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Synthesis and Characterization of Some New Main-Chain Liquid Crystalline Polymers with Tetrakis(oxyethylene) and Decamethylene Spacers

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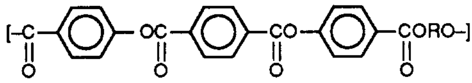
ABSTRACT: Two series of liquid crystalline, main-chain polyesters were synthesized having mesogenic triads based on substituted hydroquinones to form the center of the triad and two residues of *p*-hydroxybenzoic acid at either side. The two series differed only in the nature of the spacer; in one series it was the decamethylene and in the other the tetrakis(oxyethylene) unit. Both the type of lateral substituent and the type of spacer had a profound influence on the mesogenic properties compared to that of the unsubstituted polymer. The methyl substituent increased the temperature range of the mesophase. The ethyl substituent had a similar effect for the polymer with the decamethylene spacer, but its presence led to a marked decrease in the thermotropic properties for the polymer with the poly(oxymethylene) spacer.

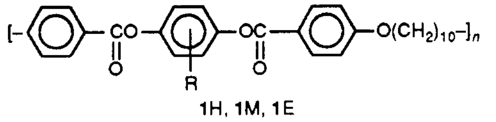
Introduction

One of the more interesting aspects of the structure–property relationships of main-chain liquid crystalline polymers[1-11] is the effect of flexible spacers on their thermotropic properties.[5-14] Earlier studies in this laboratory compared the effects of the type and length of the flexible spacer[5,6] in two series of polyesters, both of which contained a triad ester mesogenic group of the following structure:



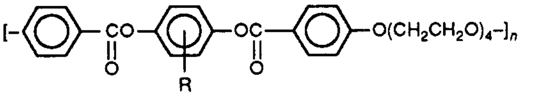
in which R was either $(-CH_2-)_n$, with n = 2–12, or $(-CH_2CH_2O-)_n$, with n = 1–4, 8.7, 13.2, and 22.3. The polymers of the former series with polymethylene spacers formed either a nematic or smectic phase on melting, but not both. The latter series with poly(oxyethylene) spacers formed both smectic and nematic phases sequentially on melting for n = 1–4 but only a nematic phase for n = 8.7. In the present study a different triad ester mesogen was selected, and the liquid crystalline properties were compared for polymers either with a decamethylene spacer or with a $(-CH_2CH_2O-)_4$ spacer. The effect of substituents in the mesogenic group on the thermotropic properties was also evaluated. The two series of polyesters prepared for this study had the following structures:

series I



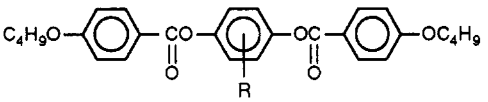
1H, 1M, 1E

series II



2H, 2M, 2E

A series of low molecular weight model compounds with the same mesogenic structure (series III) was also prepared and characterized:



3H, 3M, 3E

The substituent "R" on the hydroquinone residue in all these series was either H or CH_3 or C_2H_5, so the polymers and the model compounds in each series are designated as H, M, or E, respectively, in the structures above. The polymers in series I with R = H and CH_3, 1H, and 1M, were previously synthesized and characterized in our laboratory[5,6] and also by Strzelecky and van Luyen.[8]

Most of the polymers in both series were characterized by both intrinsic viscosity and molecular weights, the latter by gel permeation chromatography, with the results collected in Table I. The mesogenic properties of the polymers and of the model compounds were studied by differential scanning calorimetry (DSC) and by polarized light microscopy.

Results and Discussion

Polymer 1H was a tough, hard-to-dissolve, ivory-colored solid, but polymer 2E was recovered as a tacky semisolid presumably because of its low molecular weight. The chemical composition of polymer 1H was determined only by elemental analysis, but the compositions and structures of the other polymers were determined by proton NMR as well. As seen from the data in Table I, the molecular weights of the series II polymers were somewhat lower than those of the series I polymers, but the values may have been high enough so as not to affect too strongly the thermal properties of the polymers based on previous results by others for a comparable system.[11,15]

The polymer solubilities were evaluated in different solvents, and the results are summarized in Table II. In general, the polymers containing oxyethylene spacers were more soluble in common solvents than polymers containing decamethylene spacers.

On examination of samples on the hot stage of a polarizing microscope, all polymers and model compounds

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Table I
Intrinsic Viscosities and Molecular Weights of Series I and II Polymers

sample	[η], dL/g	M_w[a]	M_n[a]	M_w/M_n
1H	0.91[b]			
1M	0.57[c]			
1E	0.51[c]	39 500	28400	1.39
2H		10 500	7700	1.36
2M	0.15[c]	12 100	9400	1.30
2E		9 200	6700	1.36

[a] By gel permeation chromatography. [b] In *p*-chlorophenol at 45 °C. [c] In chloroform at 25 °C.

Table II
Solubilities of Series I and II Polymers[a]

sample	*p*-chlorophenol	TCE	$CHCl_3$	THF	acetone	methanol
1H	+	–	–	–	–	–
1M	+	+	+	–	–	–
1E	+	+	+	+	–	–
2H	+	+	+	+	–	–
2M	+	+	+	+	+	–
2E	+	+	+	+	+	–

[a] + = soluble; – = insoluble.

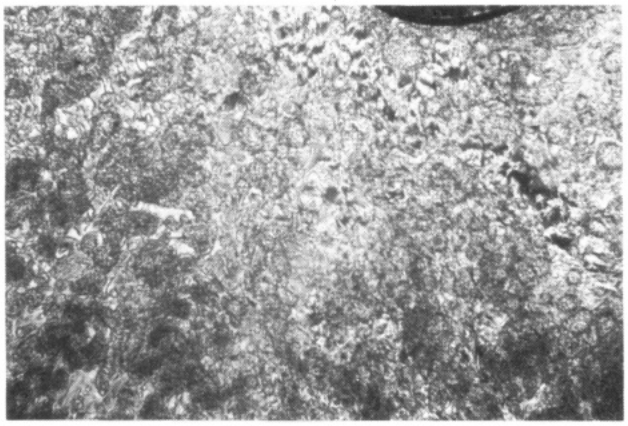


Figure 1. Photomicrograph of polymer 1H at a magnification of 200× and at 277 °C.

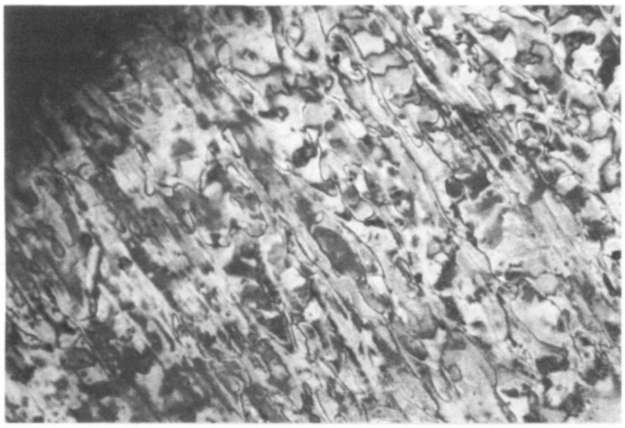


Figure 2. Photomicrograph of polymer 2M at a magnification of 200× and at 119 °C.

showed highly birefringent molten phases with threaded textures typical of nematic liquid crystalline polymers (Figure 1 and 2). Polymer 1H was reported by Strzelecky and van Luyen to exhibit two smectic phases,[8] but such phases were not observed in the present work. Nevertheless, a softening was observed for this and for some other polymers prior to the transition from the crystalline phase to the nematic phase.

Photomicrographs of series II polymers showed well-resolved textures[13] with large domains that when broken and reoriented upon shearing, were able to re-form and recover their original orientation in a very short time. A tendency toward homeotropism was observed, especially in the case of polymer **2E**. This sample was liquid crystalline at room temperature and quite viscous because it was very close to its glass transition temperature of 14 °C. The textures of the series I polymers were less well-resolved and required longer times, from 10 to 30 s depending on the temperature, to recover from shearing.

The melting transition T_m and isotropization transition T_i of all of the polymers in both series were determined by differential scanning calorimetry (DSC), with the results reported in Table III. Both of these transitions were taken at the peak maximum. The values of the enthalpies and entropies ΔH and ΔS are also included in Table III, and typical representative thermograms are given in Figures 3 and 4.

Multiple endothermic peaks were observed in the thermograms of the first heating cycle for some polymers. This behavior is commonly observed for polyesters and has been reported for many other systems.[6,7,10] In the second heating, some of the melting peaks were not reproducible, but the thermograms observed for the second and subsequent heating cycles and also for cooling cycles were reproducible.

Polymer **2M** did not crystallize on cooling from the mesophase and during standing at room temperature over 2 weeks probably because the melting transition of this polymer was too close to the glass transition temperature. A melting endotherm was not observed for polymer 1E in both the first and second heating cycles, and the thermograms were reproduced exactly for both heatings. In all three series, both transition temperatures T_m and T_i were lowered substantially by the increase in the size of the lateral substituent on the central unit of the mesogen as expected.

The effects of the lateral substituents on the mesophase properties of series II polymers and of the model compounds in series III were similar to those of series I polymers. The width of the mesophase temperature range was unaffected by the presence of a methyl substituent in both series, but it was noticeably smaller for the polymers with ethyl substituents on the central mesogenic unit. A similar substituent effect was observed on the values of ΔH_i and ΔS_i for the two series of polymers. The values of ΔH_i and ΔS_i for the polymers of series II were much smaller than those for the polymers of series I. This result agrees well with the results obtained by other workers.[12,13]

The presence of the methyl substituent in the central mesogenic unit of the series I polymers caused a substantial increase in the mesophase temperature range and in the values of ΔH_i and ΔS_i, but a further increase in the size of the substituent to the ethyl group did not have a significant additional effect on these properties.

In the series I polymers, the differences in ΔH_i and ΔS_i values of the unsubstituted polymer (1H) and the substituted polymers (1M and 1E) were rather large. This result is in agreement with previous reports on the same polymers[6] in which much higher values of ΔH_i and ΔS_i were observed for the polymers containing substituted mesogenic units with a single substituent than for polymers containing either an unsubstituted or a symmetrically disubstituted mesogen. This effect was observed only for the series I polymers and was not found either for the series II polymers or for the model compounds of series III. This result indicates that the type of flexible spacer also plays an important role in controlling the mesomorphic properties of the liquid crystalline polymers, along

Table III
Transition Temperatures and Thermodynamic Parameters of Polymers and Model Compounds

sample	T_g, °C	T_m, °C	ΔH_{m1},[a] kcal/mol	ΔH_{m2},[a] kcal/mol	T_i, °C	ΔH_i, kcal/mol	ΔS_i, cal/K mol
1H	31	253	2.35	1.58	305	1.08	1.85
1M	24	187	2.89	3.74	280	1.84	3.33
1E	25	130	0.42	0.20	234	1.61	3.17
2H	25	108	0.88	0.85	193	0.46	0.98
2M	17	78	3.02		158	0.44	1.02
2E	14				79	0.22	0.64
3H		156	8.72		245	0.77	1.48
3M[b]		115	7.50		206	0.77	1.61
3E		89	5.84		158	0.59	1.38

[a] ΔH_{m1} and ΔH_{m2}: enthalpies of melting from each of the two peaks in the first cycle thermograms. [b] According to ref 21.

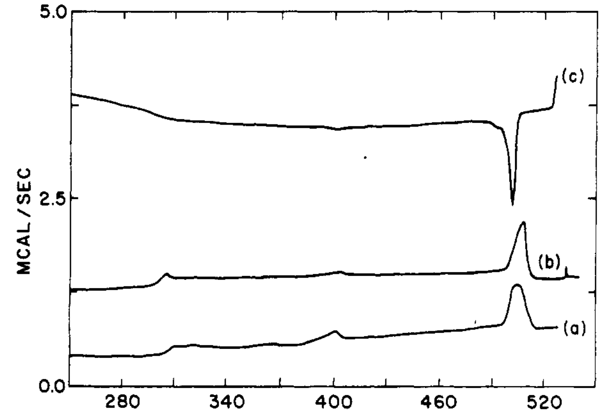


Figure 3. DSC scan of sample 1E: (a) first heating cycle, (b) second heating cycle, (c) first cooling cycle.

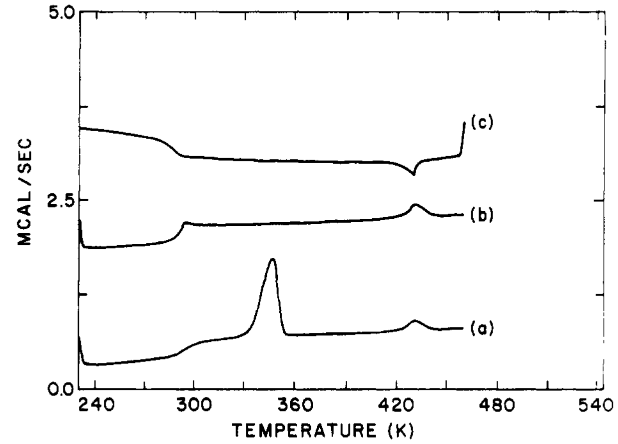


Figure 4. DSC scan of sample 2M: (a) first heating cycle, (b) second heating cycle, (c) first cooling cycle.

with the contribution of the steric effect of the lateral substituent.

Experimental Section

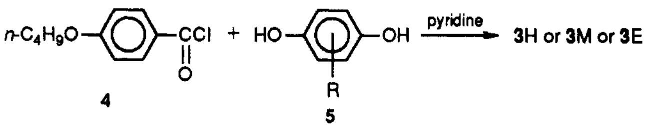
Materials. Ethyl *p*-hydroxybenzoate (Aldrich, 99%), 1,10-dibromodecane (Aldrich, 97%), potassium carbonate (Fisher, certified), thionyl chloride (Aldrich, 99+%, gold label), tosyl chloride (Aldrich, 98%), triethylborane (Aldrich, 1.0 M solution in THF), hydroquinone (Aldrich, 98.5%), and 4-*n*-butoxybenzoic acid (Aldrich, 98%) were reagents used without further purification. Tetraethylene glycol (Aldrich, 99%) was dried by azeotropic distillation with benzene. Benzoquinone (Eastman, practical grade) was sublimed under reduced pressure. Methylhydroquinone (Aldrich, 99+%, gold label) was recrystallized once from toluene.

Solvents. Dimethylformamide (DMF; Fisher, spectroanalyzed) and 1,2-dichloroethane (Aldrich, 99%) were used without further purification. Pyridine (Aldrich, 99+%, gold label) was distilled over NaOH and stored in the dark under nitrogen. Tetrahydrofuran (THF; Fisher, HPLC grade) was distilled over sodium and stored under nitrogen. 1,1,2,2-Tetrachloroethane was distilled over calcium hydride and stored under nitrogen.

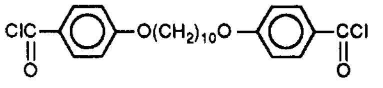
Characterization: Intrinsic viscosities [η] of the polymers were determined with a Cannon-Ubbelohde viscometer in a constant-temperature water bath. The solvents and the corresponding temperatures used were given in Table I.

Molecular weights were determined by a Waters 201 GPC, using THF as a solvent, with a flow rate of 1.34 mL/min. Narrow molecular weight polystyrene standards were used for calibration. Visual examinations of the textures and phase transiton of the polymers were made with a Leitz Ortholux polarizing microscope, and a Mettler FP-2 hot stage at a magnification of 320×. Figures 1 and 2 are the photomicrographs of polymers 1H and 2M, respectively, taken at a magnification of 200× on an Olympus BH polarizing microscope equipped with Mettler FP-800 hot stage. Thermal analysis was studied with a Perkin-Elmer Thermal Analysis System (DSC-2), equipped with a thermal analysis data station. The heating and cooling cycles were followed at a rate of 10 °C/min. The transition temperatures in Table III were taken at the peak maximum, and the values of ΔH and ΔS were calculated by integrating the peaks using indium as a reference standard.

Syntheses: The mesogenic triad was prepared by reacting the appropriate derivative of *p*-hydroxybenzoic acid with the appropriate hydroquinone. The model compounds of series III were prepared by reacting *p*-butoxybenzoyl chloride with the appropriate hydroquinone in the presence of pyridine as shown. 3H has R = H, 3M has R = CH_3, and 3E has R = C_2H_5.



Polymers 1M and 1E were synthesized by an analogous reaction using the diacid dichloride 8 in a method similar to that described by Galli et al.[13]

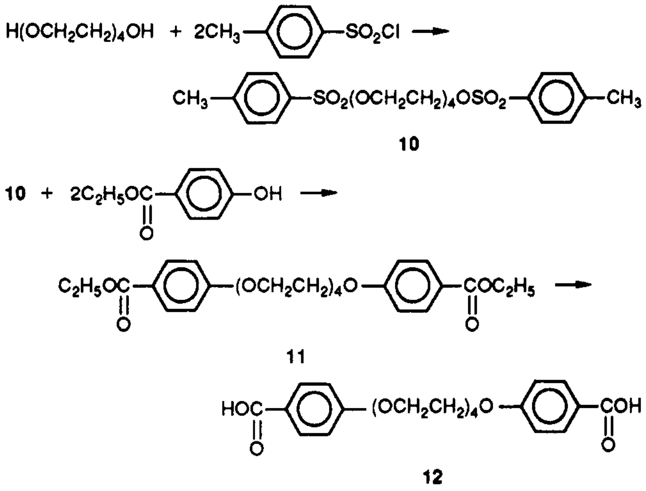


8

This diacid dichloride was synthesized according to the method described by Griffin and Havens.[7]

Ethylhydroquinone was prepared by reacting benzoquinone with triethylborane in THF. Hydroquinone, methylhydroquinone, and ethylhydroquinone were converted to the corresponding diacetates 9 by acylation with acetic anhydride. Hydroquinone diacetate was reacted with the dicarboxylic form 7 of the compound 8 for the preparation of polymer 1H.

This method is similar to that reported by Strzelecky and van Luyen.[8] The polymers of series II were prepared by an analogous reaction, in which the diacid 7 was replaced by the dicarboxylic acid 12, which was prepared by the following series of reactions:



1,10-Bis(4-carbethoxyphenoxy)decane (6). To a solution of 46.0 g (277 mmol) of ethyl *p*-hydroxybenzoate, dissolved in 60 mL of dimethylformamide in a flask fitted with a condenser and a mechanical stirrer, were added 20.0 g (132 mmol) of 1,10-dibromodecane and 34.5 g of K_2CO_3, and the heterogeneous mixture was stirred for 4 h at 150 °C. The contents in the flask, after cooling to room temperature, were poured into 2 L of distilled water and stirred for a while. The resulting aqueous suspension was refrigerated for 1 day, and the solid product, recovered by filtration, was recrystallized subsequently from ethanol and from methanol (yield 34.4 g, 60%).

1,10-Bis(4-carboxyphenoxy)decane (7). A heterogeneous mixture of 18.7 g (39.7 mmol) of 6 in 360 mL of a 10% w/v solution of KOH in 95% ethanol was refluxed for 5 h, diluted with 6 L of distilled water, and warmed to 65 °C. The dicarboxylic acid, after neutralization of the potassium salt by careful addition of concentrated HCl, was allowed to precipitate, then filtered, thoroughly washed with distilled water, and dried at 120 °C (yield 82%). The diacid was recrystallized once from DMF/95% ethanol and once from Cellosolve.

1,10-Bis[4-(chloroformyl)phenoxy]decane (8). A mixture of 1.0 g (4.8 mmol) of 7, 1.1 mL (15 mmol) of thionyl chloride, and 6 mL of 1,2-dichloroethane was refluxed in a nitrogen atmosphere for 1 h. Two drops of DMF was used as a catalyst. The acid chloride was precipitated by adding about 300 mL of hexane, stirred for about 2 h at room temperature, filtered, and dried at room temperature under reduced pressure.

Tetraethylene Glycol Ditosylate (10). The synthetic method employed was one reported in the literature,[16-18] but physical properties of the product were not reported previously. Several attempts were made without success to crystallize this compound and only an oil was obtained in each case, so the crude ditosylate was used for further reaction with ethyl *p*-hydroxybenzoate.

1,11-Bis(4-carbethoxyphenoxy)-3,6,9-trioxaundecane (11). To a solution of 8.82 g (41.0 mmol) of ethyl *p*-hydroxybenzoate, dissolved in 15 mL of DMF, were added 10.0 g (20.5 mmol) of crude tetraethylene glycol ditosylate and 7.0 g (50.6 mmol) of K_2CO_3, and the mixture was kept at 90 °C for 5 h with vigorous stirring. It was cooled and poured into 200 mL of distilled water. The viscous organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic layer was dried, and the ethyl acetate was removed by a rotary evaporator to yield 9.8 g of a viscous organic liquid. From NMR analysis, it was found that the liquid contains mostly 11 and about 10% of unconverted tosylate. Assumption of equal reactivity of the two tosylate groups in the same molecule gives the following composition of the mixture: 81% by weight of compound 11 (79% yield), 18% monotosylate, and 1% of unreacted ditosylate. Crystallization of the product was unsuccessful in several attempts. The product was soluble in methanol, ethanol, isopropyl alcohol, ethyl ether, toluene, and chloroform; it was insoluble in hexane and water; cooling of the hot solutions of solvent–nonsolvent mixtures led to emulsions.

1,11-Bis(4-carboxyphenoxy)-3,6,9-trioxaundecane (12). A solution containing 20.8 g (45 mmol) of crude 11 and 420 mL of a 10% w/v solution of KOH in 95% ethanol was refluxed for 4 h. The suspension was allowed to cool and poured into 100 mL of water. The basic solution was neutralized by careful addition of concentrated HCl. The white precipitate obtained during the neutralization was found to be KCl. On dilution of the solution by a 1 to 5 ratio with distilled water, the KCl was dissolved and the compound 12 precipitated. It was filtered, washed with distilled water, and dried. A total of 11.2 g of crude 12 was recovered (yield 64%) and purified by three recrystallizations from isopropyl alcohol: mp 186–188 °C; ^1H NMR (DMSO-d_6 and TMS as reference standard): 3.60 (s, 8 H), 3.95 (d, 8 H), 6.95 (d, 4 H), 7.90 (d, 4 H).

Ethylhydroquinone. The reductive alkylation of benzoquinone described by Hawthorne and Reintjes[19] was followed for the synthesis of this compound. A solution of 9.72 g (90 mmol) of benzoquinone in 100 mL of THF was added through a dropping funnel into 100 mL of a 1 M ethylborane solution in THF with vigorous stirring under a nitrogen atmosphere. The rate of the addition was controlled to allow the exothermic reaction to maintain the temperature of the contents in the flask around 40 °C. After the addition, the solution was kept at 60 °C for 2 h and the resulting product was steam distilled in order to hydrolyze the ethylhydroquinone diethyl-borinic monoester and to remove the borinic and boronic acids, the solvent, and other volatile materials. The ethylhydroquinone was solidified upon cooling and was recrystallized from hexane/diphenyl ether, from hexane/toluene, and then from chloroform. A total of 9.5 g of pure ethylhydroquinone was obtained (yield 69%; mp = 120 °C).

Alkylhydroquinone Diacetates (9). All the diacetates were prepared according to the method described by Majnusz and Lenz,[20] by refluxing the corresponding hydroquinone with a 50% excess of acetic anhydride in the presence of 10 mol % of anhydrous sodium acetate for 6–8 h. The products, recovered by pouring the reaction mixtures into iced water, were recrystallized 2–3 times from 70% ethanol. The yields were quantitative.

Model compounds (3H, 3M, 3E): A mixture of 2.0 g (10.0 mmol) of 4-*n*-butoxybenzoic acid, 2 mL (27.4 mmol) of thionyl chloride, and 6 mL of 1,2-dichloroethane was refluxed in the presence of 2 drops of DMF as catalyst under a nitrogen atmosphere for 1 h. The solvent and the residual thionyl chloride were removed under reduced pressure. Thionyl chloride was completely removed under reduced pressure after adding 2 mL of toluene. The resulting 4-*n*-butoxybenzoyl chloride was dissolved in 3 mL of THF, and a solution of 5.1 mmol of the appropriate hydroquinone dissolved in 4 mL of pyridine was added slowly with stirring. After 2 h, the contents of the flask were poured into 25 mL of 1 M HCl. The products of 3H and 3M were recovered and recrystallized from ethyl acetate and methanol. In the case of a derivative of ethylhydroquinone, the product appeared as a colloid. Hence, it was dissolved and extracted from the aqueous phase by ethyl acetate; the solvent was removed under reduced pressure and 3E was crystallized three times from methanol. The yields after purification were 41% in the case of hydroquinone bis(4-*n*-butoxybenzoyl) and methylhydroquinone bis(4-*n*-butoxybenzoyl) and 40% in the cases of ethylhydroquinone bis(4-*n*-butoxybenzoyl).

Polymers: Polymers 1M and 1E were synthesized by reacting the diacid chloride 6 with either methylhydroquinone or ethylhydroquinone in solution in the presence of pyridine.[13] A solution of 0.566 g (41.0 mmol) of ethylhydroquinone dissolved in 7 mL of pyridine was added during about 2 h through a dropping funnel under a nitrogen atmosphere at room temperature with constant stirring to a solution of 1.85 g (41.0 mmol) of 6 dissolved in 15 mL of 1,1,2,2-tetrachloroethane. The next day the polymer was precipitated into acetone and dried in the vacuum oven at 40 °C. A total of 1.91 g of dry polymer was obtained (yield 92%). A similar synthesis of 1M gave an identical yield.

The transesterification method[8] was used for the synthesis of polymers 1H, 2H, 2M, and 2E. Equimolar amounts of diacid 7 or 12 and an appropriate hydroquinone diacetate were ground together with 0.07 mol % of Sb_2O_3 (antimony trioxide) and calcium diacetate in a mortar. The mixture was charged into the polymerization flask that was previously evacuated and purged with nitrogen three times; then the mixture was heated at 220–260 °C under nitrogen in a fused salt bath. In the case of polymer 1H, most of the acetic acid was removed by distillation in this step. In the case of polymers 2H, 2M, and 2E, the acetic acid may have been kept from distilling by its interaction with the oxyethylene residues of the diacid. The pressure was gradually reduced after 2 h, and the mixture was heated at 260–270 °C for 1–2 h at a pressure of 0.05 Torr. Polymer 1H was obtained in a quantitative yield. It was dissolved in *p*-chlorophenol and precipitated in methanol. Polymers 2H, 2M, and 2E were obtained in a very low yield (20–30%) due to the extensive sublimation of the diacetate under reduced pressure. They were precipitated from chloroform solution using excess methanol.

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Registry No. **1E** (copolymer), 138835-45-7; **1E** (SRU), 138923-49-6; **1H** (copolymer), 76607-17-5; **1H** (SRU), 74790-57-1; **1M** (copolymer), 138835-44-6; **1M** (SRU), 78691-14-2; **2E** (copolymer), 138835-43-5; **2E** (SRU), 138923-48-5; **2H** (copolymer), 138835-41-3; **2H** (SRU), 76607-79-9; **2M** (copolymer), 138835-42-4; **2M** (SRU), 138923-47-4; **3E**, 85121-90-0; **3H**, 1818-98-0; **3M**, 66786-95-6; 4, 33863-86-4; **5E**, 2349-70-4; **5H**, 123-31-9; **5M**, 95-71-6.