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Thermotropic Hydrocarbon Main-Chain Liquid Crystalline Polymers Based on a Biphenyl Mesogen. Synthesis and Characterization

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ABSTRACT: A new homologous series of hydrocarbon oligomers having biphenyl mesogenic units and polymethylene spacers in the main chain were prepared by a carbon–carbon coupling reaction. Polymers with number-average molecular weights in the range of 4000–6000 have been obtained. Homopolymers with spacer units varying from 6 to 10 methylene units and equimolar copolymers with 6/8, 6/10, and 8/10 methylene spacers were found to exhibit smectic mesophases. The effect of the variation of the lengths of the methylene spacers on liquid crystalline properties is discussed. In general, increasing the length of the methylene spacers is accompanied by a decrease in the isotropization temperature. An alternating odd–even effect in transition temperatures is also observed, with the even members having higher isotropization temperatures than the odd members. Two different X-ray diffraction patterns for odd- and even-membered homopolymers were observed for unoriented samples.

Introduction

Early explanations for the existence of liquid crystals have usually followed two main schools of thought. As early as 1949, Onsager[1] did model calculations on the isotropic–nematic phase transition by considering a fluid of long thin rods with no forces between them except for steric interactions. He concluded that excluded volume alone is sufficient to cause an entropy-driven transition from the isotropic to the anisotropic phase when the concentration of rods exceeds a critical value. By contrast, Maier and Saupe[2] have emphasized the role of anisotropic attractive interaction in the stabilization of the mesophase. They postulated that the liquid crystalline phase transition is energy-driven by anisotropic attractions only. However, more recent theories[3,4] have shown that intermolecular attractive forces are not necessary for the formation of liquid crystalline phases. These theories predict that molecular asymmetry alone is sufficient to induce an ordered phase. This view has been supported by the discovery of liquid crystallinity in poly(tetrafluoroethylene) whiskers[5] and by the numerous examples[6] of hydrocarbon liquid crystals that have been reported. Since hydrocarbon liquid crystals contain only very weak dispersion forces, the existence of liquid crystalline phases can be attributed mainly to the anisotropic molecular shape.

Low molecular weight hydrocarbon liquid crystals have been known for some time. A review of the effects of various structural elements on the properties of low molecular weight hydrocarbon liquid crystals may be found in the literature.[7] However, with the exception of the work being performed in our laboratory,[8-10] all-hydrocarbon liquid crystalline polymers have received relatively little attention. A recent report by Memeger[11] describes substituted poly(phenylenevinylene) polymers that were characterized as liquid crystalline. This paper describes the synthesis and characterization of a series of thermotropic all-hydrocarbon main-chain liquid crystalline polymers with biphenyl as the mesogenic unit. The polymers were prepared by a nickel-catalyzed carbon–carbon coupling reaction. Preliminary results which did not include synthetic details have been reported previously.[12]

Experimental Section

Materials. Bromobenzene obtained from Aldrich Chemical Co. was distilled before use. Ethylene glycol was purchased from Baker Scientific and used without further purification. Tetrahydrofuran (THF) was purchased from Baker Scientific and was freshly distilled from Na–benzophenone under Ar before use.

The α,ω-alkanedicarbonyl dichlorides were prepared from the corresponding dicarboxylic acids by treatment with thionyl

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Table I
Characterization Data for Monomers 2

m (yield,[a] %)	mp, °C	elem anal., % found (calcd) C	H	^{1}H NMR chemical shifts, ppm
5	50	53.49	4.72	7.4 (d, 4 H), 7.0 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 2 H)
(39)		(53.43)	(4.75)	
6	65	56.82	5.70	7.4 (d, 4 H), 7.0 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 4 H)
(56)		(56.63)	(5.73)	
7	31	55.67	5.30	7.4 (d, 4 H), 7.0 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 6 H)
(41)		(55.63)	(5.41)	
8	67	56.80	5.68	7.4 (d, 4 H), 7.0 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 8 H)
(57)		(56.62)	(5.70)	
9	32	57.37	5.88	7.4 (d, 4 H), 7.1 (d, 4 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 10 H)
(47)		(57.55)	(5.98)	
10	39	58.25	6.11	7.4 (d, 4 H), 7.1 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 12 H)
(51)		(58.42)	(6.24)	
12	40	60.11	6.79	7.4 (d, 4 H), 7.1 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 16 H)
(46)		(60.01)	(6.72)	
14	42	61.54	7.19	7.4 (d, 4 H), 7.1 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 20 H)
(42)		(61.42)	(7.14)	

[a] Based on the α,ω-alkanedicarbonyl dichloride. The yields of the diketones 1 were generally 50–55%.

chloride.[13] Aluminum chloride was purchased as a Gold Label product from Aldrich Chemical Co. and was used without further purification. Potassium hydroxide was obtained from Fisher Scientific and was used without further purification. Hydrazine hydrate was obtained as a 55% aqueous solution from Aldrich Chemical Co. and was used as received. Magnesium metal was obtained from Aldrich as a Gold Label product and was used without further purification. 1,3-Bis(diphenylphosphino)propanenickel(II) chloride ($NiCl_2$(dppp)) was purchased from Strem Chemicals and also was used as received.

Measurements. Melting points were taken on a Fisher-Johns Melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory at the University of Massachusetts. ^{1}H NMR spectra were obtained in $CDCl_3$ solvent on a Varian XL-200 spectrometer (200 MHz) with tetramethylsilane (0.00 ppm) as an internal standard. Solid-state ^{13}C NMR spectra were obtained using cross-polarization (CP) and magic angle spinning (MAS) techniques at 50.3 MHz on an IBM 200 AF spectrometer equipped with an IBM solids accessory.

The molecular weights of the polymers were determined by using gel permeation chromatography (GPC). A Waters 201 liquid chromatograph with Ultrastyragel columns was employed to determine the molecular weights relative to polystyrene standards.

Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC-IV at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. The instrument was calibrated with standard samples of indium. To assure that all samples had equivalent thermal histories, the results of the second heating and cooling scans have been reported throughout.

Polarized light optical microscopy (POM) studies were carried out on a Leitz-Wetzler microscope equipped with a Mettler hot stage at a magnification of 320×. Photomicrographs were taken at a magnification of 120× with crossed polarizers.

X-ray diffraction experiments were carried out on a Statton flat-film camera using Ni-filtered Cu Kα radiation. The samples were sealed in glass capillaries, and a homemade hot stage was used to control the sample temperature to within 1 °C.

General Procedure for the Preparation of α,ω-Bis(4-bromophenyl)-α,ω-alkanedione (1). A 1000-mL three-neck round-bottomed flask was equipped with a thermometer, a magnetic stirring bar, and a 125-mL dropping funnel protected by a calcium chloride guard tube. A total of 600 mL of bromobenzene and 60 g (0.45 mol) of anhydrous aluminum chloride were added, and the mixture was cooled to 0 °C in an ice/salt bath. An amount of 0.2 mol of freshly distilled α,ω-alkanedicarbonyl dichloride was slowly added to the stirred mixture so that the temperature was kept between 0 and 5 °C. After the addition was completed, the mixture was allowed to warm to room temperature and stirred overnight.

The contents of the flask was poured into 500 g of ice/40 mL of concentrated HCl in a large beaker. Excess bromobenzene was removed by steam distillation to give a yellow solid. The solid was recrystallized from chloroform/hexane to give white flaky crystals which contained 1 and a small amount of *p*-dibromobenzene.

In general, the α,ω-bis(4-bromophenyl)-α,ω-alkanediones 1 were not purified further and were used directly. Thus, no characterization data were obtained for these compounds. The main impurity, *p*-dibromobenzene, could be removed very easily in the next step.

General Procedure for the Preparation of α,ω-Bis(4-bromophenyl)alkane (2). A total of 0.05 mol of α,ω-bis(4-bromophenyl)-α,ω-alkanedione, 120 mL of ethylene glycol, 40 g (0.6 mol) of 85% potassium hydroxide, and 42 mL (0.6 mol) of hydrazine hydrate were placed in a 500-mL three-neck round-bottomed flask with a stirring bar. A Dean-Stark trap equipped with a reflux condenser was attached, and the flask was heated and stirred at 100 °C for 1 h. The temperature was then raised slowly to 180 °C. Excess hydrazine hydrate and a small amount of *p*-dibromobenzene were codistilled from the reaction mixture and were collected in the Dean-Stark trap. Refluxing at ca. 200 °C was continued for 3 h. At the end of the heating period the reaction mixture was cooled to about 100–110 °C and was then poured into 150 mL of water. The mixture was extracted with diethyl ether (100 mL × 3). The combined ethereal solution was washed with dilute sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent gave a yellow solid. The solid was purified first by distillation on a Kugelrohr apparatus followed by recrystallization from ether/ethanol to yield a white, crystalline solid. The characterization data for the α,ω-bis(4-bromophenyl)alkanes 2 are shown in Table I.

Polymerization. A total of 0.122 g of magnesium turnings (5 mmol) was placed into an oven-dried 50-mL three-neck round-bottomed flask with a stirring bar. A reflux condenser was attached, and the apparatus was flushed with Ar for 30 min. Freshly distilled THF (25 mL) was transferred via cannula to the flask. A total of 5 mmol of monomer 2 and a small amount of iodine were added to the THF/Mg mixture under Ar. The reaction mixture was refluxed under Ar until all the Mg was reacted (ca. 2 h). A total of 5 mg of $NiCl_2$(dppp) was added to initiate the polymerization reaction. Refluxing was continued overnight as the polymer precipitated from the reaction mixture. The reaction mixture was poured into methanolic hydrogen chloride to destroy unreacted Grignard reagents. The solid polymer was removed by filtration and extracted in a Soxhlet extractor with methanol for 8 h to remove magnesium bromide and low molecular weight products. A light yellow powder was obtained in 59–72% yield (calculated on the basis of the carbon content of monomer and polymer). The characterization data for the polymers 4 are given in Tables II–IV.

Results and Discussion

Synthesis. The hydrocarbon polymers with the general structure 4 were synthesized as shown in Scheme I. The

Table II
Yields and Elemental Analyses for the Homopolymers 4

m	yield,[a] %	elem anal., % found (calcd) C	H	Br
5	72	88.52 (91.84)	8.29 (8.16)	3.25
6	65	88.06 (91.47)	8.52 (8.53)	3.51
7	69	88.16 (91.14)	8.62 (8.86)	3.02
8	63	87.97 (90.85)	8.75 (9.15)	3.46
9	68	88.64 (90.59)	8.71 (9.41)	2.78
10	61	87.02 (90.35)	9.52 (9.65)	3.59
12	59	87.06 (89.93)	9.39 (10.07)	3.65
14	62	87.52 (89.59)	8.94 (10.41)	3.67

[a] Calculated on the basis of the carbon content of the monomers and polymers.

Table III
Molecular Weight and DP for the Homopolymers 4

m	M_n[a]	M_n[b]	M_w[b]	M_w/M_n[b]	DP[c]
5	4918	4670	7705	1.65	21.4
6	4553				18.6
7	5292	4556	7625	1.67	20.5
8	4619				16.9
9	5749	4665	7498	1.61	20.1
10	4452				14.7
12	4379				13.2
14	4355				12.0

[a] Calculated on the assumption that both end groups of the polymer chain are bromine atoms. [b] GPC MW (polystyrene standard; eluent, chloroform). The even members of the series were not readily soluble for GPC analysis. [c] Based on M_n in the second column.

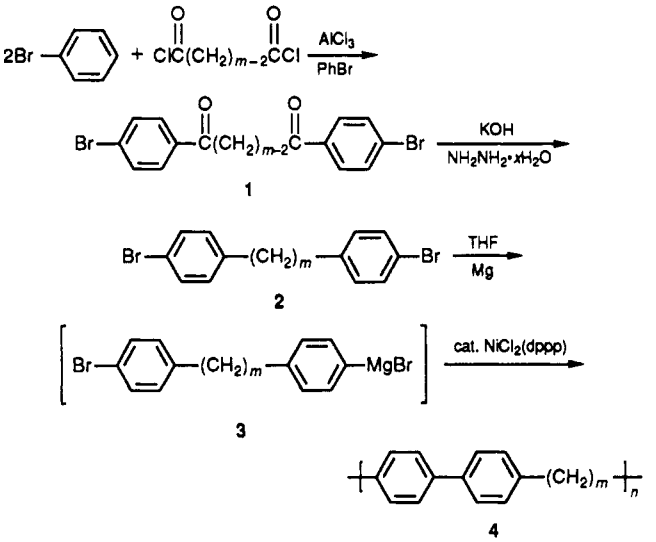
Table IV
Yields, Elemental Analyses, Molecular Weights, and DP for the Copolymers

m	yield,[a] %	M_n[b]	DP	elem anal., % found (calcd) C	H	Br
6/8[c]	65	4814	18.6	87.11 (91.14)	8.63 (8.86)	3.32
6/10[d]	68	5897	21.7	88.97 (90.85)	8.63 (9.15)	2.71
8/10[e]	72	5240	18.3	88.21 (90.59)	8.51 (9.41)	3.05

[a] Calculated on the basis of the carbon content of the monomers and polymers. [b] Calculated on the assumption that both end groups of the polymer chain are bromine atoms. [c] Copolymer from 50 mol % of two monomers **2** with m = 6 and 8. [d] Copolymer from 50 mol % of two monomers **2** with m = 6 and 10. [e] Copolymer from 50 mol % of two monomers **2** with m = 8 and 10.

syntheses of monomers **2** were modifications of a two-step process developed by Jaunin.[14] The first step consists of the acylation of bromobenzene with α,ω-alkanedicarbonyl dichloride. An excess of bromobenzene was used as both solvent and reactant to afford α,ω-bis(4-bromophenyl)-α,ω-alkanedione (**1**). These diketones **1** were generally not isolated in the pure state because they were always contaminated with a small amount of *p*-dibromobenzene, which is a well-known side product during the preparation of bromobenzene. Since *p*-dibromobenzene could easily be removed in the next step, no attempts were made to obtain the pure α,ω-bis(4-bromophenyl)-α,ω-alkanedione (**1**). Thus, no characterization data were obtained for these compounds, and they were used in the subsequent step after one recrystallization.

Scheme I[a]
Synthesis of Main-Chain Hydrocarbon Liquid Crystalline Polymers



[a] m = 5, 6, 7, 8, 9, 10, 12, 14, 6/8, 6/10, and 8/10. dppp = $Ph_2PCH_2CH_2CH_2PPh_2$.

The second step is a typical Wolff–Kishner reduction reaction of the benzylic ketone which generally produced the monomers **2** in over 90% yield. Azine formation is often a major side reaction for Wolff–Kishner reduction; however, this complication could be avoided by using excess hydrazine. Removal of the *p*-dibromobenzene impurity was also achieved at this stage because it was codistilled with hydrazine from the reaction mixture. The monomers **2** with m = 5, 7, 12, and 14 are new compounds. Table I contains the characterization data for the monomers. Both the ^1H NMR spectra and elemental analyses are in excellent agreement with the proposed structures and indicate that the compounds are pure.

The polymers **4** were synthesized by a nickel-catalyzed carbon–carbon (C–C) coupling between the aryl bromide bond and the aryl magnesium bromide group formed in the reaction mixture. In contrast to the low yield generally obtained from uncatalyzed C–C coupling reactions, the transition-metal-catalyzed C–C coupling reaction proceeds selectively under mild conditions to give the desired product in high yield.[15] The nickel catalyst used in this work has been widely utilized to prepare conductive polymers such as polyphenylene and polythiophene.[16] The polymerization reaction is performed in tetrahydrofuran (THF) since the Grignard intermediate **3** is insoluble in diethyl ether but soluble in THF. It is also well-known that the di-Grignard reagent is only soluble in THF. The reaction of the monomer with an equimolar amount of Mg does not give the sole product **3**, as shown in Scheme I, but gives a mixture of di-Grignard and mono-Grignard in addition to unreacted starting material. Similar results have been reported before.[16,17] The important consideration is that when an equivalent amount of monomer and Mg was employed, the coupling reaction proceeded without losing the stoichiometric relationship required for the polycondensation.

Eight homopolymers with m = 5, 6, 7, 8, 9, 10, 12, and 14 have been prepared as shown in Scheme I. These polymers were generally obtained in 60–70% yield from the reaction in THF, from which they precipitated as the polymerization proceeded. The yields and elemental analyses of the homopolymers are given in Table II. All polymers contain 3–4% of bromine, and the sum of carbon, hydrogen, and bromine is nearly 100%. The high bromine

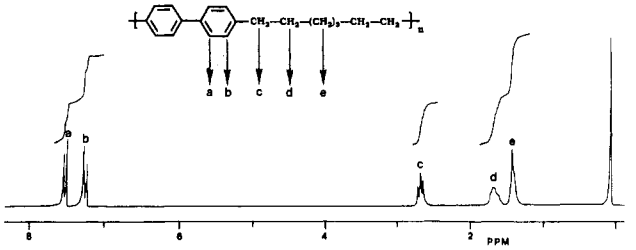


Figure 1. ^{1}H NMR spectrum for polymer 4 with m = 7.

content suggests that the precipitated polymers stop growing and that the insolubility of the polymers limits the molecular weight. Because of the insolubility of the even members of the homopolymers in common organic solvents, their molecular weights (MWs) could not be obtained by solution methods such as GPC. However, the approximate number-average degree of polymerization (DP) and MW could be calculated from the bromine analyses, assuming that both end groups of the polymer chain are bromine atoms. These results are summarized in Table III. The calculated MWs and DPs would be less if some of the bromine chain ends were replaced by hydrogen atoms. Hydrogen end groups may occur when unreacted Grignard groups are hydrolyzed at the end of the reaction during subsequent workup. In contrast to the even homologous series, the series of odd polymers where m = 5, 7, and 9 are soluble in chloroform. Their GPC MWs relative to a polystyrene standard and polydispersities are also shown in Table III. The modest MWs of both the odd- and even-membered polymers are most likely due to the insolubility of the propagating Grignard intermediates **3** in THF solution.

To increase the solubility and MW, three copolymers with 50 mol % of each monomer with m = 6/8, 6/10, and 8/10 were prepared. However, these copolymers also precipitated as the polymerization proceeded. Like the even-membered homopolymers, they were insoluble in common organic solvents. The yields, elemental analyses, MW, and DP of the copolymers are given in Table IV.

The chemical structures of polymers have been established by NMR in addition to elemental analyses. A representative ^{1}H NMR spectrum as well as the peak assignments of a homopolymer with m = 7 is shown in Figure 1. Solid-state ^{13}C CP/MAS (cross polarization/magic angle spinning) NMR spectra were obtained for polymers that are insoluble in organic solvents (i.e., the even-membered homopolymers and the copolymers). The ^{13}C CP/MAS spectra of these polymers are similar, and the spectrum of a homopolymer with m = 12 is given as an example in Figure 2. The assignments of signals due to the biphenyl mesogen were determined by comparison with known spectra and by dipolar dephasing experiments.[18]

Liquid Crystalline Properties. The liquid crystalline properties of these polymers have been studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction. The DSC results for these polymers are summarized in Table V. Temperatures T_1, T_2, T_3, and T_i refer to peak temperatures of successive endotherms observed upon a second heating of the sample at 10 °C/min, while values given in parentheses refer to the corresponding exotherms when the sample was cooled from the melt at 10 °C/min. Temperature T_i refers to the isotropization temperature. The same subscript notation is used to designate the corresponding enthalpy changes. All the polymers exhibit multiple melting transitions on DSC analysis except the homopolymer with m = 14. Representative DSC scans

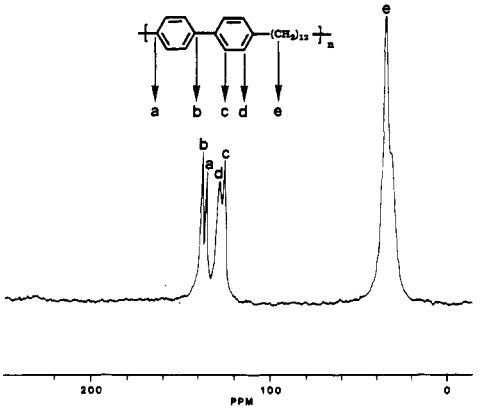


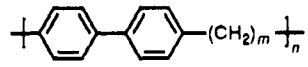
Figure 2. Solid-state ^{13}C NMR spectrum for polymer 4 with m = 12.

for an odd-membered polymer with m = 5, two even-membered polymers with m = 8 and m = 12, and an equimolar copolymer with m = 8/10 are shown in Figures 3–6, respectively. On the basis of DSC data, it appears that copolymers have broader mesomorphic ranges than the homopolymers and both the melting points (T_1) and isotropization temperatures (T_i) are lower than for the homopolymers.

With the exception of homopolymers with m = 12 and 14, all the polymers formed turbid melts upon heating, and the melts exhibited strong stir opalescence at temperatures up to their transition into the isotropic melt phase. Upon cooling from the isotropic melt state, smectic-type textures were observed under POM. Figure 7a shows a typical photomicrograph for the homopolymers. Upon cooling from the isotropic melt state, and characteristic of many smectogenic polymers, batonnets began to appear on the dark background, increasing gradually in number and size over a period of minutes to an hour. No appreciable change was observed upon subsequent cooling. The texture persisted even after cooling to room temperature. A representative photomicrograph for the copolymers is shown in Figure 7b. Unlike the homopolymers, however, the photomicrograph in Figure 7b exhibits only a weak indication of smectic-type textures. In general, POM provided no evidence for the existence of nematic-type textures for both the homopolymers and copolymers. Homopolymers with m = 12 and 14 did not exhibit any birefringence.

The nature of the mesophases was also investigated by X-ray diffraction at the appropriate temperatures. The diffraction patterns of the mesophases were obtained for the polymers while held in a capillary tube in which the polymer was heated from the crystalline phase to the mesophase. The diffraction pattern, representatively shown for the homopolymer with m = 8 in Figure 8a, consists of one sharp inner reflection and a single sharp outer ring. The inner ring is attributable to the layer spacing and varies from 14.7 to 18.3 Å as a function of the number of flexible methylene spacers. On the other hand, the sharp outer reflection corresponds to the distance between the neighboring mesogens within a layer. Its spacing of around 4.5 Å is approximately equal to the value observed for the corresponding low molar mass model compounds.[8] Both the copolymers and even members of homopolymers with m = 6, 8, and 10 yielded the same X-ray diffraction patterns when the temperature was kept between the first transition temperature (T_1) and the isotropization temperature (T_i). Therefore, these temperatures (T_1) are interpreted as crystal to smectic phase transition temperatures for the corresponding polymers. A representative X-ray diffrac-

Table V
Polymer Thermal Properties[a]



structures	T_1	T_2	T_3	T_i	ΔH_1	ΔH_2	ΔH_3	ΔH_i
$m = 5$	136 (105)[b]			178 (158)	0.58 (0.92)			0.41 (0.55)
$m = 6$	104		228 (223)	270 (259)	1.05		0.48 (0.54)	0.15 (0.10)
$m = 7$	126 (96)			154 (146)	0.58 (0.42)			0.31 (0.23)
$m = 8$	127 (104)	155	184 (180)	218 (208)	0.66 (1.48)	0.48	0.63 (0.47)	0.22 (0.24)
$m = 9$	119 (101)			149 (132)	0.66 (0.43)			0.32 (0.25)
$m = 10$	143 (136)			181 (172)	0.86 (0.76)			0.55 (0.47)
$m = 12$	145 (137)	152 (146)	158 (156)	170 (165)				6.75[c] (7.27)[c]
$m = 14$				153 (143)				7.00 (6.93)
$m = 6/8$	88			242 (234)	1.03			2.11 (2.13)
$m = 6/10$	100			211 (204)	1.39			2.04 (2.06)
$m = 8/10$	114 (89)			194 (184)	1.53 (1.23)			2.35 (2.22)

[a] Temperature, °C. ΔH, kcal/mol. [b] Values in parentheses refer to the results from the cooling scans. [c] The reported ΔH is for the enthalpy of the composite peak. Separation of enthalpy was difficult due to peak overlapping.

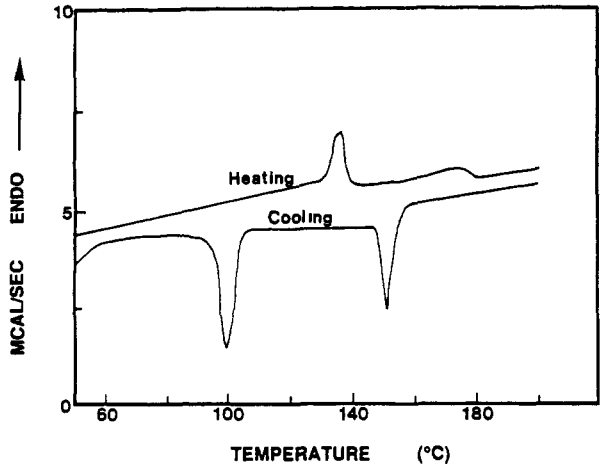


Figure 3. Second heating and cooling DSC scans for polymer 4 with $m = 5$.

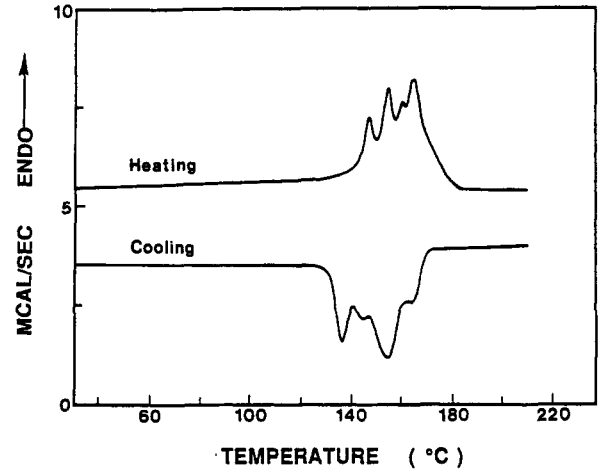


Figure 5. Second heating and cooling DSC scans for polymer 4 with $m = 12$.

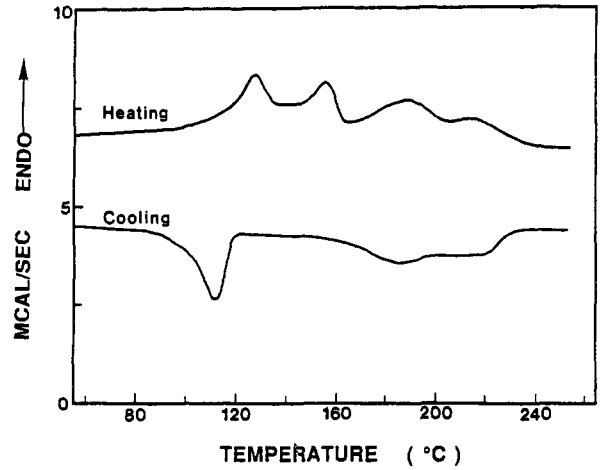


Figure 4. Second heating and cooling DSC scans for polymer 4 with $m = 8$.

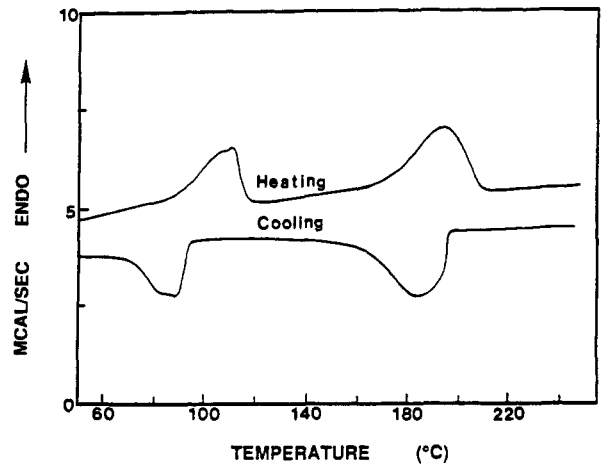


Figure 6. Second heating and cooling DSC scans for equimolar copolymer 4 with $m = 8/10$.

tion pattern taken in the mesomorphic temperature range for the odd-membered polymers is shown in Figure 8b. One principal difference between the odd and even series is that the outer reflections for the odd series are split into two sharp rings, one at 4.3 Å and the other at 4.7 Å, whereas the even-membered polymers have only one ring at 4.5 Å. Similar results for another series of liquid crystalline polymers have been previously reported by Watanabe et al.[19] From their X-ray results obtained on highly oriented samples, they concluded that the difference between these two X-ray patterns can be attributed to the different arrangement of mesogenic groups along the polymer chains. In the polymer chains of even-membered polymers, the mesogenic groups are approximately parallel to the chain axis, while in odd-membered polymers the mesogenic groups are tilted from the polymer chain. A relevant paper on the solid-state structure of azomethine ether polymers discusses tilting of mesogens as a function of odd and even spacers.[20] The X-ray patterns of oriented samples could not be obtained in our case because the MW of our polymers was too low to draw fibers from the mesophase. We could not confirm the above interpretation of the observed difference between the odd and even series. The X-ray diffraction data are summarized in Table VI.

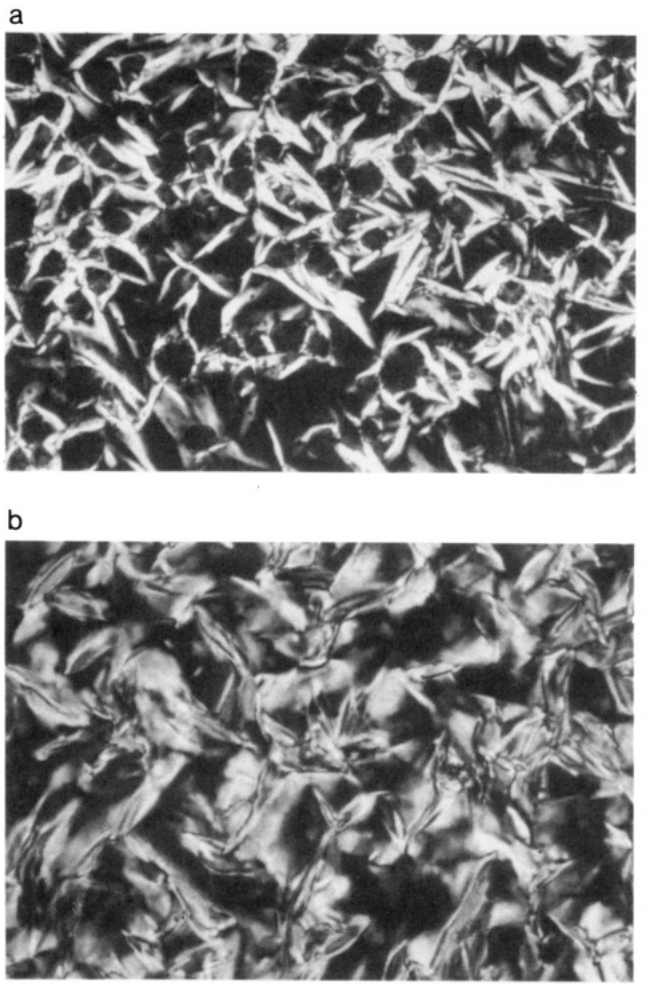


Figure 7. Photomicrograph under crossed polarizers: (a) polymer **4** with $m = 10$ at 150 °C; (b) equimolar copolymers with $m = 8/10$ at 150 °C.

Table VI
X-ray Diffraction Results

		layer spacing, Å	
m	intermolecular spacing, Å	obsd	calcd
5	4.3, 4.7	10.2	12.3
6	4.5	14.7	14.8
7	4.3, 4.7	14.8	16.3
8	4.5	16.1	16.8
9	4.3, 4.7	17.6	18.3
10	4.5	18.3	18.8
6/8	4.5	15.2	
6/10	4.5	15.7	
8/10	4.5	16.1	

The calculated layer spacings were obtained assuming an all-trans conformation for the methylene spacers. The observed layer spacings are comparable to the calculated length of the molecule for the even-membered polymers and indicate that the molecules are not tilted within the layers. However, the observed layer spacings are always less than the calculated spacings for the odd-membered polymers. This would suggest that either the molecules are tilted in the layer or that some of the carbon–carbon bonds are in the gauche conformation. Because our samples are unoriented we cannot delineate between these two possibilities. All the evidence indicates that the polymers with $m = 5$–10, 6/8, 6/10, and 8/10 are liquid crystalline while polymers with $m = 12$ and 14 are not liquid crystalline. This is probably due to the lower mesogenic content, <50%, for polymers with $m = 12$ and 14. The homopolymer with $m = 12$ is not liquid crystalline

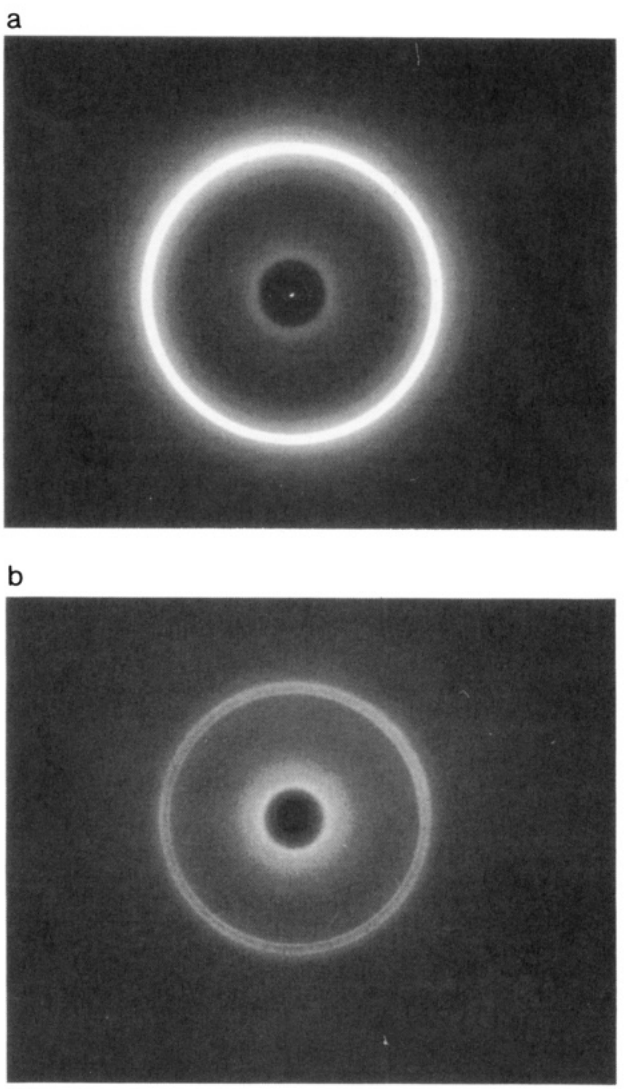


Figure 8. X-ray diffraction patterns: (a) even-membered polymer **4** with $m = 8$ at 140 °C; (b) odd-membered polymer **4** with $m = 5$ at 145 °C.

but gives multiple phase transitions by DSC as shown in Figure 5. Birefringent texture was not observed by POM even after annealing the sample for 1 week at 160 °C. X-ray scattering experiments also do not show evidence for the existence of liquid crystalline phases. The multiple peaks in Figure 5 probably represent crystal–crystal transitions or melting peaks of crystals with different degrees of crystal perfection.

For our series of hydrocarbon polymers, the isotropization temperature measured by DSC analysis decreased regularly in a zigzag manner as the length of the methylene units increased. As generally observed for other liquid crystalline polymers, those with an even number of methylene units showed higher isotropization temperatures than those with an odd number as shown in Figure 9. Another effect of lengthening the flexible spacer was to narrow the temperature range over which the mesophase formation occurred. It is also interesting to note that lengthening the flexible spacer caused a decrease in the melting point (T_1) for the odd-membered polymers but an increase in the melting point for the even-membered polymers and copolymers. On the other hand, isotropization temperatures decrease as a function of the number of methylene spacers for both the even- and odd-membered series. The melting and isotropization temperatures from the DSC results for the even and for the odd series of homopolymers and copolymers are presented as a function

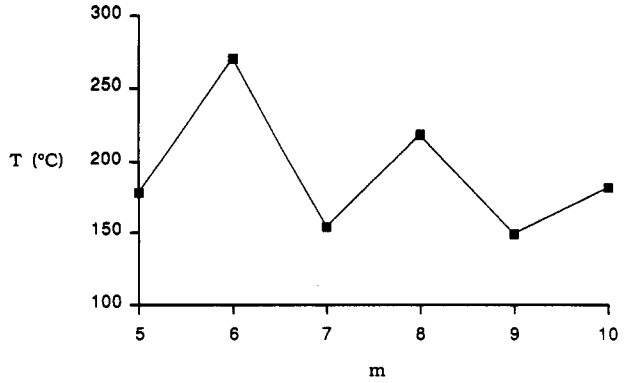


Figure 9. Isotropization temperatures for homopolymers versus the number of methylene spacers, *m*.

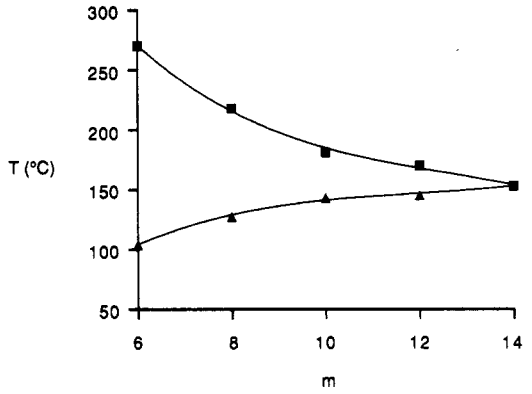


Figure 10. Melting points T_1 (▲) and isotropization temperatures T_i (■) for even-membered homopolymers versus the number of methylene spacers, *m*.

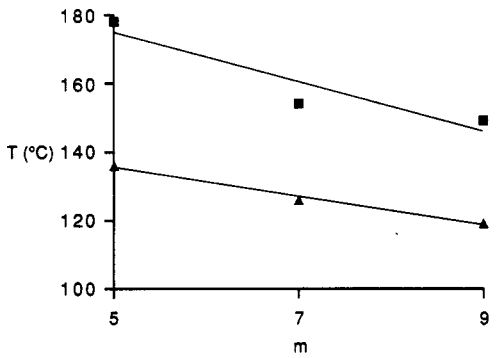


Figure 11. Melting points T_1 (▲) and isotropization temperatures T_i (■) for odd-membered homopolymers versus the number of methylene spacers, *m*.

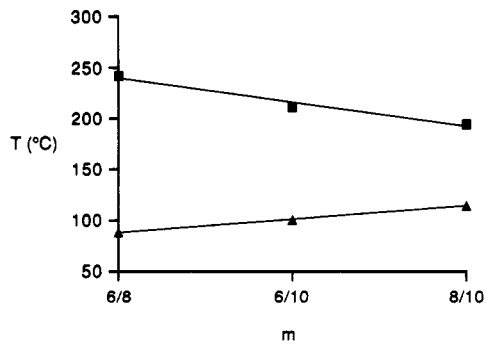


Figure 12. Melting points T_1 (▲) and isotropization temperatures T_i (■) for copolymers versus the number of methylene spacers, *m*.

of methylene spacers in Figures 10–12. It must be kept in mind that these generalizations are tentative since molecular weights have a large effect on transition temperatures, particularly at low or intermediate molecular weights. However, the molecular weights of our polymers are in similar ranges, allowing for valid comparisons to be made.

Conclusion

A new homologous series of hydrocarbon oligomers having biphenyl mesogenic units and polymethylene spacers in the main chain were prepared and characterized for their liquid crystalline properties. The observations made with the DSC, POM, and X-ray diffractions indicate that these oligomers exhibited smectic phases when 6–10 methylene units were incorporated while polymers with 12 and 14 methylene units are not liquid crystalline. Our results indicate that approximately 50% of mesogenic content is needed to give liquid crystalline properties. An odd–even effect in the isotropization temperatures was detected as the spacer length changed, with higher values being obtained for the polymers with an even number of methylene spacers. There is a definite difference in the structure of the even- and odd-membered series as evidenced by the X-ray diffraction results.

Three equimolar copolymers were synthesized to test the concept that copolymerization should disrupt the regularity required for the smectic-layered structure and might therefore lead to the formation of nematic phases. However, all the evidence indicated that these copolymers also exhibited only smectic phases. It is interesting to note that all the previously reported hydrocarbon liquid crystals containing biphenyl mesogen exhibited smectic mesophases. The anisotropic molecular shape of this biphenyl mesogen and the attractive forces between the biphenyl rings apparently stabilize smectic phases relative to nematic phases.

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