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Thermotropic Hydrocarbon Side-Chain Liquid Crystalline Polymers. 1. Synthesis and Characterization of Monomers and Model Compounds

Joseph J. Mallon and Simon W. Kantor*

Department of Polymer Science and Engineering, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003. Received July 26, 1988

ABSTRACT: A series of six new hydrocarbon monomers has been prepared by a versatile synthetic procedure. The new monomers are 1-alkene derivatives containing a biphenyl mesogen. Six new hydrocarbon twinlike model compounds have also been prepared. The synthesis permits facile variation of the length of flexible spacers as well as the alkyl substituents on the biphenyl mesogens. The liquid crystalline properties of the monomers and model compounds have been studied with differential scanning calorimetry, polarized light optical microscopy, and X-ray diffraction. Four of the six monomers and three of the six model compounds were found to exhibit smectic B liquid crystalline phases. The effect of the variation of the alkyl substituent on liquid crystalline properties is discussed. Substitution of the biphenyl mesogen by alkyl groups in the para positions appears necessary for the development of liquid crystallinity.

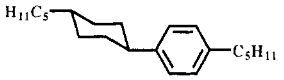
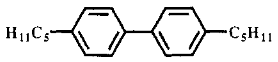
Introduction

The incorporation of a mesogenic group into the side chain of a flexible polymer often results in a polymer which exhibits liquid crystalline behavior. The structural elements common to most of these side-chain liquid crystalline polymers (SCLCP) are shown in Figure 1. These structures include flexible spacers separating the rigid mesogens from the main chain and para substitution of the mesogen with terminal units (tails). Recent reviews[1–8] show that the vast majority of SCLCPs prepared thus far are based on poly(siloxane)s, poly(acrylate)s, poly(methacrylate)s, poly(acrylamide)s and poly(methacrylamide)s. Typically, mesogens such as biphenyl, phenylbenzoate, and benzalaniline have been connected to the polymer backbone via alkylene, oxyalkylene, or ester spacer groups. Tails such as nitrile, alkoxy, and alkyl seem to predominate. The polymers may be prepared by attaching the mesogenic group to a polymer chain or by polymerizing a monomer which contains a mesogenic group. In either case, the presence of heteroatoms such as N or O facilitates the syntheses and may also contribute to mesophase stability through hydrogen bonding or dipole–dipole attractive forces.

Although the presence of intermolecular attractive forces may stabilize the liquid crystalline phase, they are not believed to be necessary for mesophase formation. The works of Onsager,[9] Isihara,[10–11] and Flory[12] predicted that solutions of rods would separate into an isotropic and an anisotropic phase depending on the axial ratio and concentration of the rods. Intermolecular attractive forces were shown to be unnecessary for the phase separation if the axial ratio and concentration were high enough. Although Flory's theory predicted the formation of a nematic phase, recent calculations by Frenkel, Lekkerkerker, and Stroobants[13] suggest that hard spherocylinders can also form a smectic phase in the absence of intermolecular attractions. This view has been supported by the discovery of liquid crystallinity in poly(tetrafluoroethylene) whiskers[14] and by the numerous examples[15] of hydrocarbon liquid crystals that have been reported. Hydrocarbons do not contain hydrogen bonds or strong dipoles which could contribute to mesophase stability.[16,17] Dispersion or London forces are the dominant attractive forces between the molecules of these compounds.

The transition temperatures of the liquid crystalline dipentyl derivatives of bicyclohexane, phenylcyclohexane, and biphenyl are shown in Table I. The clearing temperatures decrease in the order alicyclic mesogen > aromatic mesogen > mixed aromatic and alicyclic mesogen.

Table I
Transition Temperatures of Dipentyl Mesogens

structure	transition temp, °C
	$K \xrightarrow{40} S \xrightarrow{110.4} I$
	$K \xrightarrow{-0.8} S \xrightarrow{(-8)} N \xrightarrow{(-5)} I$
	$K \xrightarrow{26} S_E \xrightarrow{47.6} S_B \xrightarrow{52.2} I$

Although the biphenyl mesogen is more polar than, for example, the bicyclohexane mesogen, the biphenyl mesogen was selected in our study because of its synthetic versatility and lower melting transitions and to avoid cis and trans isomers inherent with substituted cyclohexane groups. The general structures of monomers and polymers chosen for this work are shown in Figure 2.

In this report the synthesis and characterization of hydrocarbon monomers and model compounds containing biphenyl mesogens are described. The characterization of twinlike liquid crystalline hydrocarbon model compounds, either isolated as side products from the monomer syntheses or synthesized by a modified procedure, is also described. The synthetic route employed for the synthesis allows the spacer length and tail length of the monomers and model compounds to be varied over a wide range. Preliminary results which did not include synthetic details have been reported previously.[15]

Experimental Section

Materials. Methylene chloride obtained from Baker Scientific was stirred with $AlCl_3$ and filtered 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.

Acetyl chloride and butyryl chloride were Aldrich Chemical Co. Gold Label quality and were used as received. Potassium hydroxide was obtained from Baker Scientific and used without further purification. Hydrazine hydrate was obtained as a 55% solution in water from Aldrich Chemical Co. and was used as received. Aluminum chloride was purchased as a Gold Label product from Aldrich Chemical Co. and used without further purification. 4-Bromobiphenyl was purchased from Aldrich Chemical Co., recrystallized from 2-propanol, and dried under vacuum before use. 1,4-Dibromobutane, 1,6-dibromohexane, and 1,8-dibromooctane were purchased from Aldrich and vacuum

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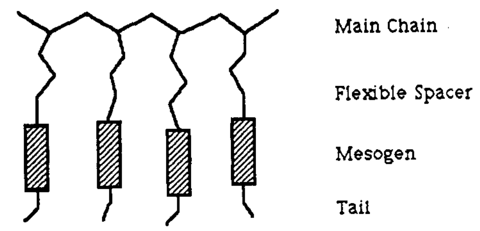


Figure 1. Main structural features of most side-chain liquid crystalline polymers.

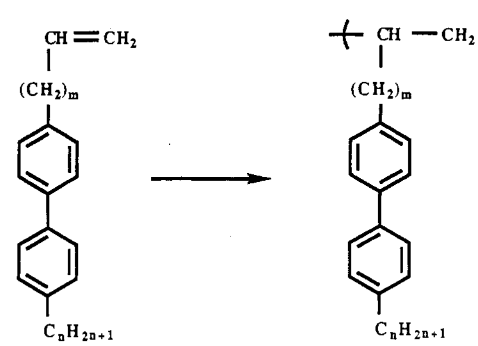


Figure 2. General monomer and polymer structure.

distilled from CaH_2 before use. Magnesium metal and 1,2-dibromoethane were obtained from Aldrich as Gold Label products and used without further purification. LiBr and $CuBr_2$ were obtained from Aldrich and dried under vacuum prior to use. Trimethylamine purchased from Eastman Kodak as a 25% solution in methanol was used as received. Silver oxide obtained from Aldrich was used as received.

All Grignard reagents were prepared and used under a dry Ar atmosphere in glassware that had been oven-dried at 110 °C. Standard procedures for the correct transfer of reagents sensitive to air and water were used. The melting behavior of the monomers and model compounds is discussed in the Results and Discussion section.

Preparations. 4-Acetyl-4′-bromobiphenyl. A clean, dry 2000-mL three-neck round-bottom flask was fitted with a reflux condenser; 1000 mL of CH_2Cl_2 and a stir bar were added, and the flask was cooled in an ice bath under Ar purge until the contents reached 5 °C. $AlCl_3$ (0.72 mol, 96.0 g) was added to the flask with a powder funnel. Acetyl chloride (51.8 g, 0.66 mol) was slowly added to the stirred mixture. After the contents of the flask had again cooled to 5 °C, 140 g (0.6 mol) of 4-bromobiphenyl was added with a powder funnel over the course of 10 min. The resulting red suspension was allowed to warm to room temperature and stirred overnight.

The contents of the flask were poured into 1000 g of ice/60 mL of concentrated HCl in a large beaker. The beaker contents were stirred and heated to drive off CH_2Cl_2. After the mixture cooled, the crystalline solid was removed by filtration. The solid was recrystallized from 50/50 2-propanol/$CHCl_3$ to yield, after drying, 127.3 g of white crystals, mp 130–131 °C [lit. mp 131–133 °C,[18] 131 °C,[19] 129–130 °C[20]]. The yield was 77%, based on 4-bromobiphenyl.

4-Ethyl-4′-bromobiphenyl. 4-Acetyl-4′-bromobiphenyl (123.8 g, 0.45 mol), 500 mL of ethylene glycol, 66 g (1.0 mol) of 85% potassium hydroxide, and 95 mL (1.35 mol) of hydrazine hydrate were placed into a 1-L three-neck round-bottom flask with a stir bar. A still head was attached, and the flask was heated and stirred at 110 °C for 1 h. The temperature was raised to 180 °C by further heating, which was accompanied by the distillation of water. The distillation was discontinued at 180 °C, and the dark solution was allowed to reflux for 3 h and then cooled to 100 °C and poured into a beaker. After cooling to room temperature, the solid material was removed with tongs and crushed in a mortar and pestle. The liquid remaining in the beaker was extracted with benzene. The benzene extract and crushed crysalline solid were stirred together to dissolve most of the crystals. A yellow solid insoluble in benzene was removed by filtration and discarded. The remaining solution was washed with dilute $NaHCO_3$, dried over Na_2SO_4, and decolorized with activated charcoal to give a yellow benzene solution. Evaporation of the solution gave a yellow solid.

The yellow solid was either recrystallized several times from ethanol or codistilled with ethylene glycol to yield a white, crystalline solid. (The codistillation process generally gave higher purity product than recrystallization from ethanol.) Recrystallization of the codistilled product from ethanol yielded 46.6 g (yield 40%) of product, mp 128–129 °C [lit.[21] mp 125–126 °C].

4-Butyryl-4′-bromobiphenyl. The preparation of this compound was similar to that of 4-acetyl-4′-bromobiphenyl except that butyryl chloride was used in place of acetyl chloride. Three recrystallizations from ethanol gave 117.5 g (69% yield) of light yellow crystals, mp 104–105 °C [lit.[22] mp 104–104.5 °C].

4-Butyl-4′-bromobiphenyl. The preparation of this compound was similar to that of 4-ethyl-4′-bromobiphenyl. The light yellow crystals obtained after benzene evaporation were recrystallized 3 times from ethanol to yield 71.3 g (64% yield) of 4-butyl-4′-bromobiphenyl, mp 104–105 °C [lit.[22] mp 102–102.5 °C].

0.1 M Li_2CuBr_4/THF solution: 0.17 g (0.002 mol) of LiBr and 0.22 g (0.001 mol) of $CuBr_2$ were placed into a dry 50-mL single neck round-bottom flask. The flask was septa-capped and flushed with Ar, and 10 mL of dry THF was added via syringe. The resulting dark green solution was stored under dry Ar.

1-(4-Biphenyl)-6-bromohexane: 3.65 g of magnesium turnings (0.15 mol) was placed into an oven-dried 250-mL three-neck round-bottom flask with a stir bar. A graduated 100 mL addition funnel was attached, and the apparatus was flushed with Ar for 30 min. A solution of 23.3 g (0.1 mol) of 4-bromobiphenyl in 50 mL of THF was prepared under Ar in a 100-mL round-bottom flask. Fifty milliliters of THF was transferred via cannula to the 250-mL round-bottom flask containing the Mg. 1,2-Dibromoethane (0.2 mL) was added via syringe to the 250-mL flask to activate the magnesium. After activation was complete (about 30 min), the solution of 4-bromobiphenyl was transferred to the dropping funnel via cannula. The 4-bromobiphenyl solution was added dropwise to the activated magnesium over the course of 1 h. The resulting orange solution was stirred for an additional hour.

1,6-Dibromohexane (73.2 g, 0.30 mol) was placed into a 500-mL three-neck round-bottom flask with a stir bar. The flask was fitted with a reflux condenser and an adapter containing a coarse fritted disk. The system was septa-capped, and Ar was bubbled through the liquid for at least 1 h. The Grignard reagent previously prepared was transferred via cannula to the adapter. The solution flowed through the coarse fritted disk into the 1,6-dibromohexane. The resulting yellow solution was heated to gentle reflux, and 3 mL of previously prepared 0.1 M Li_2CuBr_4/THF solution was added via syringe. After about 10 min of gentle reflux, the solution turned dark green over the course of about 1 min. The dark-green solution was refluxed for 2 h and then allowed to cool to room temperature.

The reaction mixture was poured into a beaker containing 50 g of ice/10 mL of concentrated HCl. The THF was removed via rotary evaporation. Diethyl ether was added, and the resulting three-phase mixture was filtered to remove a white precipitate. The water and ether layers were separated, and the aqueous layer was washed with ether. The ether extracts were combined and washed with water, dilute $NaHCO_3$, and water. The clear-yellow ether solution was dried over $CaCl_2$ and the solvent removed via rotary evaporation.

The residual yellow oil was vacuum distilled. The first fraction boiling from 50–150 °C (100 mTorr) was excess 1,6-dibromohexane. The second fraction boiling at 165–175 °C was a light-yellow oil. The oil was recrystallized from ethanol by placing its hot ethanol solution in the freezer. The resulting white solid was dried under vacuum to yield 19.5 g of product, mp 28–29 °C. The yield, based on 4-bromobiphenyl, was 61%.

In general, the 1-[4-(4′-alkylbiphenyl)]-*n*-bromoalkanes were not purified further. They were difficult to distill or recrystallize, so they were used in the subsequent step in a crude state. Thus, no characterization data were obtained for these compounds. Water-insoluble organic impurities were removed in the next step when the 1-(4,4′-alkylbiphenyl)-*n*-bromoalkanes were converted into water-soluble salts and filtered.

1-(4-Biphenyl)-8-bromooctane. The procedure used to prepare this compound was similar to that used to prepare 1-

(4-biphenyl)-6-bromohexane except that 81.6 g (0.3 mol) of 1,8-dibromooctane was used in place of 1,6-dibromohexane. The white precipitate insoluble in ether was removed via filtration and recrystallized twice from 50/50 $CHCl_3$/ethanol to yield 0.8 g of white crystalline product. This product was identified by ^1H NMR as 1,8-bis(4-biphenyl)octane (BP8BP). After the excess 1,8-dibromooctane was distilled off, the major product was vacuum distilled at 600 mTorr and 190–200 °C to yield 21.6 g (62%) of a pale-yellow oil that crystallized on cooling, mp 34–35 °C.

6-(4-Biphenyl)-1-hexene (MEBP04): 20.6 g (0.06 mol) of 1-(4-biphenyl)-6-bromohexane was mixed at room temperature with 50 mL of 25% $N(CH_3)_3$ in methanol. The flask was heated slightly to produce a clear solution, which was allowed to stir overnight. The solvent was removed via rotary evaporation to yield a white solid. Water was added to the flask to dissolve the solid, and the solution was filtered to remove small amounts of insoluble material; 13.9 g (0.06 mol) of Ag_2O was added to the flask, and the resulting mixture was stirred overnight. The brown mixture was filtered to remove excess Ag_2O and AgBr. A few drops of Dow DB 100 antifoam agent was added to the brown filtrate, and the water was removed via rotary evaporation. The resulting brown paste was scraped from the flask and placed into a 100-mL single-neck round-bottom flask with a stir bar. A stillhead was attached, and the brown paste was heated under vacuum at an oil bath temperature of 220 °C. A liquid nitrogen trap was used to prevent $N(CH_3)_3$ from entering the vacuum pump. A mixture of water and a clear oil collected in the distillation receiver. Ether was added to the water/oil mixture, and the layers were separated. The water layer was washed with ether, and the ether extracts were combined and dried over $CaCl_2$. Rotary evaporation of the ether gave a clear oil. Vacuum distillation of the oil from CaH_2 at 140–145 °C and 75 mTorr yielded 7.4 g of clear oil, 31% yield based on 1-(4-biphenyl)-6-bromohexane.

8-(4-Biphenyl)-1-octene (MEBP06). The synthesis of this monomer from 1-(4-biphenyl)-8-bromooctane is similar to that of 6-(4-biphenyl)-1-hexene (MEBP04). The monomer was distilled from CaH_2 at 500 mTorr and 160–170 °C to give 7.9 g of clear oil, 50% yield based on 1-(4-biphenyl)-8-bromooctane.

1-[4-(4′-Ethylbiphenyl)]-6-bromohexane. This compound was prepared from 4-ethyl-4′-bromobiphenyl in a manner similar to the preparation of 1-(4-biphenyl)-6-bromohexane. The white precipitate insoluble in ether was filtered and dissolved in $CHCl_3$. The portion insoluble in $CHCl_3$ was removed via filtration. Ethanol was added to the filtrate, and the white precipitate was recrystallized from 50/50 $CHCl_3$/ethanol to yield, after vacuum drying, 400 mg of a white crystalline solid. The ^1H NMR data are consistent with 1,6-bis[4-(4′-ethylbiphenyl)]hexane (2BP6BP2). After vacuum distillation of the 1,6-dibromohexane, the yellow residue was recrystallized from ethanol by chilling in the freezer. After vacuum drying, 16.8 g of semisolid yellow product was obtained, 65% yield, based on 4-ethyl-4′-bromobiphenyl.

1-[4-(4′-Ethylbiphenyl)]-8-bromooctane. This compound was prepared from 4-ethyl-4′-bromobiphenyl in a manner similar to the preparation of 1-(4-biphenyl)-6-bromohexane. The ether-insoluble white precipitate formed in the reaction was collected by filtration. The portion soluble in $CHCl_3$ was recrystallized from 50/50 $CHCl_3$/ethanol and vacuum dried to give 490 mg of a white crystalline solid. The ^1H NMR data are consistent with 1,8-bis[4-(4′-ethylbiphenyl)]octane (2BP8BP2). After 1,8-dibromooctane was removed by vacuum distillation, the yellow residue was recrystallized from ethanol and vacuum dried to give 19.3 g (69% yield) of yellow crystals, mp 40–42 °C.

6-[4-(4′-Ethylbiphenyl)]-1-hexene (MEBP24). This compound was prepared from 1-[4-(4′-ethylbiphenyl)]-6-bromohexane in a manner similar to the preparation of 6-(4-biphenyl)-1-hexene (MEBP04). Vacuum distillation from CaH_2 yielded 3.2 g (27% yield) of a waxy white solid.

8-[4-(4′-Ethylbiphenyl)]-1-octene (MEBP26). This monomer was prepared by starting from 1-[4-(4′-ethylbiphenyl)]-8-bromooctane in a manner similar to the preparation of 6-(4-biphenyl)-1-hexene (MEBP04). Vacuum distillation from CaH_2 yielded 7.0 g (48% yield) of a waxy white solid.

1-[4-(4′-Butylbiphenyl)]-6-bromohexane. This compound was prepared from 4-butyl-4′-bromobiphenyl in a manner similar to the preparation of 1-(4-biphenyl)-6-bromohexane. After vacuum distillation of excess 1,6-dibromohexane, the yellow residue was recrystallized from ethanol by placing the ethanol solution in the freezer to yield, after vacuum drying, 15.0 g (57% yield) of a yellow, semisolid mass.

1-[4-(4′-Butylbiphenyl)]-8-bromooctane. This compound was prepared from 4-butyl-4′-bromobiphenyl analogously to the preparation of 1-(4-biphenyl)-6-bromohexane. The ether-insoluble product fromed in the reaction was dissolved in $CHCl_3$ and filtered. Ethanol was added to the filtrate, and the precipitate was recrystallized from 50/50 $CHCl_3$/ethanol and dried under vacuum to give 500 mg of white crystalline solid. The ^1H NMR spectrum was consistent with 1,8-bis[4-(4′-butylbiphenyl)]octane (4BP8BP4).

After removal of excess 1,8-dibromooctane by vacuum distillation, the yellow residue was recrystallized twice from 50/50 ethanol/methanol to yield 24.4 g (61% yield) of a white solid after vacuum drying.

6-[4-(4′-Butylbiphenyl)]-1-hexene (MEBP44). This monomer was prepared from 1-[4-(4′-butylbiphenyl)]-6-bromohexane in a manner analogous to the preparation of 6-(4-biphenyl)-1-hexene (MEBP04). Three recrystallizations from 50/50 ethanol/methanol gave 4.8 g (33% yield) of a waxy white solid after vacuum drying.

8-[4-(4′-Butylbiphenyl)]-1-octene (MEBP46). This monomer was prepared from 1-[4-(4′-butylbiphenyl)]-8-bromooctane in a manner similar to the preparation of 6-(4-biphenyl)-1-hexene (MEBP04). Several recrystallizations from 50/50 methanol/ethanol were necessary to give, after vacuum drying, 4.0 g (21% yield) of a white waxy solid.

1,4-Bis[4-(4′-Ethylbiphenyl)]butane (2BP4BP2). This compound was not obtained as a side product but was synthesized deliberately. A Grignard reagent was prepared from 2.61 g (0.01 mol) of 4-ethyl-4′-bromobiphenyl and 0.36 g (0.015 mol) of Mg in 10 mL of THF by a procedure analogous to that given for biphenylmagnesium bromide. The Grignard reagent was transferred via cannula and filter adapter to 1.08 g (0.005 mol) of 1,4-dibromobutane. The resulting solution was heated to reflux and stirred under Ar. With a syringe, 0.3 mL of 0.1 M Li_2CuBr_4 solution was added to the flask. Within 15 min, a precipitate had formed, making stirring impractical. The flask was cooled, and 10 g of ice/1 mL of concentrated HCl was added. Ether was added, and the resulting mixture was filtered to remove a white solid. The white solid was dissolved in $CHCl_3$ and filtered. Ethanol was added to the $CHCl_3$ filtrate, and the resulting precipitate was recrystallized from 50/50 $CHCl_3$/ethanol and vacuum dried to give 0.56 g (27%) of white crystalline product. The ^1H NMR spectrum is consistent with 1,4-bis-[4-(4′-ethylbiphenyl)]butane (2BP4BP2).

1,4-Bis[4-(4′-butylbiphenyl)]butane (4BP4BP4). This compound was prepared from 4-butyl-4′-bromobiphenyl and 1,4-dibromobutane analagously to the preparation of 1,4-bis-[4-(4′-ethylbiphenyl)]butane (2BP4BP2). After recrystallization from 50/50 $CHCl_3$/ethanol, 710 mg (42% yield) of vacuum-dried white crystalline solid was obtained. The ^1H NMR spectrum is consistent with 1,4-bis[4-(4′-butylbiphenyl)]butane (4BP4BP4).

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. The ^1H NMR data, elemental analyses, and synthetic yields for the monomers and model compounds are reported in Tables II and III, respectively. ^1H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), and integration.

Differential scanning calorimetry (DSC) experiments were performed on a Perkin Elmer DSC-II at a heating rate of 20 °C/min and a cooling rate of 10 °C/min, except where noted. The instrument was calibrated with standard samples of indium and naphthalene. To assure that all of the samples had equivalent thermal histories, the results of the second heating scan 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.

Table II
Characterization Data for Monomers[a]

code [formula] (yield)	analysis, % calculated [found] C	H	^{1}H NMR chemical shifts, ppm
MEBP04 [$C_{18}H_{20}$] (31%)	91.47 [91.51]	8.53 [8.50]	7.0–7.6 (m, 9 H), 5.6–5.9 (m, 1 H), 5.0 (m, 2 H), 2.5 (t, 2 H), 2.0 (m, 2 H), 1.5 (m, 2 H), 1.3 (m, 2 H)
MEBP06 [$C_{20}H_{24}$] (50%)	90.85 [91.00]	9.15 [8.91]	7.2–7.7 (m, 9 H), 5.8 (m, 1 H), 5.0 (m, 2 H), 2.6 (t, 2 H), 2.1 (m, 2 H), 1.6–1.7 (m, 2 H), 1.2–1.5 (m, 6 H)
MEBP24 [$C_{20}H_{24}$] (27%)	90.85 [90.80]	9.15 [9.12]	7.1–7.6 (m, 8 H), 5.5–6.0 (m, 1 H), 5.0 (m, 2 H), 2.6 (m, 4 H), 2.1 (m, 2 H), 1.5 (m, 2 H), 1.3 (m, 5 H)
MEBP26 [$C_{22}H_{28}$] (48%)	90.35 [90.29]	9.65 [9.52]	7.0–7.5 (m, 8 H), 5.5–6.0 (m, 1 H), 4.8–5.1 (m, 2 H), 2.5–2.9 (m, 4 H), 2.0–2.1 (m, 2 H), 1.2–1.9 (m, 11 H)
MEBP44 [$C_{22}H_{28}$] (33%)	90.35 [90.22]	9.65 [9.45]	7.1–7.6 (m, 8 H), 5.8 (m, 1 H), 5.0 (m, 2 H), 2.6 (m, 4 H), 2.1 (m, 2 H), 1.2–1.8 (m, 8 H), 1.0 (t, 3 H)
MEBP46 [$C_{24}H_{32}$] (21%)	89.94 [90.02]	10.06 [10.11]	7.2–7.6 (m, 8 H), 5.8 (m, 1 H), 5.0 (m, 2 H), 2.6 (t, 4 H), 2.0 (m, 2 H), 1.2–1.8 (m, 12 H), 0.9 (t, 3 H)

[a] Code explanation: MEBP26, for example, stands for monomer (versus polymer), ethylene (backbone type), biphenyl (mesogen type), 2 (tail length), 6 (spacer length).

Table III
Characterization Data for Model Compounds[a]

code [formula] (yield)	analysis, % calculated [found] C	H	^{1}H NMR chemical shifts, ppm
BP8BP [$C_{32}H_{34}$]	91.81 [92.03]	8.19 [8.00]	7.2–7.7 (m, 18 H), 2.5–2.8 (t, 4 H), 1.3–1.8 (m, 12 H)
2BP4BP2 [$C_{32}H_{34}$] (27%)	91.81 [91.54]	8.19 [7.98]	7.0–7.6 (m, 16 H), 2.4–2.7 (m, 8 H), 1.2–1.8 (m, 10 H)
2BP6BP2 [$C_{34}H_{38}$]	91.43 [91.30]	8.57 [8.60]	7.1–7.7 (m, 16 H), 2.5–2.8 (m, 8 H), 1.2–1.8 (m, 14 H)
2BP8BP2 [$C_{36}H_{42}$]	91.08 [91.25]	8.92 [8.73]	7.1–7.6 (m, 16 H), 2.4–2.8 (m, 8 H), 1.1–1.8 (m, 18 H)
4BP4BP4 [$C_{36}H_{42}$] (42%)	91.08 [91.05]	8.92 [8.89]	7.1–7.7 (m, 16 H), 2.2–2.6 (t, 8 H), 1.2–1.8 (m, 12 H), 0.9 (t, 6 H)
4BP8BP4 [$C_{40}H_{50}$]	90.51 [90.43]	9.49 [9.41]	7.2–7.7 (m, 16 H), 2.4–2.7 (m, 8 H), 1.2–1.7 (m, 20 H), 0.9 (t, 6 H)

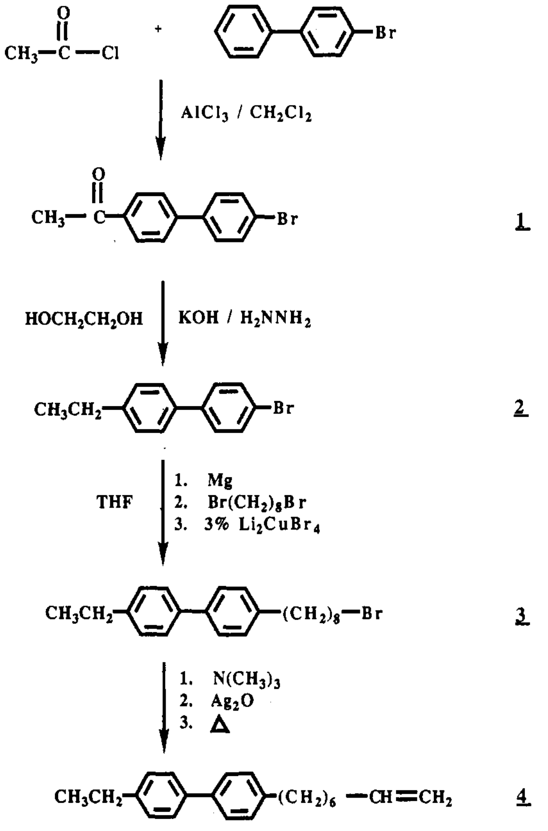
[a] Code explanation: 2BP6BP2, for example, stands for 2 (tail length), biphenyl (mesogen type), 6 (spacer length), biphenyl (mesogen type), 2 (tail length). The yields of four of the model compounds are not shown because they were isolated as side products of the monomer synthesis.

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 home-made hot stage was used to control sample temperature to within 1 °C.

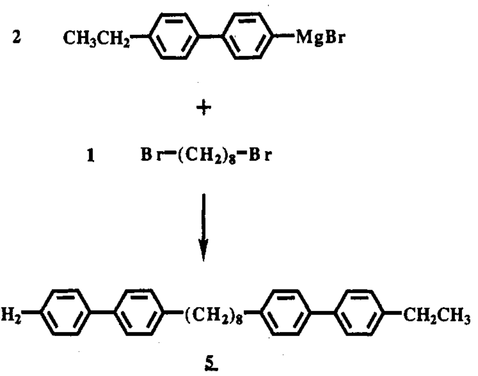
Results and Discussion

The synthetic route to the monomers is illustrated in Scheme I for a monomer with a two-carbon tail and a six-carbon spacer (MEBP26). The syntheses of 4-alkyl-4′-bromobiphenyl compounds such as **2** were modifications of procedures developed by Gray.[20-22] Methylene chloride was substituted for nitrobenzene as the solvent for the Friedel–Crafts reaction (the first reaction in Scheme I) in order to simplify the work-up procedure. The length of the alkyl tail was easily varied by choosing the appropriate acid chloride. Although only two different tail lengths were used in this work, Gray[22] has prepared numerous bromobiphenyl derivatives with a wide variety of tail lengths.

Scheme I
Monomer Synthetic Route Illustrated for MEBP26

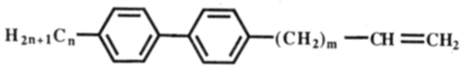


Scheme II
Reaction Pathway for Model Compound Formation Illustrated for 2BP8BP2



The coupling reaction of α,ω-dibromoalkanes with 4-alkyl-4′-biphenylmagnesium bromide derivatives followed from the work of Tamura and Kochi[23] and Friedman and Shani.[24] The third step of the reaction sequence shown in Scheme I illustrates this reaction for 1,8-dibromooctane and 4-ethyl-4′-biphenylmagnesium bromide. The length of the spacer group was varied by appropriate choice of α,ω-dibromoalkane. An excess of α,ω-dibromoalkane was used to favor the formation of **3**, but some reaction with both ends of the α,ω-dibromoalkane occurred by the reaction pathway shown in Scheme II. Products with the general structure of **5** were insoluble in diethyl ether, a solvent for compounds with a structure similar to **3**, so separations were easily achieved. 1-4-(4′-Alkylbiphenyl)-*n*-bromoalkanes such as **3** were generally not isolated in the pure state because they were difficult to distill or recrystallize. Removal of hydrocarbon impurities was achieved during the last step of the reaction sequence shown in Scheme I when **3** was converted to a water-soluble trimethylammonium bromide salt and filtered prior to reaction with silver oxide. The 1-alkene monomer product **4** was formed by thermally decomposing the tri-

Table IV
Monomer Thermal Properties



code	n	m	transition temp, °C	ΔH, kJ/mol	ΔS, J/(mol K)
MEBP04	0	4	$K \xrightarrow{1.3} I$	15.1	55.1
MEBP06	0	6	$K \xrightarrow{18.3} I$	21.0	71.9
MEBP24	2	4	$S_B \xrightarrow{26.3} I$	8.4	28.0
MEBP26	2	6	$K \xrightarrow{9.4} S_B$	4.8	16.8
			$S_B \xrightarrow{28.2} I$	7.9	26.3
MEBP44	4	4	$K \xrightarrow{24.4} S_B$	0.8	2.5
			$S_B \xrightarrow{38.5} I$	7.2	23.1
MEBP46	4	6	$K \xrightarrow{-24.6} S_B$	2.2	9.0
			$S_B \xrightarrow{42.4} I$	9.6	30.5

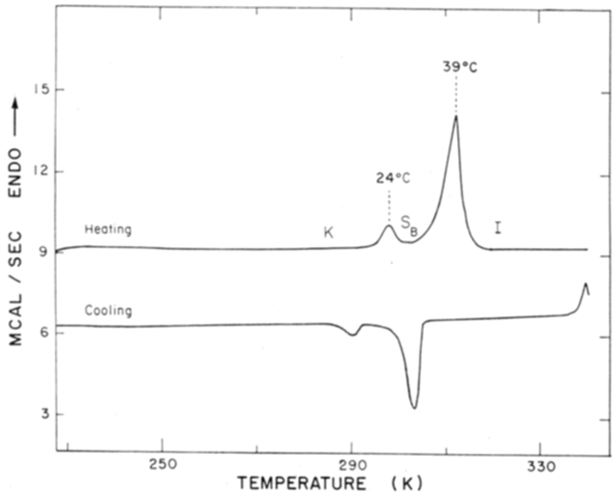


Figure 3. Second heating and cooling DSC scans for MEBP44: heating rate, 20 °C/min; cooling rate, 10 °C/min.

methylammonium hydroxide derivative formed from the reaction with silver oxide (Hoffman elimination).[25] The deliberate synthesis of model compounds such as **5** was achieved by employing the reaction stoichiometry shown in Scheme II.

Tables II and III contain the characterization data for the monomers and model compounds, respectively. The elemental analyses and ^1H NMR data are in excellent agreement with the proposed structures and indicate that the compounds are highly pure. No attempts were made to optimize the yields, which ranged from 20% to 50%. Yields are not given for four of the model compounds because they were isolated as side products from the monomer syntheses.

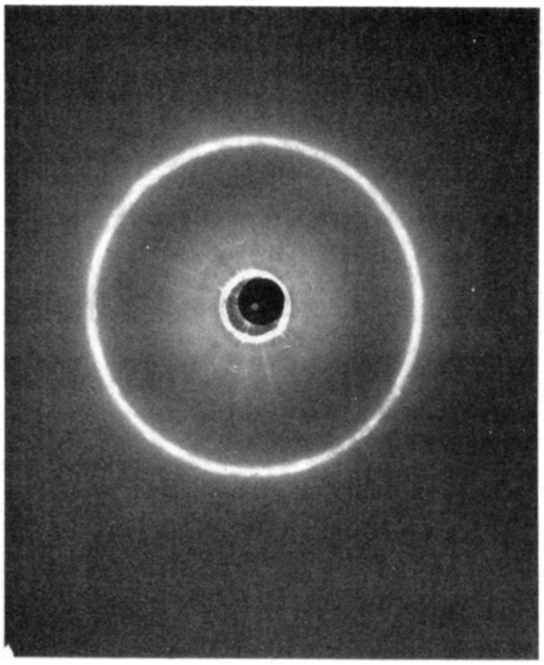


Figure 4. X-ray diffraction pattern for MEBP44 at 35 °C.

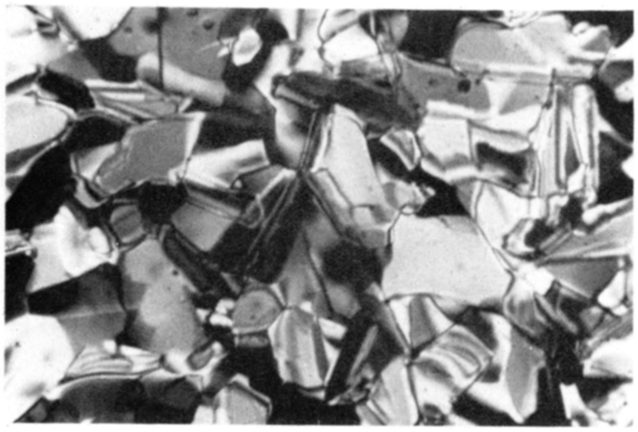


Figure 5. Photomicrograph under crossed polarizers of MEBP44 at 35 °C showing mosaic texture indicative of smectic B phase.

Table V
X-ray Diffraction Results for Liquid Crystalline Monomers and Model Compounds

code	intermolecular spacing, Å	observed layer spacing, Å	calculated molecule length, Å
MEBP24	4.6	18.8	16.3
MEBP26	4.6	21.3	18.8
MEBP44	4.6	21.5	18.8
MEBP46	4.6	24.5	21.2
4BP4BP4	4.6	32.7	29.3
4BP8BP4	4.6	37.5	34.1

The liquid crystalline properties of the monomers prepared in this work are summarized in Table IV. Four of the six monomers display the smectic B phase, a type of layered packing with hexagonal order within the layers. A representative DSC scan, flat film X-ray diffraction pattern, and POM photomicrograph for MEBP44 are shown in Figures 3, 4, and 5, respectively. The small peak at 24 °C in the DSC scan shown in Figure 3 shows that the crystalline to smectic B transition involves a small change in enthalpy. The transition from the highly ordered smectic B mesophase to the disordered isotropic state results in a relatively larger change in enthalpy at 39 °C. The flat film X-ray diffraction pattern for MEBP44 shown in Figure 4 shows an inner ring corresponding to the layer spacing of 21.5 Å and an outer ring corresponding to the intermolecular spacing of 4.6 Å. The layer spacing is comparable to the calculated length of the molecule (18.8 Å) and shows that the molecules are not tilted within the layers, as would be expected for a smectic C phase. The difference of 2.7 Å between the layer spacing and the length of the molecule is attributed to the space between the ends of the molecules.[26] The X-ray diffraction data obtained for the liquid crystalline monomers and model compounds are shown in Table V. An intermolecular

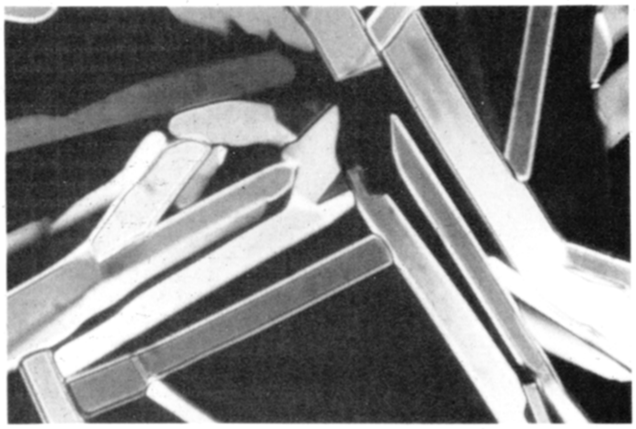


Figure 6. Photomicrograph under crossed polarizers of MEBP26 at 25 °C showing rod-shaped grains typical of smectic B phase.

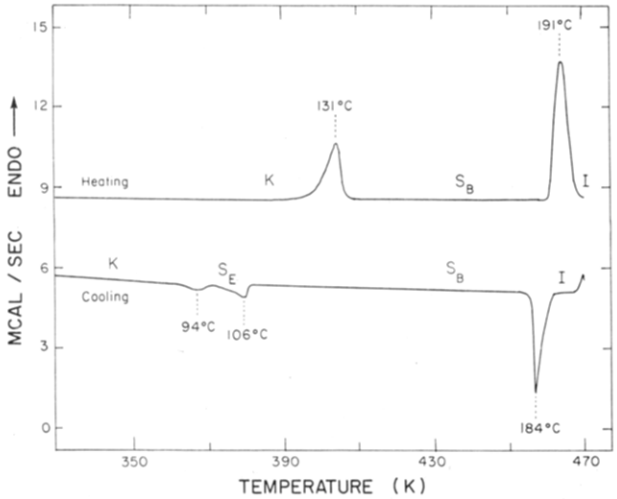


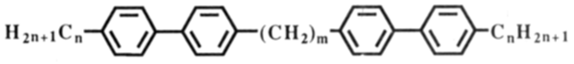
Figure 7. Second heating and cooling DSC scans for 4BP4BP4: heating rate, 20 °C/min; cooling rate, 10 °C/min.

spacing of 4.6 Å is observed for all of the smectic B phases exhibited by the monomers and model compounds. This spacing is less than the 4.9–5.0-Å spacing that has been reported[27] for the smectic B phase and indicates that the effective width of these hydrocarbon liquid crystals is smaller than usual.

The photomicrograph of MEBP44 under crossed polarizers in Figure 5 shows a birefringent mosaic texture typical of that often observed for a smectic B mesophase. Figure 6 is a photomicrograph under crossed polarizers of MEBP26 showing the familiar rod-shaped grains that are also characteristic of a smectic B phase type.[28–29] Similar textures have been observed for MEBP46 and MEBP24. The DSC, POM, and X-ray diffraction results are consistent with smectic B phase assignments for all of the dialkyl substituted monomers prepared in this work. MEBP24 was not observed to crystallize, even on cooling to −40 °C. The failure of dialkylbiphenyl liquid crystals to crystallize has been noted previously be Petrzilka.[30]

MEBP04 and MEBP06, the two monomers that do not have alkyl tails, are not liquid crystalline. These data are consistent with the conclusion that disubstitution of the biphenyl mesogen is necessary for the achievement of a liquid crystalline phase. No examples of monoalkyl-substituted biphenyl liquid crystals have been found in the literature.[15] The monomer with the longest substituents, MEBP46, has the highest clearing temperature (42 °C) and the broadest liquid crystalline range (67 °C). The liquid crystalline monomer with the shortest substituents has the lowest clearing temperature (26 °C). Apparently, a normal alkyl tail group adopts a favored transconformation in the liquid crystalline phase, which leads to an enhanced aspect ratio for the mesogenic group.

Table VI
Model Compound Thermal Properties



code	n	m	transition temp, °C	ΔH, kJ/mol	ΔS, J/(mol K)
BP8BP	0	8	$K \xrightarrow{142} I$	56	135
2BP4BP2	2	4	$K \xrightarrow{181} I$	46	101
			$(\xrightarrow{174} S_B \xrightarrow{152} K)$		
2BP6BP2	2	6	$K_1 \xrightarrow{120} K_2$	3.9	10
			$K_2 \xrightarrow{149} I$	35	84
2BP8BP2	2	8	$K_1 \xrightarrow{129} K_2$	8.4	21
			$K_2 \xrightarrow{140} I$	42	101
4BP4BP4	4	4	$K \xrightarrow{131} S_B$	12	31
			$S_B \xrightarrow{191} I$	24	52
			$(\xrightarrow{94} S_E \xrightarrow{106} S_B)$		
4BP8BP4	4	8	$K \xrightarrow{125} S_B$	13	31
			$S_B \xrightarrow{141} I$	27	66

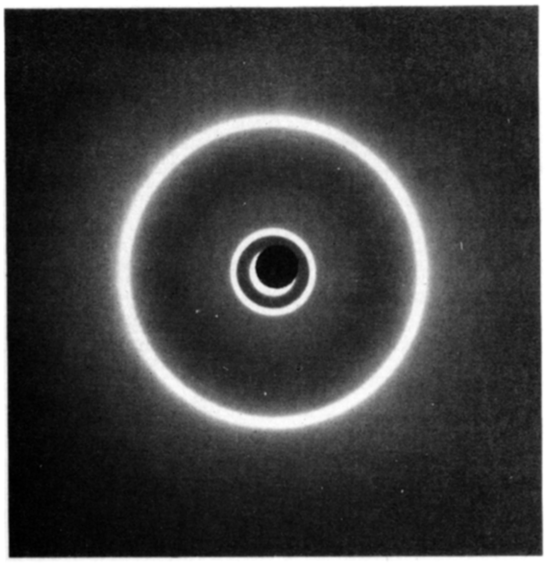


Figure 8. X-ray diffraction pattern for 4BP4BP4 at 150 °C.

The liquid crystalline properties of the model compounds prepared in this work are summarized in Table VI. Three of the model compounds, 2BP4BP2, 4BP4BP4, and 4BP8BP4, display smectic liquid crystalline phases. The liquid crystalline phase exhibited by 2BP4BP2 is a monotropic smectic B phase observed only on cooling. The DSC scan of 4BP4BP4 is shown in Figure 7. A smectic B mesophase is observed between 131 and 191 °C on heating, while both a smectic B and a monotropic smectic E mesophase are found on cooling. The flat film X-ray diffraction pattern of the smectic B mesophase in 4BP4BP4 is shown in Figure 8. The smectic B and smectic E characteristic textures observed by POM on cooling for 4BP4BP4 are shown in Figures 9 and 10, respectively. Similar DSC, POM, and X-ray diffraction data

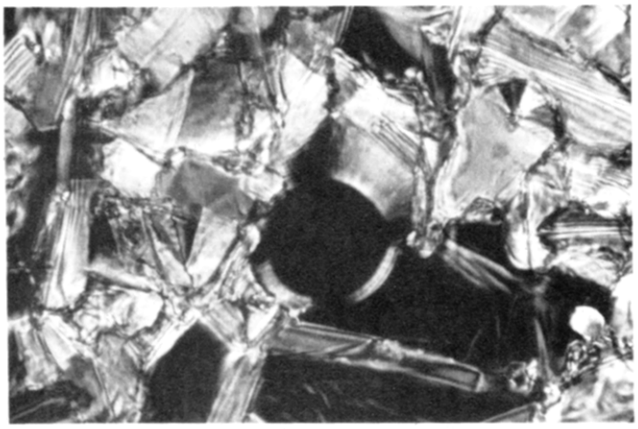


Figure 9. Photomicrograph under crossed polarizers of 4BP4BP4 at 140 °C on cooling showing smectic B texture (same area as Figure 10).

Figure 10. Photomicrograph under crossed polarizers of 4BP4BP4 at 100 °C on cooling showing smectic E texture (same area as Figure 9).

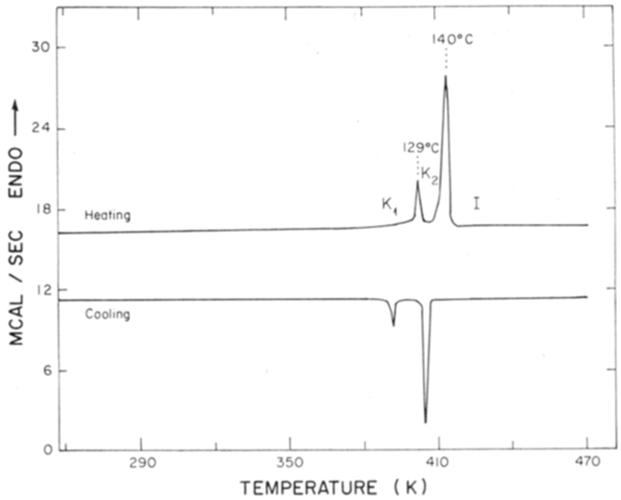


Figure 11. Second heating and cooling DSC scans for 2BP8BP2: heating rate, 20 °C/min; cooling rate, 10 °C/min.

confirm that 4BP8BP4 displays a smectic B mesophase between 125 and 141 °C.

The model compounds 2BP6BP2 and 2BP8BP2 are not liquid crystalline, but both give DSC scans, which exhibit two peaks. The DSC scan of 2BP8BP2 is shown in Figure 11. A texture change is observable by POM at the lowest temperature peak. The intermediate phase was tentatively labeled as smectic in an earlier publication,[15] but recent X-ray experiments indicate that a change in crystal structure occurs at the lower temperature peak. The peak at 129 °C in Figure 11 probably represents a crystal–crystal transition, but the possibility that the peak is due to the melting of small crystallites or impurities has not been eliminated. BP8BP is definitely not liquid crystalline, lending further support to the idea that disubstitution of the biphenyl mesogen is necessary to achieve liquid crystallinity, even in this class of model compounds.

Two trends are apparent from the data obtained on the model compounds. The first is that shorter spacers lead to more stable liquid crystalline phases. 4BP4BP4 has higher transition temperatures than 4BP8BP4 and exhibits an "extra", albeit monotropic, liquid crystalline phase. 2BP4BP2 is the only member of the two-carbon tail category to show a liquid crystalline phase and has the highest melting point of the group. The second trend is that longer tails lead to greater mesophase stability. The model compound without tails is not liquid crystalline, and the model compounds with two-carbon tails are only weakly liquid crystalline or exhibit crystal–crystal transitions. The model compounds with four-carbon tails exhibit the most stable liquid crystalline phases. 4BP4BP4, the model compound with the shortest spacer and the longest tails, has the highest clearing temperature (191 °C) and the broadest liquid crystalline range (60 °C) and exhibits two different liquid crystalline phases (smectic B and smectic E). These general trends have been noted previously[31,32] for twinlike ester model compounds.

The liquid crystalline monomers and model compounds prepared in this investigation show only smectic B and/or smectic E mesophases. Other dialkyl-substituted biphenyl liquid crystals and dialkyl-substituted bicyclohexane liquid crystals reported in the literature (see Tables I and IV in ref 15) also show only smectic phases. Only a few of the large number of dialkylbiphenyl and dialkylbicyclohexane derivatives have been reported, however, so it is possible that nematic phases may be present in compounds that have not yet been prepared. Further work in this area is needed.

Conclusion

A versatile synthetic route has been developed to prepare six new hydrocarbon monomers and six new twinlike hydrocarbon model compounds based on the biphenyl mesogen. Four of the monomers and three of the model compounds were shown to be liquid crystalline. Dialkyl substitution of the biphenyl mesogen appears to be necessary, although not sufficient, for liquid crystallinity, as monoalkyl-substituted biphenyl compounds were not liquid crystalline. Longer alkyl tails and shorter spacers resulted in more stable liquid crystalline phases. Only smectic phases (smectic B and/or smectic E) were observed in the new liquid crystalline materials and in other dialkyl-substituted biphenyl liquid crystals that have been previously reported. Attractive forces between the polarizable electrons of the biphenyl rings apparently stabilize smectic phases relative to nematic phases. The polymerization of the monomers and the properties of the resulting polymers will be reported in a future publication.

Acknowledgment. The support of the National Science Foundation for the Materials Research Laboratory at the University of Massachusetts is gratefully acknowledged.

Registry No. MEBP04, 115181-05-0; MEBP06, 115181-07-2; MEBP24, 116422-68-5; MEBP26, 115181-09-4; MEBP44, 115181-11-8; MEBP46, 115181-13-0; BP8BP, 116422-69-6; 2BP4BP2, 116422-70-9; 2BP6BP2, 116422-71-0; 2BP8BP2, 116422-72-1; 4BP4BP4, 116445-91-1; 4BP8BP4, 116422-73-2; 1-(4-biphenyl)-6-bromohexane, 118798-31-5; 1,6-dibromohexane, 629-03-8; 4-bromobiphenyl, 92-66-0; 1-(4-biphenyl)-8-bromooctane,

Macromolecules 1989, *22*, 2077–2082

118798-32-6; 1,8-dibromooctane, 4549-32-0; 1-[4-(4′-ethylbiphenyl)]-6-bromohexane, 118798-33-7; 1-[4-(4′-ethylbiphenyl)]-8-bromooctane, 118798-34-8; 1-[4-(4′-butylbiphenyl)]-6-bromohexane, 118798-35-9; 1-[4-(4′-butylbiphenyl)]-8-bromooctane, 118798-36-0; 4-ethyl-4′-bromobiphenyl, 58743-79-6; 1,4-dibromobutane, 110-52-1.

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Thermotropic Hydrocarbon Side-Chain Liquid Crystalline Polymers. 2. Polymer Synthesis and Tacticity

Joseph J. Mallon and Simon W. Kantor*

Department of Polymer Science and Engineering, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: Thermotropic hydrocarbon liquid crystalline α-olefin monomers have been polymerized with $AlEt_3/TiCl_4$ to form high molecular weight polymers. The properties of side-chain liquid crystalline polymers and poly(1-alkene)s are known to be highly dependent on tacticity. The tacticities of the new polymers range from 65% ± 10% to 90% ± 10% isotactic as determined by high-field ^{13}C nuclear magnetic resonance (NMR) spectroscopy. A model system employing poly(1-octadecene) has been used to identify the proper polymerization catalyst for the preparation of atactic liquid crystalline polymers. ^{13}C NMR has been used to show that atactic and isotactic poly(1-octadecene) can be distinguished on the basis of solubility and melting behavior. Preliminary experiments have not been successful in preparing atactic polymers from the new mesogenic monomers.

Introduction

A broad variety and number of side-chain liquid crystalline polymers have been prepared in recent years. Although the tacticities of most of the polymers have not been specified, some workers have studied the influence of backbone stereochemistry on liquid crystalline polymer properties. Newman, Frosini, and Magagnini have shown[1] that the transition temperatures of syndiotactic-rich poly(*p*-biphenyl acrylate) are much higher than the transition temperatures of isotactic polymer. In 1981, Ringsdorf et al. demonstrated[2] that the transition temperatures of a liquid crystalline poly(methacrylate) derivative were also influenced by tacticity.

In 1968, Aubrey and Barnatt reported[3] that poly(1-octadecene) prepared with $Et_3Al/TiCl_4$ catalyst displayed two melting points, 42 and 68 °C. The portion of the polymer soluble in hexane had only one melting point, at 42 °C, whereas the portion insoluble in hexane displayed a melting point of 68 °C. Aubrey and Barnatt proposed that the higher melting fraction was isotactic and the lower melting fraction atactic but offered no direct evidence for the tacticity assignment. In a series of papers, Magagnini and co-workers have investigated[4-7] the influence of tacticity on the side-chain packing of poly(1-eicosene). They used a variety of techniques to show that isotactic and atactic poly(1-eicosene) have different melting points, different crystal structures, and different solubility behavior. Data compiled by Porter, Wang, and Knox show[8] that poly(1-alkene)s with side chains of 11–14 carbon atoms also display two melting points.

The thermotropic hydrocarbon liquid crystalline monomers described in the first paper[9] of this series have been polymerized with Ziegler–Natta catalysts. In the present work, six new hydrocarbon polymers containing biphenyl mesogens in the side chain have been prepared from corresponding mesogenic monomers with a $Et_3Al/TiCl_4$ catalyst. The molecular weights of the six polymers and of a polymer prepared with a different catalyst (described below) have been measured by gel permeation chromatography (GPC), and the tacticities have been determined

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