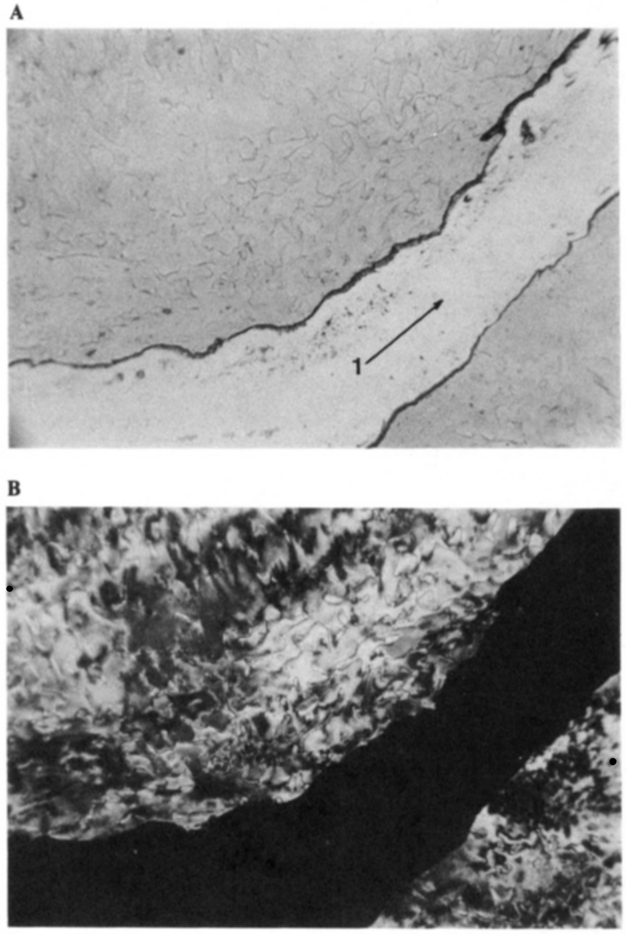


Figure 18. Photomicrographs showing the nematic gel structure of PDA1 at 300 °C. These photomicrographs were taken after the nematic melt was held 1 h in air and at 300 °C: (A) polarized light; (B) cross polarizers. The gel was broken at 300 °C with the point of a spatula in the direction of break line 1→, after it was held for 15 min in air at this temperature (magnification ×100).

compounds to give rise to homeotropic texture.

The thermodynamic properties of these model compounds are given in Table V. A comparison between Tables V and II shows that there are correlations between the phase transition temperatures, the mesophase range, and the type of liquid crystalline phase for model compounds and analogous polymers of series 1.

Compound M1 with an unsubstituted ortho-linked unit as the rigid link between the mesogenic units was only monotropic, and analogous polymer P1 had the shorter mesophase range among the polymers of series 1. However, model compounds M2–M5 and analogous polymers P2–P5 containing substituted ortho-linked units as the rigid links between the mesogenic units formed stable smectic phases over a relatively broad range of temperatures. The substituent groups of the ortho-linked units CH_3, CHO, NO_2, and fused phenyl ring are the terminal groups of the mesogenic units (Figure 2b). It is known that terminal groups which extend the mesogenic units along the molecular axis without broadening the molecule too much increase the thermal stability of the mesophases. Terminal groups which are conjugated with the aromatic ring of the mesogenic units particularly increase the T_i's by increasing the polarizability along the molecular axis.[28a] The terminal group efficiency order reported for nematic phases in aromatic systems is Ph > NO_2 > CH_3 > H.[28b] Consequently, a methyl terminal group produces the transformation of a monotropic compound M1 into an enantiotropic one M2 with a mesophase range of 17 °C and the transformation of a nematic polymer P1 into a smectic one P2 with a T_i 15 °C higher. Also, compounds M3–M5 and P3–P5 with conjugated terminal groups show very high T_i's. Figure 16 is a schematic illustration of the structure of the smectic layers suggested for polymers P2–P5 in which the mesogenic units are represented as "U".

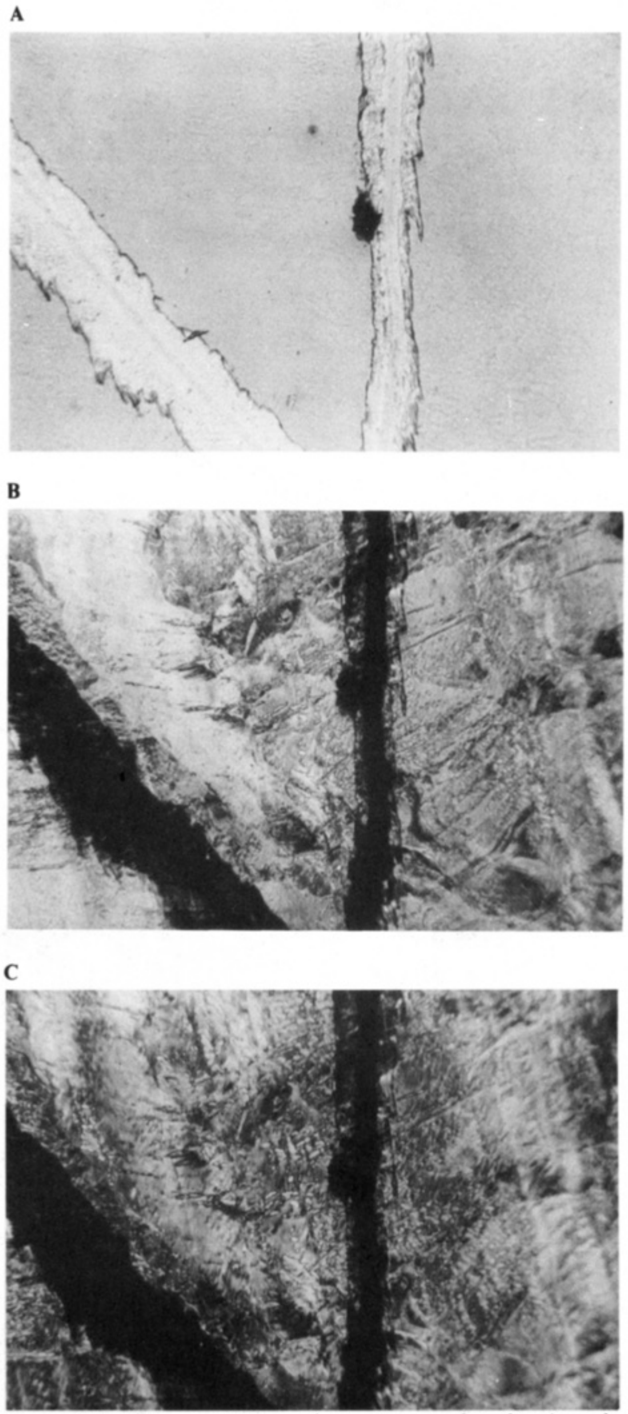


Figure 19. Representative photomicrographs showing the variation of the birefringence in the multidomain texture of the nematic gel of PDA6 in air and at 330 °C: (A) Gels after 10 min in air at 330 °C (polarized light). (B) and (C) gels viewed between crossed polarizers after 10 and 30 min in air at 330 °C, respectively. Gels broken at 330 °C after 5 min in air at this temperature (magnification ×100).

III.6. Thermal Stability and Thermal Cross-Linking of Polymers. Although the melts of polymers proved to be very stable on the hot stage of the polarizing microscope in air and below 250 °C, most of the polymers of series 1 and 2 underwent some degradation at tem-

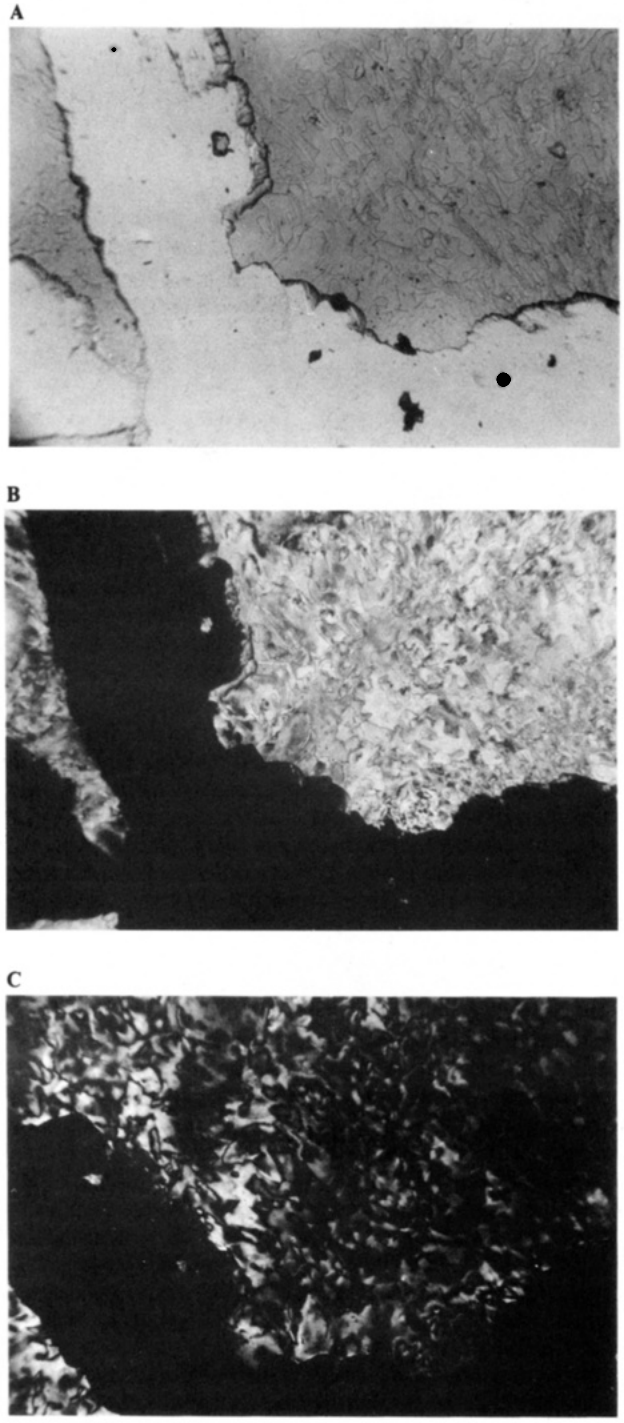


Figure 20. Representative photomicrographs showing the variation of the birefringence in the multidomain texture of the nematic gel of PDA1 in air and at 330 °C. (A) Gels after 10 min in air at 330 °C (polarized light). (B) and (C) gels viewed between crossed polarizers after 10 and 30 min in air at 330 °C, respectively. Gels broken at 330 °C after 5 min in air at this temperature (magnification ×100).

peratures above 300 °C. The melts turned yellow and the color darkened with time; also some gas bubbles could be observed. In addition, most of the copolymers spontaneously formed homeotropic textures at high temperatures, usually above 275 °C for series 2 (Figure 15B) and above 330 °C for series 3, which suggests that the number of chain ends increases as a consequence of degradation of the sample.[17a]

The thermal stability of polymers in air from 25 to 330 °C was studied by TGA at the heating rate of 10 °C/min. All the polymers of series 1 and 2 showed weight loss higher than 5% at 330 °C while weight loss of the polymers of series 3 was around 5%. Thermogravimetric analysis of series 1 and 2 polymers showed around 12% and 20% weight loss after 15 and 60 min in air at 330 °C, respectively, while series 3 polymers showed around 8% and 16% weight loss respectively on the same conditions. These results show that although the polymers of series 3 were more thermally stable than those of series 1 and 2 their thermal stability in air at 330 °C was not very great.

On the other hand, the thermal stability of polymer double bonds in air at 300 °C was also not very great. Under these conditions the viscosity of the polymer's melts increased rapidly as a consequence of a gelation process of the sample. One characteristic of these gelled melts was its pronounced tendency to form very homogeneous textures when the sample was subjected to mechanical stress on the hot stage of the polarizing microscope. Attempts to reduce the thickness of these gels by pressing the cover glass with a spatula produced the formation of a transparent film with a very homogeneous texture, while releasing the pressure over the cover produced the rapid return to the initial thickness of the preparation. These gels proved to be insoluble in all common organic solvents although they were swollen by solvents such as chloroform, dichloromethane, DMF, and dioxane.

Thermogravimetric analysis of the polymers of series 3 revealed small weight loss (5%) even after 60 min in air at 300 °C, implying that thermal degradation of these polymers was not very great under these conditions. This, together with the thermal stability of nematic phases of the polymers of series 3 at 300 °C, allowed the direct observation of their gelation process on the polarizing microscope. Gelation of these nematic melts did not change their multidomain textures. Figures 17 and 18 are photomicrographs showing the gel structure of PDA6 and PDA1 nematic melts after they were held in air at 300 °C for 60 min. These nematic gels could be detached from the glass slide at 300 °C as mematic free-standing films which were insoluble in all common organic solvents and showed certain resistance to be swollen by these solvents. IR spectra of these films were essentially the same as those of PDA6 and PDA1 (Table I). These results show that the gelation process of these nematic melts consists of the development of cross-linked structures due to thermal cross-linking reaction between the conjugated double bonds. In photomicrographs of Figure 17, two different break lines of PDA6 melt at 300 °C can be appreciated. This nematic melt was twice broken at 300 °C with the point of a spatula: first after 10 min at 300 °C in the direction of break line 1→ and then after 30 min at 300 °C in the direction of break line 2→. From the round edges of break line 1→ it can be deduced that the melt was not completely gelled. However, it can be seen from the sharp edges of break line 2→ that at this point the melt had the consistency of a thick gel at 300 °C. Photomicrographs D and E in Figure 17 show that after the melt was held in air at 300 °C for 60 min it has been converted into a solid film which can be easily detached from the glass slide with the point of a spatula. Figures 19 and 20 show the variation of the birefringence with the time of the nematic gels of PDA6 and PDA1 in air and at 330 °C. These figures show that the polydomain texture was preserved while the birefringence of the nematic gels decreased with time at 330 °C.

III.7. Photo-Cross-Linking of Polymeric Films. The presence of cinnamate ester or *p*-phenylenediacrylate ester chromophores in the synthesized polymers and model compounds was confirmed by UV spectral analysis.

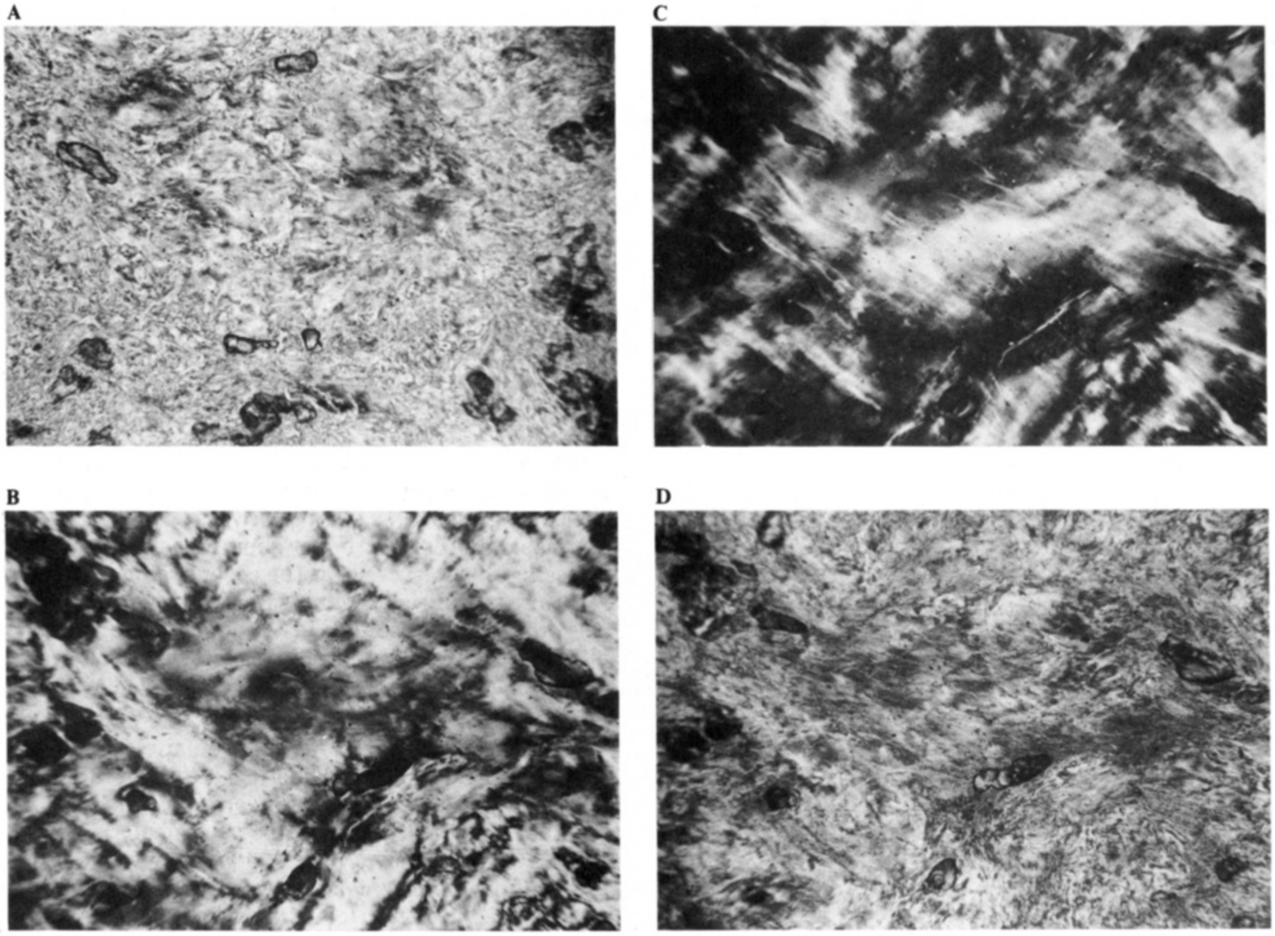


Figure 21. Representative optical polarization photomicrographs showing the variation of the birefringence of a thick sample of P1c with the temperature. Heating cycle: (A) at 90 °C, (B) at 115 °C, and (C) at 130 °C. Cooling cycle: (D) at 90 °C (magnification ×100).

A typical UV spectrum of these compounds in chloroform solution shows maxima at about 305 and 315 nm and a shoulder at about 275 nm (Tables I and II). The cross-linking of photochemically reactive cinnamate and *p*-phenylenediacrylate ester chromophores containing polymers was carried out by irradiation in air for several intervals of time at room temperature of solvent-cast films of these polymers with a low-pressure mercury arc lamp with maximum light emission centering at 300 nm. Photolysis of these films produced cross-linked films resistant to solvents which softened above 100 °C but did not melt below 350 °C. These cross-linked films appeared birefringent when observed between glass plates on the polarizing microscope, and their birefringence decreased as the time of irradiation was increased. IR spectra of the photoirradiated films showed that the 1630-cm^{-1} peak assigned to the C=C stretching mode had almost disappeared. All these results suggest that the C=C bonds in the cinnamate and *p*-phenylenediacrylate moieties photodimerize to form cyclobutane units. A similar cycloaddition process has been described for other liquid crystalline polycinnamates and poly(*p*-phenylenediacrylates).[20a,b]

III.8. Synthesis of Some Insoluble Cross-Linked Polymers of Series 1–3 by Melt Transesterification. Intents to prepare LC cross-linked polymers by melt transesterification were based on two facts stated in section III.6. First, most of the polymers showed weight loss lower than 5% at 300 °C, and, second, cross-linked polymers were obtained on the hot stage of the microscope by thermal cross-linking of the nematic melts of the polymers of series 3 at 300 °C.

Although the synthesis and study of polymers of series 1–3 with a cross-linked structure is still outstanding, some results can be given in advance. Dicarboxylic diacid monomers, 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) and *p*-phenylenediacrylic diacid, introduce reactive conjugated double bonds in the chains of polymers of series 1–3. These polymers were synthesized as described above using a low-temperature solution method in order to avoid thermal cross-linking. However, polymers P1, P2, P6, PBP1, PBP6, and PDA1 were also obtained by melt transesterification at high temperatures which caused the gelation of the reaction mixtures due to the development of cross-linked structures. These gels contained between 15 and 35 wt % of chloroform-soluble polymers. Extraction of the sol afforded insoluble cross-linked polymers P1c, P2c, P6c, PBP1c, PBP6c, and PDA1c, some of their properties were studied, and the results were compared with those of the un-cross-linked polymers P1, P2, P6, PBP1, PBP6, and PDA1.

The IR spectra and elemental analyses of the cross-linked and un-cross-linked polymers were essentially identical. Cross-linked polymers were insoluble in all organic solvents although they were highly swollen by common organic solvents such as chloroform, dichloromethane, DMF, and dioxane.

Observation of samples of the cross-linked polymers on the hot stage of the polarizing microscope showed that they formed highly birefringent phases at temperatures above their T_g's and below their T_i's. The birefringence of the samples gradually decreased as the temperature was increased (Figure 21). T_i's of these cross-linked polymers were much lower than the T_i's of the un-cross-linked ones (typically about 50 °C lower). Moving the cover glass of the preparations in the isotropic phase caused an orientational birefringence like in ordinary elastomeric network materials. At temperatures above their T_g's and below 350 °C samples of cross-linked polymers showed certain stability of shape, did not flow under stress, and showed reversible elastic deformations if the cover glass was moved.

All these results show that these polymers synthesized by melt transesterification have cross-linked structures with a high degree of chemical heterogeneity. They seem to show reversible liquid-crystalline-like phases although much less stable than the liquid crystalline phases of the un-cross-linked polymers.

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Registry No. P1 (copolymer), 136795-35-2; P1 (SRU), 136795-32-9; P1 acetate (copolymer), 136795-53-4; P2 (SRU), 136892-69-8; P2 (copolymer), 136795-36-3; P2 acetate (copolymer), 136795-54-5; P3 (SRU), 136892-68-7; P3 (copolymer), 136795-37-4; P4 (SRU), 136892-67-6; P4 (copolymer), 136795-38-5; P5 (SRU), 136795-33-0; P5 (copolymer), 136795-39-6; P6 (SRU), 136892-70-1; P6 (copolymer), 136795-40-9; P6 acetate (copolymer), 136795-55-6; PBP1 (copolymer), 136795-41-0; PBP1 acetate (copolymer), 136795-56-7; PBP2 (copolymer), 136795-42-1; PBP3 (copolymer), 136795-43-2; PBP4 (copolymer), 136795-44-3; PBP (copolymer), 136795-45-4; PBP6 (copolymer), 136795-46-5; PBP6 acetate (copolymer), 136795-57-8; PDA1 (copolymer), 136795-47-6; PDA1 acetate (copolymer), 136822-52-1; PDA2 (copolymer), 136795-48-7; PDA3 (copolymer), 136795-49-8; PDA4 (copolymer), 136795-50-1; PDA5 (copolymer), 136795-51-2; PDA6 (copolymer), 136795-52-3; M1, 136795-26-1; M2, 136795-27-2; M3, 136795-28-3; M4, 136795-29-4; M5, 136795-30-7; M6, 136795-31-8; HOC_6H_4-*o*-OH, 120-80-9; 4-(decyloxy)cinnamic acid, 55379-98-1.