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Functional polymers and sequential copolymers by phase transfer catalysis

29[a]. Synthesis of thermotropic side-chain liquid crystalline polymers containing a poly(2,6-dimethyl-1,4-phenylene oxide) main chain

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SUMMARY

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing pendant mesogenic units separated from the polymer main-chain through spacers of three to ten methylene units were synthesized and characterized. The synthetic pathway used for the chemical modification of PPO involved the radical bromination of its methyl groups followed by phase transfer catalyzed esterification of the resulting bromobenzyl groups with potassium ω-(4-oxybiphenyl)alkanoates and potassium ω-(4-methoxy-4'-oxybiphenyl)-alkanoates. Only the resulting polymers containing ten methylene units as spacer and 4,4'-methoxybiphenyl as mesogen present thermotropic liquid crystalline mesomorphism.

INTRODUCTION

Finkelmann and Ringsdorf proposed the spacer concept in 1978 as a systematic method for obtaining side-chain liquid crystalline polymers, with the idea that a spacer must be introduced to partially decouple the mobility of the main chain from that of the mesogenic groups (1-4). If this is so, then it should be possible to obtain side-chain liquid crystalline behavior from even very rigid polymer backbones. The goal of this paper is to determine the length of the spacer that is required to obtain side-chain liquid crystalline polymers from the rigid polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by introducing mesogenic units to the PPO backbone through spacers of from three to ten methylene groups via polymer analogous reactions.

The synthetic procedure used for the chemical modification of PPO involved in the first step the radical bromination of PPO methyl groups to provide a polymer containing bromobenzyl groups. The bromobenzyl groups were then esterified under phase-transfer-catalyzed (PTC) reaction conditions with potassium 4-(4-oxybiphenyl)butyrate, potassium 4-(4-methoxy-4'-oxybiphenyl)butyrate, potassium 5-(4-oxybiphenyl)valerate, potassium 5-(4-methoxy-4'-oxybiphenyl)valerate, potassium 11-(4-oxy-biphenyl)undecanoate, and potassium 11-(4-methoxy-4'-oxybiphenyl)-undecanoate. The esterification of PPO is presented in Scheme 1.

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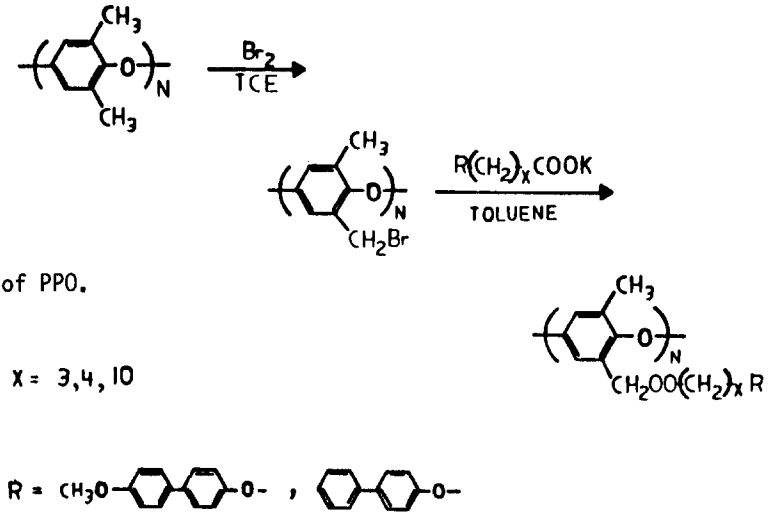

Scheme 1.
Esterification of PPO.

EXPERIMENTAL

A. Methods and Materials

Commercially available PPO (Aldrich, $\bar{M}n$=19,000, $\bar{M}w$=49,000) was purified by precipitation with methanol from chloroform solution, and brominated as described previously (5). Sodium hydroxide, potassium hydroxide, tetrabutylammonium hydrogen sulfate (TBAH) and all solvents were reagent grade and were used as received. Ethyl 4-bromobutyrate (Aldrich, 95%), ethyl 5-bromovalerate (Aldrich, 99%), 5-bromovaleronitrile (Aldrich, 95%), and 11-bromoundecanoic acid (Aldrich, 99%) were used without further purification. 4-Phenylphenol (Aldrich) was recrystallized from a toluene/ethanol solution, and 4,4'-dihydroxybiphenyl (Polysciences) was recrystallized from methanol. 4-Methoxy-4'-hydroxybiphenyl was synthesized as described previously (6).

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer and 60 MHz ^{1}H-NMR spectra were recorded on a Varian EM 360A spectrometer, both in $CDCl_3$ solutions with TMS as internal standard. Calculation of the percent substitution of PPO has been described previously (5). A Perkin Elmer 1320 Infrared Spectrophotometer was used to record IR spectra from KBr pellets. Thermal analysis was performed with a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a Perkin-Elmer TADS thermal analysis data station. Heating and cooling rates were 20°C/min, and Indium was used as the calibration standard. All samples were heated to just above Tg and quenched before the first heating scan was recorded. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor was used to analyze the anisotropic textures.

B. Synthesis of Ethyl 4-(4-oxybiphenyl)butyrate, Ethyl 4-(4-methoxy-4'-oxybiphenyl)butyrate, Ethyl 5-(4-oxybiphenyl)valerate, Ethyl 5-(4-methoxy-4-oxybiphenyl)valerate, n-Propyl 11-(4-oxybiphenyl)undecanoate, and n-Propyl 11-(4-methoxy-4'-oxybiphenyl)undecanoate.

The sodium salts of 4-phenylphenol and 4-methoxy-4'-hydroxybiphenyl were first prepared by stoichiometric reaction of sodium hydroxide with a methanol solution of the corresponding phenol, followed by solvent evaporation and drying. These sodium salts were used without further purification, as in the following example. Ethyl 4-(4-oxybiphenyl)butyrate was prepared by the addition of ethyl 4-bromobutyrate (9.8 ml, 0.068 mol) to a solution of sodium 4-phenyl-4'-phenoxide (9.8g, 0.05 mol) and TBAH (1.7g, 5.0 mmol) in dimethylformamide (DMF) (200 ml). The reaction mixture was stirred at 82°C for 3.5 h, and then precipitated in water. The precipitate was filtered, dried, and recrystallized three times from methanol, yielding 8.3 g (58%) white crystals: m.p. 51-52°C. IR: 1735 cm^{-1} ($\upsilon_{C=O}$). ^{1}H-NMR (60 MHz, $CDCl_3$, δ, ppm): 1.3 (t, $-CH_3$), 1.9-2.7 (m, $-CH_2CH_2COO$), 3.8-4.4 (m, $-CH_2O-$, $-CH_2OOC$), 7.0 (d, 2 aromatic protons), 7.5 (m, 7 aromatic protons).

Ethyl 4-(4-methoxy-4'-oxybiphenyl)butyrate: m.p. 94-97°C. IR: 1730 cm^{-1} ($\upsilon_{C=O}$). ^{1}H-NMR (60 MHz, $CDCl_3$, δ, ppm): 1.3 (t, $-CH_3$), 1.8-2.8 (m, $-CH_2CH_2COO$), 3.9 (s, $-OCH_3$), 3.9-4.4 (m, $-CH_2OOC$, $-CH_2O-$), 7.0 (d, 4 aromatic protons), 7.5 (m, 4 aromatic protons).

Ethyl 5-(4-oxybiphenyl)valerate: m.p. 73-75°C. IR: 1735 cm^{-1} ($\upsilon_{C=O}$). ^{1}H-NMR (200 MHz, $CDCl_3$, , ppm): 1.3 (t, $-CH_3$), 1.8 (m, $-CH_2CH_2-$), 2.4 (t, $-CH_2COO$), 4.0 (t, $-CH_2O-$), 4.1 (q, $-CH_2OOC$), 6.9 (d, 2 aromatic protons), 7.4 (m, 7 aromatic protons).

Ethyl 5-(4-methoxy-4'-oxybiphenyl)valerate: m.p. 93-95°C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.2 (t, $-CH_3$), 1.8 (m, $-CH_2CH_2-$), 2.4 (t, $-CH_2COO$), 3.85 (s, $-OCH_3$), 4.0 (t, $-CH_2O-$), 4.1 (q, $-CH_2OOC$), 6.9 (q, 4 aromatic protons), 7.5 (m, 4 aromatic protons).

n-Propyl 11-(4-oxybiphenyl)undecanoate: m.p. 73-75°C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 0.9 (t, $-CH_3$), 1.2-2.4 (m, $-(CH_2)_9COO$, $-CH_2-$), 3.96 (t, $-CH_2O-$), 4.02 (t, $-CH_2OOC$), 6.9 (d, 2 aromatic protons), 7.5 (m, 7 aromatic protons).

n-Propyl 11-(4-methoxy-4'-oxybiphenyl)undecanoate: m.p. 108-110°C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 0.9 (t, $-CH_3$), 1.2-2.4 (m, $-(CH_2)_9COO$, $-CH_2-$), 3.8 (s, $-OCH_3$), 3.97 (t, $-CH_2O-$), 4.02 (t, $-CH_2OOC$), 6.9 (q, 2 aromatic protons), 7.4 (m, 4 aromatic protons).

C. Synthesis of 4-(4-oxybiphenyl)butyric acid, 4-(4-methoxy-4'-oxybiphenyl)butyric acid, 5-(4-oxybiphenyl)valeric acid, 5-(4-methoxy-4'-oxybiphenyl)valeric acid, 11-(4-oxybiphenyl)undecanoic acid and 11-(4-methoxy-4'-oxybiphenyl)undecanoic acid.

The acids were best prepared by refluxing the corresponding esters overnight with excess potassium hydroxide (8 fold excess) in aqueous ethanol. The acids were isolated by first acidifying, (because the carboxylates themselves displayed limited solubility in water and in cold

aqueous ethanol), and then precipitating in water. Following filtration and drying, the acids were recrystallized from methanol, or from toluene to avoid esterification.

5-(4-Methoxy-4'-oxybiphenyl)valeric acid was also prepared from 5-bromovaleronitrile (1.75 ml, 0.015 mol) by reaction with the sodium salt of 4-methoxy-4'-hydroxybiphenyl (2.9g, 0.014 mol) and TBAH (0.52g, 1.5 mmol) in DMF (75 ml) at 85°C. After 4 h, the solvent was removed, and potassium hydroxide (7g, 0.12 mol) in aqueous ethanol (250 ml, 1:1) was added. The reaction mixture was refluxed overnight to hydrolyze the cyano group to a carboxylic acid, and then worked up as described in the previous paragraph.

4-(4-Oxybiphenyl)butyric acid: m.p. 137-139°C. IR: 3300-2500 (υ_{OH}), 1700 ($\upsilon_{C=O}$), and 900 cm^{-1} (υ_{OH}).

4-(4-Methoxy-4'-oxybiphenyl)butyric acid: m.p. 178-179°C. IR: 3300-2700 (υ_{OH}), 1700 ($\upsilon_{C=O}$), and 900 cm^{-1} (υ_{OH}).

5-(4-Oxybiphenyl)valeric acid: m.p. 141-142°C. IR: 3360-2400 (υ_{OH}), 1695 ($\upsilon_{C=O}$), and 900 cm^{-1} (υ_{OH}).

5-(4-Methoxy-4'-oxybiphenyl)valeric acid: m.p. 178.5-179°C. IR: 3400-2300 (υ_{OH}), 1690 ($\upsilon_{C=O}$), and 900 cm^{-1} (υ_{OH}).

11-(4-Oxybiphenyl)undecanoic acid. IR: 3300-2400 (υ_{OH}), 1680 ($\upsilon_{C=O}$), and 900 cm^{-1} (υ_{OH}).

11-(4-Methoxy-4'-oxybiphenyl)undecanoic acid: m.p. 150-152°C. IR: 3300-2400 (υ_{OH}), 1720 ($\upsilon_{C=O}$), and 910 cm^{-1} (υ_{OH}).

D. Synthesis of Potassium 4-(4-oxybiphenyl)butyrate, Potassium 4-(4-methoxy-4'oxybiphenyl)butyrate, Potassium 5-(4-oxybiphenyl)valerate, Potassium 5-(4-methoxy-4'-oxybiphenyl)valerate, Potassium 11-(4-oxybiphenyl)undecanoate and Potassium 11-(4-methoxy-4'-oxybiphenyl)-undecanoate.

The potassium salts were all prepared by approximately stoichiometric reaction of potassium hydroxide with a methanol solution of the corresponding carboxylic acid, followed by solvent evaporation and drying. The salts were used without further purification.

E. Esterification of Brominated PPO with Potassium 4-(4-oxybiphenyl)-butyrate (Ph3COO-PPO), Potassium 4-(4-methoxy-4'-oxybiphenyl)butyrate (Me3COO-PPO), Potassium 5-(4-oxybiphenyl)valerate (Ph4COO-PPO), Postassium 5-(4-methoxy-4'-oxybiphenyl)valerate (Me4COO-PPO), Potassium 11-(4-oxybiphenyl)undecanoate (Ph10COO-PPO) and Potassium 11-(4-methoxy-4'-oxybiphenyl)undecanoate (Me10COO-PPO).

The general procedure used for the esterification of PPO is presented in the following example. Brominated PPO (0.74 bromobenzyl groups per structural unit) (0.23g, 0.97 mmol Br) was dissolved in toluene (20 ml), and TBAH (0.07g, 0.21 mmol) and potassium 4-(4-oxybiphenyl)butyrate (0.51g, 1.7 mmol) were added. The reaction mixture was stirred at 60°C for 46h and then poured into methanol. The obtained polymer was purified by

precipitation from tetrahydrofuran (THF) solution into methanol. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.8-2.5 (m, $-CH_2-$, $-CH_2CH_2COO$), 3.9 ($-CH_2O-$), 5.0 (s, $-CH_2OOC$), 6.4-6.8 (m, 2 aromatic PPO protons), 6.9 (d, 2 aromatic protons), 7.2-7.6 (m, 7 aromatic protons).

Me3COO-PPO. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.7-2.5 (m, $-CH_3$, $-CH_2CH_2COO$), 3.8 (s, $-OCH_3$), 3.96 (s, $-CH_2O-$), 5.0 (s, $-CH_2OOC$), 6.3-6.8 (m, 2 aromatic PPO protons), 6.9 (s, 2 aromatic protons), 7.4 (s, 4 aromatic protons).

PH4COO-PPO. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.6-2.5 (m, $-CH_2-$, $-CH_2CH_2CH_2COO$), 3.9 (s, $-CH_2O-$), 6.4-6.8 (m, 2 aromatic PPO protons), 6.9 (d, 2 aromatic protons), 7.2-7.6 (m, 7 aromatic protons).

Me4COO-PPO. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.5-2.5 (m, $-CH_2-$, $-CH_2CH_2CH_2COO$), 3.8 (s, $-OCH_3$), 3.94 (s, $-CH_2O-$), 5.0 (s, $-CH_2OOC$), 6.4-6.8 (m, 2 aromatic PPO protons), 6.9 (s, 2 aromatic protons), 7.5 (s, 4 aromatic protons).

Ph10COO-PPO. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.0-2.5 (m, $-CH_2-$, $-(CH_2)_9COO$), 3.9 (t, $-CH_2O-$), 4.3 (s, $-CH_2Br$), 5.0 (s, $-CH_2OOC$), 6.3-6.8 (m, 2 aromatic PPO protons), 6.9 (d, 2 aromatic protons), 7.2-7.6 (m, 7 aromatic protons).

Me10COO-PPO. ^{1}H-NMR (200 MHz, $CDCl_3$, δ, ppm): 1.1-2.3 (m, $-CH_2-$, $-(CH_2)_9COO$), 3.8 (s, $-OCH_3$), 3.9 (t, $-CH_2O-$), 4.3 (s, $-CH_2Br$), 5.0 (s, $-CH_2OOC$), 6.4-6.8 (m, 2 aromatic PPO protons), 6.9 (d, 2 aromatic protons), 7.4 (d, 4 aromatic protons).

Table I summarizes the experimental conditions and the results of substitution of PPO for all reactions performed.

Table I. Reaction Conditions and Results of Synthesis of PPO Containing Biphenyl Groups.

#	Nucleophile	Mole Fraction Structural Units Containing $-CH_2Br$	Moles per Mole $-CH_2Br$ Nucleophile	Moles per Mole $-CH_2Br$ TBAH	Reaction Temp. (°C)	Reaction Time (hr)	%CH_2Br Substituted
1	biPhO-$(CH_2)_3$COOK	0.52	2.2	0.22	25	45	25
2		0.74	1.8	0.24	25	45	26
3		0.74	1.8	0.12	60	46	100
4	MeO-biPhO-$(CH_2)_3$COOK	0.52	2.0	0.19	25	40	15
5		0.74	2.0	0.19	25	40	12
6		0.74	1.7	0.39	60	61.5	100
7	biPhO-$(CH_2)_4$COOK	0.52	2.0	0.21	25	62	87
8		0.74	1.9	0.07	25	62	93
9		0.74	1.9	0.14	60	46	100
10	MeO-biPhO-$(CH_2)_4$COOK	0.52	2.1	0.14	25	62	50
11		0.74	2.1	0.10	25	62	61
12		0.74	2.0	0.39	60	61.5	100
13	biPhO-$(CH_2)_{10}$COOK	0.52	2.0	0.12	25	96	25
14		0.74	1.9	0.21	25	96	24
15	MeO-biPhO-$(CH_2)_{10}$COOK	0.74	0.9	0.24	60	54.5	71
16		0.74	0.9	0.24	60	139.5	75

RESULTS AND DISCUSSION

Polymer analogous reactions have been used previously to synthesize liquid crystalline polymers. For example, liquid crystalline polyacrylates, polymethacrylates, and polyacrylamides have been prepared by conventional esterification or amidation of poly(acryloyl chloride) and poly(methacryloyl chloride) with a mesogenic alcohol or amine in the presence of triethylamine (7-9). Similarly, liquid crystalline polyacrylates, polymethacrylates, and polyitaconates have been prepared by phase-transfer-catalyzed reactions on the sodium salts of the corresponding polycarboxylates (10-12). In addition, alternating poly(methylvinyl-ether-co-maleate) copolymers were prepared by the PTC reactions of poly(methylvinylether-co-disodium maleate) with mesogens containing bromoalkylesters (13). The most important use of this class of reactions, however, is in the preparation of liquid crystalline polysiloxanes, which cannot be obtained by any other method. It involves the platinum catalyzed hydrosilation reaction of vinyl substituted mesogenic molecules with poly(hydrogen methylsiloxane) or its copolymers. The synthesis of liquid crystalline polysiloxanes was recently reviewed (3,14).

We believe the polymer analogous reactions on PPO presented here are also important since it would be very difficult to obtain liquid crystalline PPO by any other method. In addition, as was demonstrated with PPO substituted similiarly with a series of alkyl side-chains, the glass transition temperature decreases with an increase in the side-chain length (15). Therefore, it is very likely that we may obtain poly(p-phenylene ethers) with low glass transition temperatures, even though unsubstituted PPO is a rigid polymer with a glass transition temperature (Tg) of 220°C.

It was previously shown that the only available procedure for the nucleophilic substitution of brominated PPO was by solid-liquid phase-transfer catalyzed reactions in nonpolar aprotic solvents (5), since PPO is not soluble in aprotic dipolar solvents which are required for conventional nucleophilic substitutions. In this case, it was necessary to use elevated temperatures (60°C) to obtain good halide displacement.

Table II summarizes the thermal characterization of substituted PPO, and demonstrates that although the Tg is easily dropped with any of the substituents, liquid crystalline behavior is not observed until 4-methoxy-4'-hydroxybiphenyl is decoupled from the PPO's backbone by ten methylenic units. Therefore, liquid crystalline behavior can be obtained from very rigid polymers, provided a long enough spacer is employed. A smectic liquid crystalline mesophase was confirmed by polarized optical microscopy for MeIOCOO-PPO, but the exact smectic phase could not be determined because some thermal crosslinking takes place during extensive annealing. This could be the result of the presence of unreacted bromobenzylic groups. In contrast to MeIOCOO-PPO, PhIOCOO-PPO is not liquid crystalline. Although there is comparatively little substitution in this case, p-biphenyl itself would not be expected to act as a mesogen in such a rigid polymer due to its low degree of anisotropy and polarizability.

In conclusion, the experiments described in this paper demonstrate that thermotropic side-chain liquid crystalline polymers can be prepared from any polymer backbone, including rigid ones, provided that a long enough spacer is employed.

Table II. Thermal Characterization of PPO Containing Biphenyl Groups.

# [a]		Temperature (°C) Heating Tg	Heating Endotherms	Cooling Tg	Cooling Exotherms
1	0.13 Ph3COO-PPO[b]	141.7	—		
2	0.19 Ph3COO-PPO	130.0	—		
3	0.74 Ph3COO-PPO	69.5	—		
4	0.08 Me3COO-PPO	172.5	—		
5	0.09 Me3COO-PPO	155.2	—		
6	0.74 Me3COO-PPO	69.4	—	58.4	—
7	0.43 Ph4COO-PPO	80.8	—		
8	0.69 Ph4COO-PPO	67.0	—		
9	0.74 Ph4COO-PPO	59.6	—		
10	0.26 Me4COO-PPO	106.2	—		
11	0.45 Me4COO-PPO	89.2	—	85.6	—
12	0.74 Me4COO-PPO	62.5	—	53.1	—
13	0.13 Ph10COO-PPO	105.5	—		
14	0.18 Ph10COO-PPO	83.7	—		
15	0.53 Me10COO-PPO	54.2	114.5	39.2	77.5
16	0.56 Me10COO-PPO	38.6	72.4, 116.8, 129.0	c	40.4, 101.4

a) from Table I; b) mole fraction of mesogen substituted structural units; c) buried in peak

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