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

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ABSTRACT: A series of thermotropic hydrocarbon liquid-crystalline oligomers contained a tolan mesogenic unit connected by a flexible polymethylene spacer were prepared. The oligomers were synthesized by a palladium-catalyzed carbon–carbon coupling reaction between aryl iodide and aryl acetylene monomers. Polymers with number-average molecular weights in the range of 3000–4000 have been obtained. Four tolan polymers with 6, 8, 10, and 12 methylene spacers were prepared and characterized by DSC, polarized light optical microscopy, X-ray diffraction, and solid-state ^{13}C NMR. The polymers were liquid-crystalline, but their mesophases could not be definitively characterized. Lengthening the polymethylene spacers between the tolan mesogenic groups decreased both the melting points and the isotropization temperatures and also narrowed the mesomorphic ranges.

Introduction

Most of the thermotropic liquid-crystalline polymers known today contain heteroatoms such as N, O, or Si in their structures. These heteroatoms not only provide simple and versatile synthetic methods but also contribute to mesophase stability through hydrogen bonding or dipole–dipole interactions. It is generally believed that both the attractive interactions between the molecules and the anisotropy of molecular shape are responsible for the formation of liquid-crystalline phases.[1,2] However, considerable evidence[3-5] has been obtained recently that it is sufficient to consider only the anisotropic interactions for the development of liquid crystallinity. In other words, the existence of a liquid-crystalline phase can be governed by shape anisotropy alone. All-hydrocarbon liquid-crystalline polymers should be good candidates to test the validity of this theory because they have only weak intermolecular attractive forces. Therefore, the existence of a liquid-crystalline phase can be attributed mainly to the anisotropic molecular shape.

In our previous reports,[6,7] we described the synthesis and characterization of a series of all-hydrocarbon liquid-crystalline polymers based on a biphenyl mesogen. In this paper, we report the synthesis and characterization of another series of thermotropic all-hydrocarbon main-chain liquid-crystalline polymers with tolan (diphenylacetylene) as the mesogenic unit. The polymers prepared in this work were synthesized by a palladium-catalyzed carbon–carbon (C–C) coupling reaction. This reaction using a palladium catalyst has been widely used to prepare conductive polymers such as poly(arylene-acetylenes).[8,9]

Experimental Section

Materials. Hexamethylphosphoramide (HMPA), copper(I) iodide, (trimethylsilyl)acetylene, and bis(triphenylphosphine)-palladium(II) chloride were obtained from Aldrich Chemical Co. and were used without further purification. Methanol, potassium hydroxide (85+%), and potassium iodide were purchased from Fisher Scientific Co. and were used without further purification.

Triethylamine was purchased from Fisher Scientific Co. and was distilled from potassium hydroxide under Ar before use. Benzene was also purchased from Fisher Scientific Co. and was distilled under Ar before use.

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. ^1H 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. Infrared (IR) spectra were taken on a Perkin Elmer FTIR-1600 spectrometer.

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 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 sample temperatures to within 1 °C.

General Procedure for the Preparation of α,ω-Bis(4-iodophenyl)alkanes 3. In a 200-mL three-necked round-bottom flask fitted with a reflux condenser were placed 0.01 mol of α,ω-bis(4-bromophenyl)alkane **2**,[6] 33 g (0.2 mol) of potassium iodide, 19 g (0.1 mol) of copper(I) iodide, 50 mL of HMPA, and a magnetic stirring bar. The mixture was stirred under Ar at 150–160 °C for 8 h. At the end of the heating period, the reaction mixture was cooled to about 50 °C and was then poured into 400 mL of water/40 mL of concentrated HCl followed by the addition of diethyl ether (300 mL) in a large Erlenmeyer flask. The insoluble inorganic salts were removed by filtration. The organic phase was separated, washed with 10% aqueous sodium sulfite solution (2 × 100 mL), and dried over magnesium sulfate. Evaporation of the solvent gave a light yellow solid. The solid was purified by recrystallization from chloroform/ethanol to yield a white crystalline solid. Yields, melting points, elemental analysis results, and ^1H NMR data for compounds **3** are summarized in Table I.

General Procedure for the Preparation of α,ω-Bis{4-[(trimethylsilyl)ethynyl]phenyl}alkanes 4. In a 100-mL three-necked round-bottom flask fitted with an addition funnel were placed 5 mmol of α,ω-bis(4-iodophenyl)alkane **3**, 28 mg (0.04 mmol) of bis(triphenylphosphine)palladium(II) chloride, 8 mg (0.042 mmol) of copper(I) iodide, 25 mL of triethylamine, and a magnetic stirring bar. The mixture was degassed by passing Ar through it for 15 min, and then 1.3 g (13 mmol) of (trimethylsilyl)acetylene was added dropwise to the mixture

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Table I. Characterization Data for Monomers 3

m (yield, %)	mp, °C	elemental anal., % found (calcd) C	H	^{1}H NMR chemical shifts, ppm
6 (77)	93	44.33 (44.11)	4.20 (4.11)	7.6 (d, 4 H), 6.9 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 4 H)
8 (80)	80	46.30 (46.36)	4.72 (4.67)	7.6 (d, 4 H), 6.9 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 8 H)
10 (73)	57	48.46 (48.37)	5.19 (5.17)	7.6 (d, 4 H), 6.9 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 12 H)
12 (75)	66	50.36 (50.19)	5.53 (5.62)	7.6 (d, 4 H), 6.9 (d, 4 H), 2.5 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 16 H)

Table II. Characterization Data for Compounds 4

m (yield, %)	mp, °C	elemental anal., % found (calcd) C	H	^{1}H NMR chemical shifts, ppm
6 (87)	103	77.97 (78.07)	8.97 (8.90)	7.4 (d, 4 H), 7.1 (d, 4 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 4 H), 0.2 (s, 9 H)
8 (90)	76	78.26 (78.53)	9.21 (9.23)	7.4 (d, 4 H), 7.1 (d, 4 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 8 H), 0.2 (s, 9 H)
10 (89)	60	78.99 (78.94)	9.49 (9.52)	7.4 (d, 4 H), 7.1 (d, 4 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 12 H), 0.2 (s, 9 H)
12 (85)	60	79.44 (79.30)	9.81 (9.79)	7.4 (d, 4 H), 7.1 (d, 4 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.2 (m, 16 H), 0.2 (s, 9 H)

under Ar. A white precipitate of triethylamine hydroiodide began to form immediately. The reaction mixture was stirred under Ar at room temperature for 8 h, and then the crystalline white solid of triethylamine hydroiodide was removed by filtration. The brown filtrate was concentrated, mixed with 100 mL of 10% aqueous sodium bicarbonate, and extracted with hexane (3 × 50 mL). The organic fractions were combined, dried over magnesium sulfate, and decolorized with activated charcoal to give a light yellow hexane solution. Evaporation of the solvent gave a light yellow solid. Recrystallization from ethanol yielded a white, crystalline solid. Yields, melting points, elemental analysis results, and ^{1}H NMR data for compounds 4 are summarized in Table II.

General Procedure for the Preparation of α,ω-Bis(4-ethynylphenyl)alkanes 5. α,ω-Bis{4-[(trimethylsilyl)ethynyl]-phenyl}alkane 4 (5 mmol) prepared above was treated with 0.9 g of potassium hydroxide in ca. 100 mL of methanol/ether (1:1 v/v) solution under Ar at room temperature for 1 h. The solvent was evaporated, and the residue was mixed with 100 mL of 10% aqueous sodium bicarbonate and extracted with ether (3 × 50 mL). The combined ethereal fractions were dried over magnesium sulfate and concentrated to yield a white solid. This white solid is essentially very pure. Yields, melting points, elemental analysis results, and ^{1}H NMR data for compounds 5 are summarized in Table III.

Polymerization. In a 100-mL three-necked round-bottom flask were placed 2.5 mmol of α,ω-bis(4-iodophenyl)alkane 3, 2.5 mmol of α,ω-bis(4-ethynylphenyl)alkane 5, 10 mL of triethylamine, and 40 mL of benzene. The mixture was degassed by passing Ar through it for 15 min, and then 14 mg (0.02 mmol) of bis(triphenylphosphine)palladium(II) chloride and 4 mg (0.02 mmol) of copper(I) iodide were added under Ar. A white precipitate of triethylamine hydroiodide began to form after 10 min. After stirring under reflux for 4 h, the reaction mixture was cooled and poured into 200 mL of ethanol. The precipitate obtained was separated by filtration and extracted in a Soxhlet extractor with methanol for 8 h to remove triethylamine hydroiodide and low molecular weight products. A light brown solid was obtained in ca. 60% yield (calculated on the basis of the carbon content of monomer and polymer). The characterization data for the polymers are given in Table IV.

Table III. Characterization Data for Monomers 5

m (yield, %)	mp, °C	elemental anal., % found (calcd) C	H	^{1}H NMR chemical shifts, ppm
6 (93)	66	92.12 (92.26)	7.82 (7.74)	7.4 (d, 4 H), 7.1 (d, 4 H), 3.0 (s, 1 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 4 H)
8 (96)	46	91.68 (91.67)	8.32 (8.33)	7.4 (d, 4 H), 7.1 (d, 4 H), 3.0 (s, 1 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 8 H)
10 (93)	41	90.97 (91.17)	8.81 (8.83)	7.4 (d, 4 H), 7.1 (d, 4 H), 3.0 (s, 1 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 12 H)
12 (95)	50	90.98 (90.75)	9.03 (9.25)	7.4 (d, 4 H), 7.1 (d, 4 H), 3.0 (s, 1 H), 2.6 (t, 4 H), 1.6 (m, 4 H), 1.3 (m, 16 H)

Table IV. Yields, Elemental Analyses, Molecular Weights, and DPs for Polymers 1

m	yields,[a] %	elemental anal., % found (calcd) C	H	I	MW[b]	DP[b]
6	62	84.23 (92.26)	7.72 (7.74)	8.1	3136	11.1
8	68	85.35 (91.61)	6.93 (8.39)	7.2	3528	11.4
10	60	84.44 (91.08)	8.14 (8.92)	6.9	3518	10.3
12	59	84.90 (93.64)	8.89 (9.36)	6.3	4032	11.0

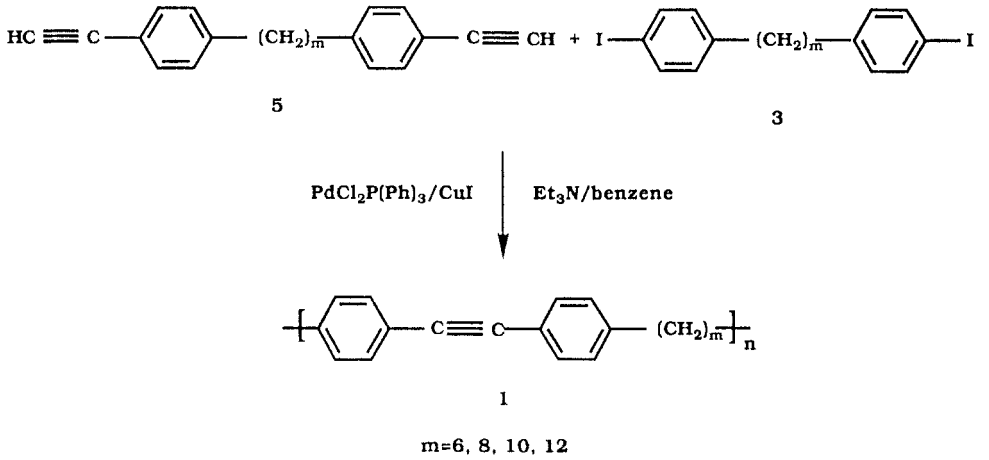
[a] Calculated on the basis of the carbon content of the monomers and polymers. [b] Calculated on the assumption that both end groups of the polymers are iodine atoms.

Results and Discussion

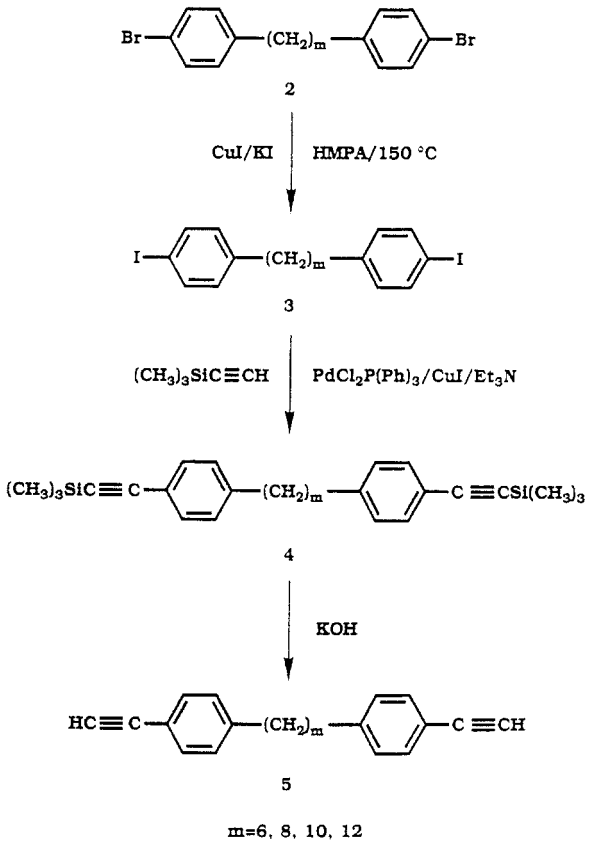
Synthesis. The hydrocarbon polymers with the general structure 1 were synthesized as shown in Scheme I. Monomers 3 and 5 were successfully prepared by the synthetic route depicted in Scheme II. This route started with compounds 2 which were first converted to the corresponding diiodides 3. Compounds 2 which we reported[6] previously were prepared in a two-step synthesis from bromobenzene. Use of a large excess of potassium iodide and copper(I) iodide effects the bromine to iodine exchange in high yields.[10] The halogen exchange is an equilibrium reaction, and an excess of iodide ion is needed to shift the reaction in the desired direction. Interestingly, aryl bromides such as 2 are inactive in the subsequent palladium-catalyzed cross coupling reaction. However, activated halides[11,12] (e.g., aryl iodides or aryl bromides with an ortho or para electron-withdrawing group on the aromatic ring or compounds such as 3) reacted smoothly and gave the expected products. This halogen exchange reaction is necessary for the success of the subsequent step. The second step shown in Scheme II is a palladium-catalyzed coupling reaction between 3 and (trimethylsilyl)-acetylene. The reaction proceeds cleanly at room temperature, and yields of 90% of 4 are generally isolated after purification. Subsequent treatment of 4 with potassium hydroxide in anhydrous methanol/ether solution at ambient temperature gave a quantitative yield of 5. Compounds 3–5 are all new compounds. The characterization data for all these new materials are summarized in Tables I–III. These compounds were not liquid-crystalline.

Four hydrocarbon polymers 1 containing tolan mesogens in the main chain have been prepared as shown in Scheme I. These polymers were generally obtained in 60–70% yield from the reaction in benzene, from which they precipitated as the polymerization proceeded. The yields and elemental analyses of the polymers are given in Table IV. All polymers contained 7–8% of iodine atoms. This high iodine content suggests that the precipitated polymers stop growing and that the insolubility of the

Scheme I. Synthesis of Hydrocarbon Liquid-Crystalline Polymers Based on a Tolan Mesogen



Scheme II. General Synthetic Route for the Monomers



polymers limits the molecular weight. Because of the insolubility of the polymers 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 number-average MWs could be calculated from the iodine analyses, assuming that both end groups of the polymer chain are iodine atoms. These results are summarized in Table IV. The calculated MWs and DPs would be less if some of the iodine chain ends were replaced by acetylenic groups. The MWs obtained in our work correspond to about 10–11 repeating units as shown in Table IV.

The chemical structures of the polymers have been established by FTIR and solid-state ^{13}C NMR. Figure 1 shows a typical IR spectrum of the polymers obtained. The absorbances at 3090, 2922, and 2851 cm^{-1} are typical C–H stretching frequencies. A weak absorbance at about 2200 cm^{-1} is in a region characteristic of unsymmetrically substituted C≡C stretching vibrations. There is no strong

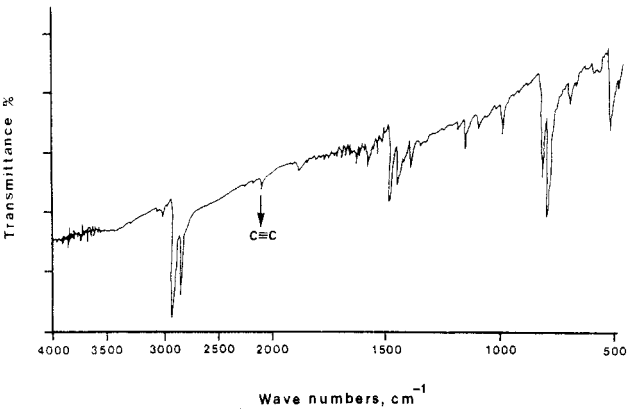
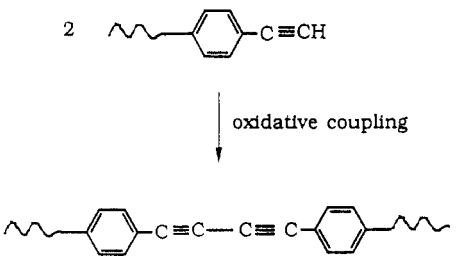


Figure 1. IR spectrum for polymer 1 with $m = 10$.

absorbance near the 3300-cm^{-1} region which is characteristic of the C–H stretching frequency in terminal alkynes. As this absorbance is reasonably strong relative to the absorbance at 2200 cm^{-1} and the absorbance at 2200 cm^{-1} is clearly observable, then a terminal acetylenic C–H should have been observed if present, as the DPs of these polymers are fairly low. Since the absorbances due to terminal acetylenes are not observed, we propose the existence a coupling type of termination reaction shown as follows:



This reaction has been used to transform terminal diynes into polymers under similar reaction conditions as shown by Hay.[13] This oxidative coupling reaction is extremely fast[14] in the presence of oxygen. Therefore, this reaction is likely to occur during the workup. Similar results have been reported earlier in the case of poly(phenyleneacetylenes).[8,9]

Figure 2 shows a representative solid-state ^{13}C CP/MAS (cross-polarization/magic angle spinning) NMR spectrum of the polymer 1 with $m = 10$. The assignments of signals due to the tolan mesogen were determined by comparison with known spectra and by calculation using standard additivity relationships.[15] Further support for assigning

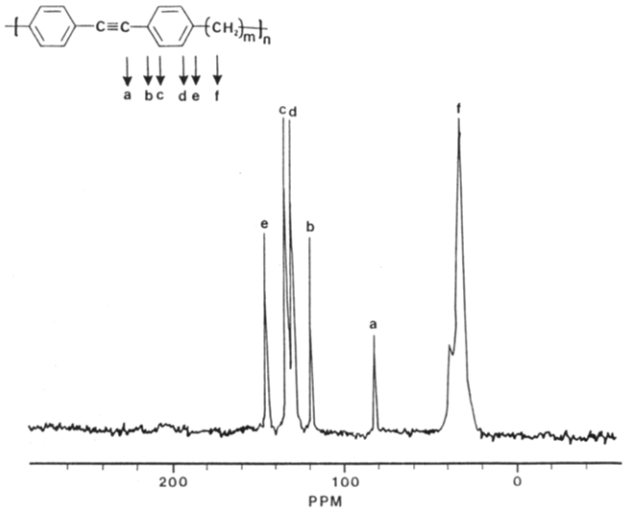


Figure 2. Solid-state ^{13}C NMR spectrum for polymer 1 with m = 10.

Table V. Polymer 1 Thermal Properties[a]

m	T_1	T_2	T_i	ΔH_1	ΔH_2	ΔH_i
6	120	241	>260[b]	0.56		–[b]
8	102	222	241	1.05	0.42	0.22
10	96	137	183	0.74	0.53	3.15
12	89		152	1.06		0.32

[a] Temperature in °C; ΔH in kcal/mol of repeating unit. [b] Decomposed.

the solid-state spectra was obtained by the dipolar dephasing experiment.[16]

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 thermal properties obtained for the polymers 1 from the DSC experiments are shown in Table V. Temperatures T_1, T_2, and T_i refer to peak temperatures of successive endotherms observed upon a second heating of the sample at 10 °C/min. Temperature T_i refers to the isotropization temperature. The same subscript notation is used to designate the corresponding enthalpy changes. The transition enthalpies were calculated by measuring the area under the respective peaks and are expressed in kilocalories per mole of repeating unit. On the basis of the low enthalpies, the polymers exhibit a low percentage of overall crystallinity.

Representative DSC scans for polymers 1 with m = 6 and m = 8 are shown in Figures 3 and 4, respectively. Upon cooling from the isotropic state, there is no distinct phase transition observed for any of the polymers. The isotropization transition for the polymer 1 with m = 6 was obscured by thermal decomposition at about 260 °C and could not be determined by DSC. Although thermogravimetric analyses (TGA) showed no weight loss until 350 °C, all of the polymers decomposed and turned black when heated on a Fisher-Johns melting point apparatus at a temperature of 260 ± 5 °C. This is probably because the polymers have very reactive acetylene groups which are known to self-condense thermally.

All polymers formed turbid melts that showed strong stir-opalescence up to the isotropization temperature (T_i). Figure 5 is a photomicrograph of the fine-grain texture displayed by polymer 1 with m = 10 under crossed polarizers. Similar textures were also observed for polymers 1 with m = 6, 8, and 12. The fine-grain texture is characteristic of either smectic or nematic liquid-crystalline polymers. The polymers were annealed in a vacuum at temperatures 5–10 °C below the isotropization temperature for periods as long as a week, but the fine-grain textures remained. The polymers may be too viscous to allow more recognizable textures to develop.

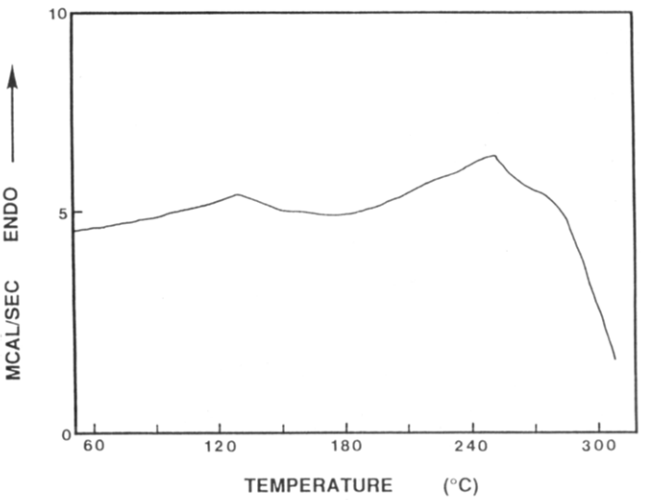


Figure 3. Second-heating DSC scan for polymer 1 with m = 6.

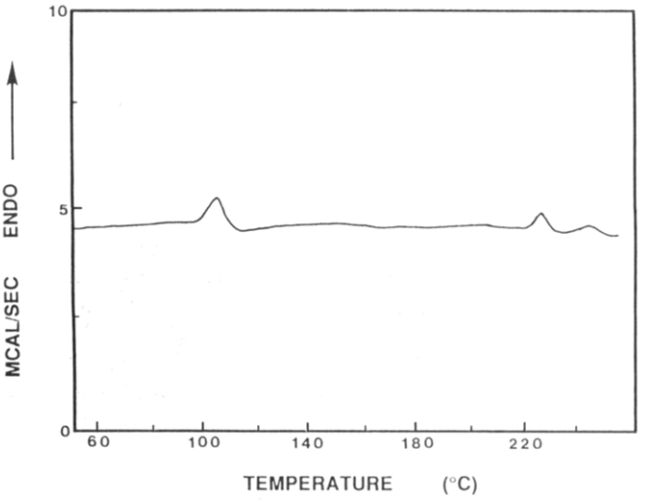


Figure 4. Second-heating DSC scan for polymer 1 with m = 8.

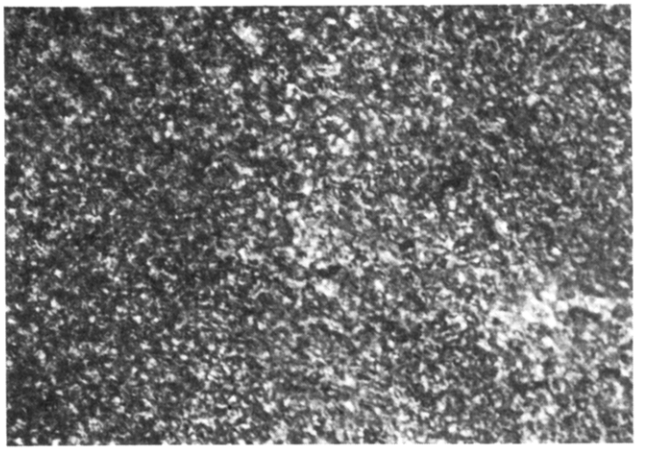


Figure 5. Photomicrograph [magnification shown 84× (originally photographed at 120×), crossed polarizers] of polymer 1 with m = 8 at 150 °C.

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

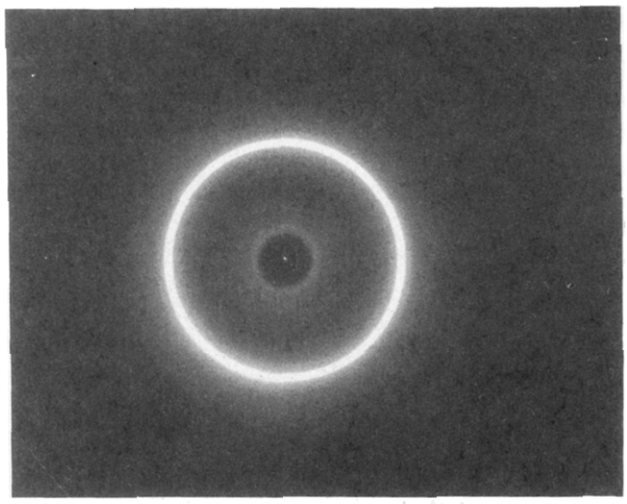


Figure 6. X-ray diffraction patterns for polymer 1 with $m = 8$ at 150 °C.

Table VI. X-ray Diffraction Results

m	intermolecular spacing, Å	obsd layer spacing, Å	calcd layer spacing, Å
6	4.5	13.7	17.6
8	4.5	15.2	19.6
10	4.5	16.8	21.7
12	4.5	18.3	23.8

mesophase. The diffraction pattern, representatively shown for the polymer 1 with $m = 10$ in Figure 6, consists of one weak but sharp inner reflection and a single sharp but very strong outer ring. The inner ring is attributable to the layer spacing and varies from 13.7 to 18.3 Å as a function of the number of flexible methylene spacers. The sharp outer reflection is attributed 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.[17] This spacing also corresponds to the intermolecular spacing in main-chain and side-chain all-hydrocarbon polymers based on a biphenyl mesogen.[7] These groups apparently show a strong driving force to stack in layers. The X-ray diffraction data are summarized in Table VI. The calculated layer spacings were obtained assuming an all-trans conformation for the methylene spacers. The observed layer spacings are always less than the calculated spacings. This is probably either because the molecules are tilted in the layer or because some of the carbon–carbon bonds are in the gauche conformation. Additional X-ray studies are needed on oriented samples to characterize the mesophases more completely.

All the evidence indicates that the polymers 1 with $m = 6$, 8, 10, and 12 are liquid-crystalline and exhibit either nematic or smectic mesophases. On the basis of the DSC data in Table V, it appears that the principal effect of lengthening the flexible spacer was to decrease the melting points (T_1) and the isotropization temperatures (T_i) and to narrow the temperature range, ΔT ($T_i - T_1$), over which thermotropic behavior of the polymers occurred. It is reasonable to expect that longer flexible spacers should be increasingly effective in increasing segmental and translational molecular mobility in the polymer melt. This increased mobility should result in both a lower isotropization temperature (T_i) and a lower melting point (T_1). The melting and isotropization temperatures from the DSC results are presented as a function of methylene spacers in Figure 7. The tolan polymers show wider mesogenic ranges when compared to similar polymers with biphenyl mesogens. This observation supports the generalization

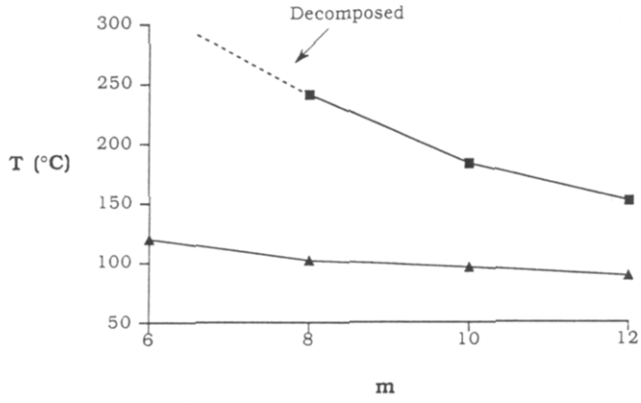


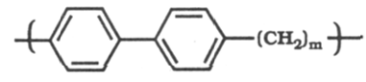
Figure 7. Melting points T_1 (▲) and isotropization temperatures T_i (■) for polymers 1 versus the number of methylene spacers, m.

that tolan is a more effective mesogen to induce liquid crystallinity. It must 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.

Conclusions

Four hydrocarbon oligomers having tolan mesogenic units and polymethylene spacers in the main chain were prepared, and their liquid-crystalline properties were investigated by DSC, POM, and X-ray diffractions. All the oligomers were found to exhibit mesophases which could not be definitely characterized. Lengthening the polymethylene spacer between the tolan mesogenic groups decreased both the melting points (T_1) and the isotropization temperatures (T_i) and also narrowed the temperature range, ΔT ($T_i - T_1$), over which thermotropic behavior of the polymers occurred. The same trend has been observed for similar polymers which were reported by others for closely related polymers.

By comparing tolan polymers 1 and with another series of hydrocarbon polymers **6** prepared in our laboratory,[6]



6

it was observed that polymer **6** with $m = 12$ was not liquid-crystalline whereas polymer 1 with $m = 12$ exhibited liquid-crystalline phases. Also polymers 1 have broader mesomorphic ranges than polymers **6**. Our work supports the conclusion that the tolan mesogen with a higher aspect ratio is more effective than the biphenyl mesogen to induce liquid crystallinity.

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