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FUNCTIONAL POLYMERS AND SEQUENTIAL COPOLYMERS BY PHASE

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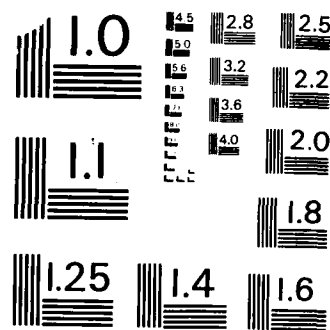
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Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis.

30. Synthesis of Liquid Crystalline Poly(epichlorohydrin) and Copolymers

By

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ABSTRACT

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Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis. 30^a.

SYNTHESIS OF LIQUID CRYSTALLINE POLY(EPICHLOROHYDRIN) AND COPOLYMERS

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^a) Part 29 in this series: C. Pugh and V. Percec, Polym. Bull., submitted.

SUMMARY

Poly(epichlorohydrin) (PECH) containing pendant mesogenic units separated from the polymer main chain through spacers of zero to ten methylene units were synthesized and characterized. The synthetic pathway used for the chemical modification of PECH involved the phase transfer catalyzed etherification and esterification of the chloromethyl groups with sodium 4-methoxy-4'-biphenoxide and potassium ω -(4-methoxy-4'-oxybiphenyl)-alkanoates. All the resulting polymers, including that with no spacer, present thermotropic liquid crystalline mesomorphism.

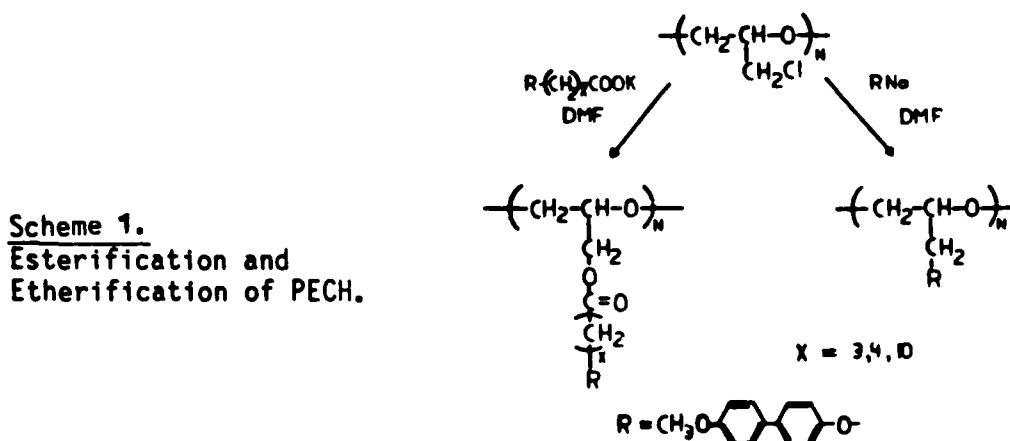
INTRODUCTION

In the previous paper in this series, we synthesized and characterized poly(2,6-dimethyl-1,4-phenylene oxide) containing mesogenic units separated from the main chain through spacers of three, four, and ten methylene units in order to determine the length of the spacer that is required to obtain thermotropic liquid crystalline mesomorphism from such a rigid polymer. It was found that only the polymers containing ten methylene units as the spacer were liquid crystalline.

The goal of this paper is to further test the spacer concept proposed by Finkelmann and Ringsdorf (1-4) when very flexible polymer backbones are employed. That is, we wish to determine the necessity and/or the length of the spacer that is required to achieve liquid crystallinity from flexible polymers, with the idea that a flexible polymer backbone may itself act as a flexible spacer, thereby eliminating the need for an additional spacer between the mesogen and the polymer main chain. In order to test this hypothesis, we have introduced mesogens to the backbone of flexible poly(epichlorohydrin) (PECH) through spacers of from zero to ten methylene groups by polymer analogous reactions.

The synthetic procedure used for the chemical modification of PECH involved the phase-transfer-catalyzed esterification of the chloromethyl groups with potassium 4-(4-methoxy-4'-oxybiphenyl)butyrate, potassium 5-(4-methoxy-4'-oxybiphenyl)valerate, and potassium 11-(4-methoxy-4'-oxybiphenyl)undecanoate. In addition, the phase-transfer-catalyzed etherification of the chloromethyl groups of PECH with sodium

4-methoxy-4'-biphenoxide was used to synthesize PECH with direct attachment of the mesogen to the polymer backbone. Esterification and etherification routes of PECH are presented in Scheme 1.



EXPERIMENTAL

A. Materials and Methods

Commercially available PECH (B. F. Goodrich, $M_n=873,000$, $M_w=10,250,000$) was purified by precipitation with methanol from chloroform solution. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 3.7 (s, $-\text{CH}_2\text{O}-$, $-\text{CH}-$, $-\text{CH}_2\text{Cl}$). 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 (5).

200 MHz $^1\text{H-NMR}$ spectra were recorded on a Varian XL-200 spectrometer and 60 MHz $^1\text{H-NMR}$ 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 PECH has been described previously (6). 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 $^\circ\text{C}/\text{min}$ unless noted otherwise, and Indium was used as the calibration standard. All samples were heated to just above T_g 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.

Table I. Reaction Conditions and Results of Synthesis of PECH
Containing Methoxybiphenyl Groups.

#	Nucleophile	Moles per Mole $-\text{CH}_2\text{Cl}$		Reaction Time (hr)	$\Sigma\text{CH}_2\text{Cl}$ Substituted
		Nucleophile	TBAH		
1	MeO-b1PhONa	0.76	0.10	92	29
2		0.76	0.10	140	36
3	MeO-b1PhO-(CH ₂) ₃ COOK	0.69	0.13	91	22
4		0.75	0.12	108.5	26
5		0.75	0.12	139.5	30
6		0.75	0.12	158.5	34
7	MeO-b1PhO-(CH ₂) ₄ COOK	0.75	0.12	19	23
8		0.75	0.12	49	42
9		0.75	0.12	83	52
10		0.73	0.11	91	51
11		0.75	0.12	115.5	62
12		0.75	0.12	140	65
13		0.75	0.12	159.5	65
14		0.75	0.12	181.5	65
15	MeO-b1PhO-(CH ₂) ₁₀ COOK	0.64	0.17	54	17

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

The carboxylic acids and their potassium salts were prepared as described previously (7).

C. Substitution of PECH with 4-methoxy-4'-hydroxybiphenyl (MeO-PECH).

PECH (0.3g, 3.2 mmol) was dissolved in DMF (20 ml), and TBAH (0.11g, 0.31 mmol) and sodium 4-methoxy-4'-biphenoxide (0.5g, 2.2 mmol) were added. The reaction mixture was stirred at 60°C for 92 h and poured into methanol. The obtained polymer was purified by precipitation from THF solution into methanol. ¹H-NMR (200 MHz, CDCl₃, δ , ppm): 3.1-4.4 (m, $-\text{CH}_2\text{O}$, $-\text{CH}-$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OC}$, $-\text{OCH}_3$), 6.9 (d, 4 aromatic protons), 7.5 (d, 4 aromatic protons). The moles of substituted chloromethyl groups per structural unit was calculated to be 0.29.

D. Esterification of PECH with Potassium 4-(4-methoxy-4'-oxybiphenyl)-butyrate (Me3COO-PECH), Potassium 5-(4-methoxy-4'-oxybiphenyl)valerate (Me4COO-PECH), and Potassium 11-(4-methoxy-4'-oxybiphenyl)undecanoate (Me10COO-PECH).

In a typical procedure, PECH (0.19g, 2.1 mmol) was dissolved in DMF (20 ml) and TBAH (0.08g, 0.24 mmol) and potassium 4-(4-methoxy-4'-oxybiphenyl)butyrate (0.52g, 1.5 mmol) were added. The reaction mixture was stirred at 60°C for 91 h and poured into methanol. The obtained polymer

was purified by precipitation from THF solution into methanol. $^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 2.1 (s, $-\text{CH}_2\text{COO}$), 2.5 (s, $-\text{CH}_2-$), 3.2-4.4 (m, $-\text{CH}_2\text{O}$, $-\text{CH}-$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OOC}$, $-\text{CH}_2\text{OC}_6$), 6.9 (d, 4 aromatic protons), 7.5 (d, 4 aromatic protons). The moles of substituted chloromethyl groups per structural unit was calculated to be 0.22.

Me4COO-PECH. $^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 1.9 (s, $-\text{CH}_2\text{CH}_2-$), 2.5 (s, $-\text{CH}_2\text{COO}$), 3.2-4.6 (m, $-\text{CH}_2\text{O}$, $-\text{CH}-$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OC}_6$, $-\text{OCH}_3$), 6.9 (d, 4 aromatic protons), 7.5 (d, 4 aromatic protons).

Me10COO-PECH. $^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 1.1-1.9 (m, $-(\text{CH}_2)_8-$), 2.3 (t, $-\text{CH}_2\text{COO}$), 3.4-4.4 (m, $-\text{CH}_2\text{O}$, $-\text{CH}-$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OC}_6$, $-\text{OCH}_3$), 6.9 (d, 4 aromatic protons), 7.5 (d, 4 aromatic protons).

Table II summarizes the experimental conditions and the results of substitution of PECH for all reactions performed.

RESULTS AND DISCUSSION

The results of the modification of PECH summarized in Table I demonstrates that we were able to obtain from 17 to 65% substitution of the chloromethyl groups. As determined previously (6), it is necessary to use elevated temperature (60°C) to achieve good halide displacement of these weakly electrophilic primary chlorides.

In contrast to the results of the previous paper in this series on PPO, Table II demonstrates that no spacer is required to obtain liquid crystalline behavior from PECH, although the thermal characteristics of Me10COO-PPO and Me10COO-PECH are very similar. Figures 1 thru 5 show some

Table II. Thermal Characterization of PECH Containing Methoxybiphenyl Groups.

#	1st Heat		Temperature ($^\circ\text{C}$)		2nd Heat	
	T_g	Endotherms	T_g	Exotherms	T_g	Endotherms
1	9.2	66.6, 82.9	- 1.6	65.7	7.0	81.2
2	17.3	60.1, 80.5	- 3.9	62.9	12.4	81.6
3	-4.1	39.8, 49.6	- 9.8	—	-2.5	—
4	-0.9	7.9, 52.3	-11.7	13.9	-0.4	43.1
5	0.1	51.6, shoulder	- 7.3	26.7	1.8	51.7
6	3.7	50.0, shoulder	- 6.9	31.6	3.7	56.8
7	-9.1	shoulder, 44.7	-13.6	—	-7.5	34.1
8	7.7	55.0, 70.3	2.0	42.0, 55.2	6.2	70.7
9	18.6	58.8, 85.4, 107.2	4.7	70.6	17.3	88.1
10	17.0	57.3, 83.5, 103.2	- 5.2	65.7	16.0	83.4
11	34.3	73.5, 100.5, 114.4	—	82.9	37.6	101.7
12	35.2	72.0, 105.0, 117.3	—	89.0	40.2	107.1
13	36.0	67.0, 107.9, 119.2	—	91.4	47.7	110.4
14	34.1	62.4, 107.8, 118.1	—	91.1	44.1	109.8
15			-20.3	34.7, 88.6	-12.9	45.7, 74.1, 105.4

* from Table I

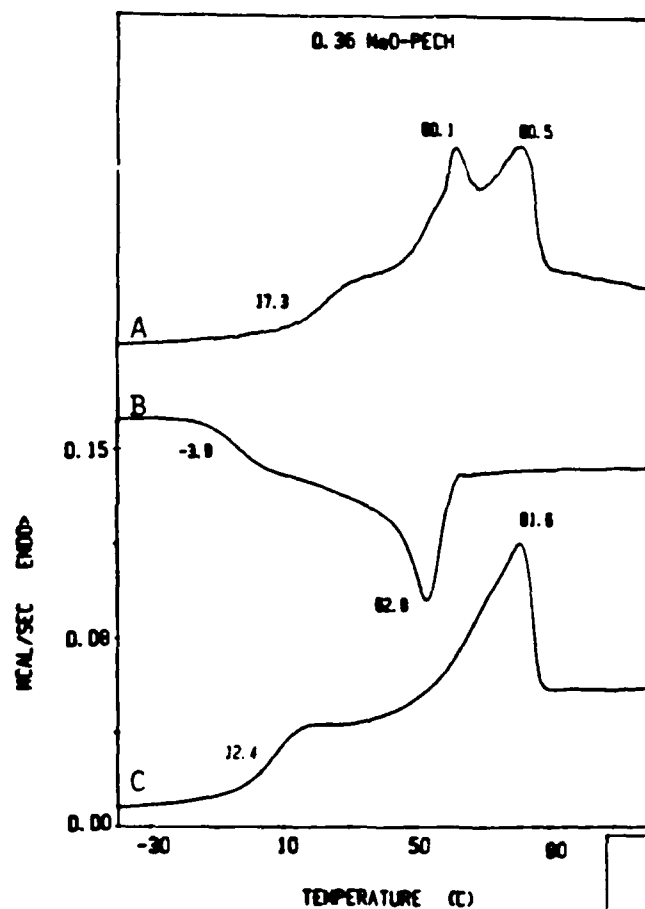
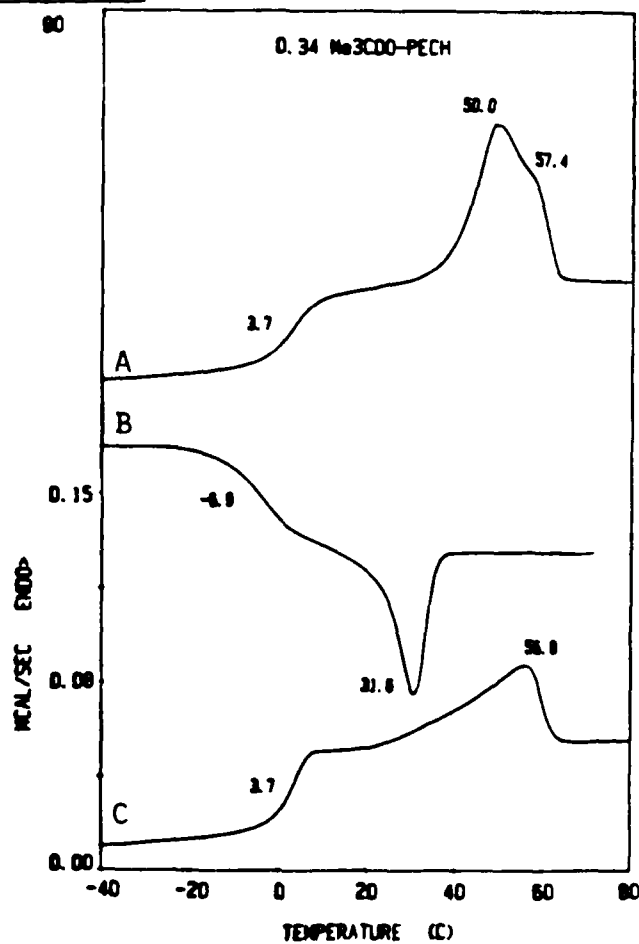


Figure 1. DSC traces of 0.36 MeO-PECH: (A) first heat; (B) first cool; (C) second heat.

Figure 2. DSC traces of 0.34 Me₃COO-PECH: (A) first heat; (B) first cool; (C) second heat.



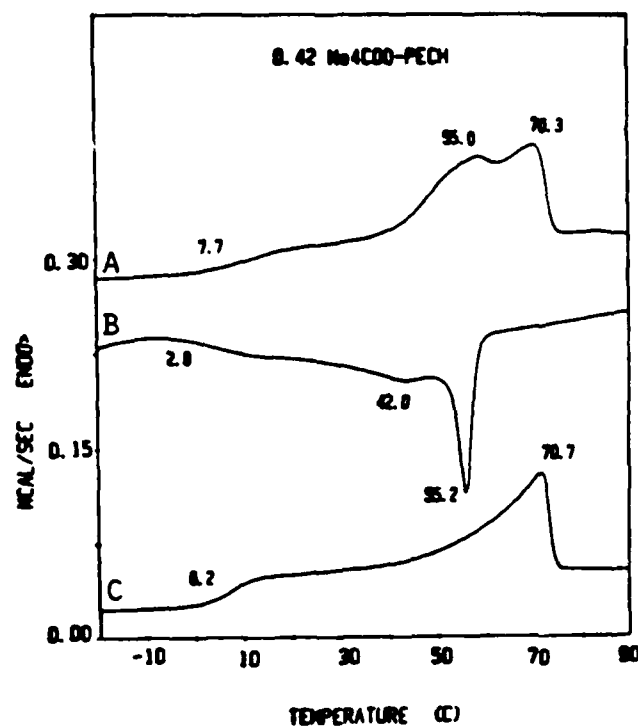
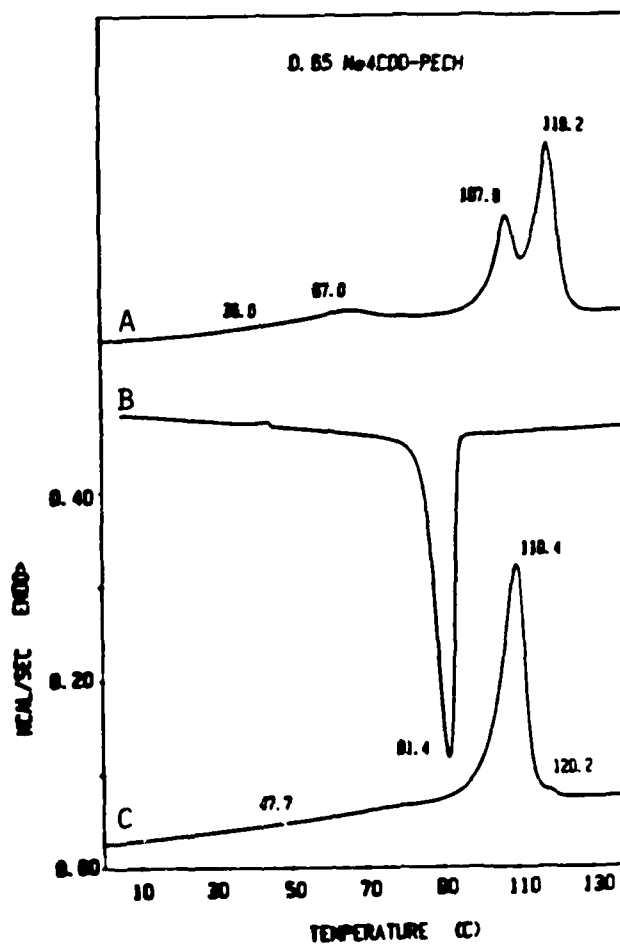


Figure 4. DSC traces of 0.42 Me₄COO-PECH: (A) first heat; (B) first cool; (C) second heat.

Figure 5. DSC traces of 0.65 Me₄COO-PECH: (A) first heat; (B) first cool; (C) second heat.



representative DSC traces for MeO-PECH, Me3COO-PECH and Me4COO-PECH. In addition to the first cooling and second heating scans, the first heating scan is also shown. This is because the multiple endotherms observed with all spacers in this scan can be reproduced simply by annealing above T_g for several hours. Therefore, these endotherms cannot be dismissed as traces of solvent or the result of thermal history, and the phases are evidently kinetically controlled. It must be noted that this is the first time liquid crystalline polymers of such high molecular weight have been obtained. We have found with main-chain liquid crystalline polymers (8) that beyond a critical molecular weight, not only are the crystalline transitions kinetically controlled, but the liquid crystalline transitions also become kinetically rather than thermodynamically controlled, presumably as the result of chain entanglements. This results in a higher degree of supercooling than is normally observed for liquid crystalline phases, especially for smectic mesophases, as is seen here.

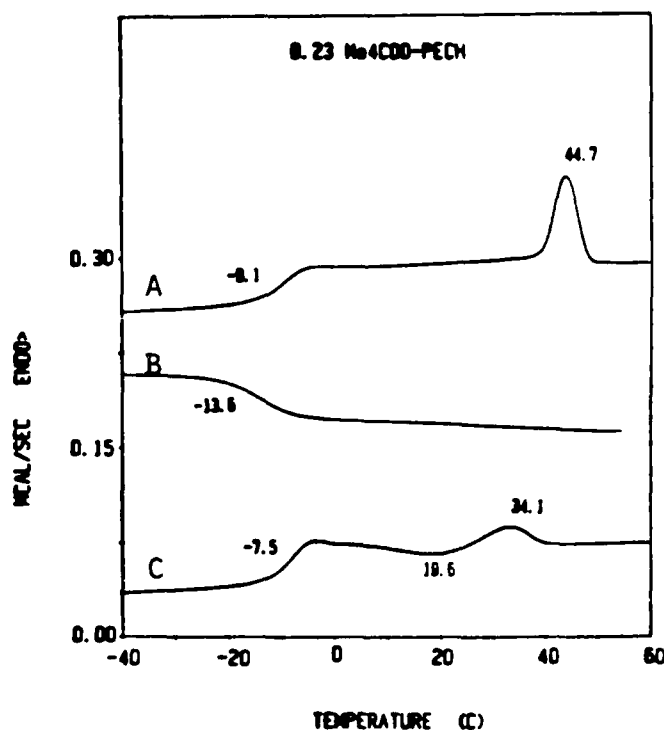
0.22 Me3COO-PECH and 0.23 Me4COO-PECH (Fig. 3) demonstrate that there is a minimum concentration limit necessary for mesophase formation in copolymers of mesogenic monomers with nonmesogenic monomers (3), since the liquid crystalline endotherm is not observed in the second heating scan. In addition, Figure 3 demonstrates that the first endotherm in each sample may be a crystalline melting. The first heating scan of 0.23 Me4COO-PECH shows a strong liquid crystalline endotherm at 44.7°C, and a weak endotherm in the form of a tail at the temperature corresponding to the weak melting endotherm in the second scan. This endotherm is obviously crystalline melting since cold crystallization of the same enthalpic content is required just prior to the melting. This, and the lack of a crystallization exotherm on cooling demonstrates that crystallization is slow and occurs over a large range of temperatures with these samples. This is probably due to the proximity of the T_g and the temperature of melting (T_m), combined with a great deal of crystalline supercooling.

Beyond the minimum mesogenic concentration limit of approximately 26% with these shorter spacers (or no spacer), isotropization is also seen in the second heating scans with melting seen only as a tail to isotropization. Once 51% substitution is reached with Me4COO-PECH, we see in addition to melting and the "normal" liquid crystalline endotherm (T_i), crystallization followed by a second endotherm at higher temperature. However, it is not observed again on reheating scans unless the sample is annealed, and the enthalpy of the endotherm in the second heating scan is equal to the total enthalpy content of the first two peaks in the first scan. When substitution is increased further, this third endotherm is seen as a minor peak in additional heating scans and therefore represents the true isotropization temperature.

Preliminary room temperature x-ray data of 0.65 Me4COO-PECH (Fig. 5) indicates that the sample presents a highly ordered smectic mesophase. The textures seen by polarized optical microscopy are also typical of undeveloped smectic phases. Due to the very high molecular weights involved, textures could not be developed within a reasonable amount of time by annealing.

In conclusion, the phase-transfer-catalyzed incorporation of mesogenic units into PECH offers a simple method for obtaining liquid crystalline elastomers whose transition temperatures can be tailored by varying the amount of substitution and the length of the spacer between the mesogen and the backbone. Liquid crystalline poly(ethylene oxide) oligomers were previously prepared by the homopolymerization of mesogenic oxiranes (9). These polymers represent an alternative to polysiloxanes for the preparation of liquid crystalline elastomers.

Figure 3. DSC traces of 0.23 Me₄COO-PECH: (A) first heat; (B) second heat; (C) second heat.



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