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THERMOTROPIC HYDROCARBON SIDE CHAIN
LIQUID CRYSTALLINE POLYMERS

A Dissertation Presented

by

JOSEPH JAMES MALLON

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1988

Polymer Science and Engineering

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JOSEPH JAMES MALLON

Approved as to style and content by:

Simon W. Kantor, Chairman of Committee

Roger S. Porter, Member

C. Peter Lillya, Member

William J. MacKnight, Department Head
Polymer Science and Engineering

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ABSTRACT

THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

SEPTEMBER 1988

JOSEPH JAMES MALLON, B. S., UNIVERSITY OF CONNECTICUT
M. S., PH. D. UNIVERSITY OF MASSACHUSETTS

Directed by: Professor Simon W. Kantor

A versatile synthesis of thermotropic hydrocarbon side chain liquid crystalline monomers and model compounds containing the biphenyl mesogen has been developed. The monomers are n -[4-(4'-alkylbiphenyl)]-1-alkene derivatives with n equal to six or eight and terminal alkyl groups (tails) consisting of H, ethyl or n -butyl. Six new monomers were prepared by a four step synthesis that allows n and the alkyl group to be easily varied. A series of six new twin-like model compounds have also been prepared by a modification of the monomer synthesis. The model compounds are 1, n -bis-[4-(4'-alkylbiphenyl)]-alkane derivatives where n is four, six or eight and the alkyl groups are H, ethyl or n -butyl. The length of the flexible n -alkylene core and the terminal n -alkyl groups may be easily varied by employing the proper synthetic conditions.

Four of the six monomers and three of the six model compounds were shown to be liquid crystalline. Disubstitution of the biphenyl mesogen was found to be a

necessary, but not sufficient, condition for liquid crystallinity in the monomers and the model compounds, in accordance with previously noted trends. The new compounds exhibited only smectic B and/or smectic E phases.

Six new polymers were prepared by polymerizing the six new monomers with transition metal (Ziegler-Natta) catalysts. The polymers had four or six carbon flexible spacers and H, ethyl or n-butyl tails. Investigation of the polymers with Differential Scanning Calorimetry, Polarized Light Optical Microscopy and X-Ray Diffraction showed that four of the polymers were liquid crystalline (smectic B and smectic E). The polymers with H tails were not liquid crystalline and the polymers with ethyl or n-butyl tails were liquid crystalline.

The tacticities of the new polymers were measured by Carbon-13 Nuclear Magnetic Resonance Spectroscopy. The polymers ranged from 65% to 90% isotactic. Attempts were made to identify a catalyst capable of polymerizing the new monomers to atactic polymers using 1-octadecene as a model monomer. Carbon-13 Nuclear Magnetic Resonance Spectroscopy was used to show that atactic and isotactic poly(1-octadecene) could be distinguished on the basis of solubility and melting behavior. A series of catalysts were used to try to prepare atactic poly(1-octadecene), but only oligomers were obtained. An attempt to polymerize one of the biphenyl-containing monomers with the most promising catalyst from the 1-octadecene experiments also resulted in the formation of low molecular weight products.

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CHAPTER I

DEFINITION, BACKGROUND AND RATIONALE FOR THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Defining the Project

The project described in this dissertation is the synthesis and characterization of thermotropic hydrocarbon side chain liquid crystalline polymers. These polymers consist of a known hydrocarbon mesogen attached to a polyethylene backbone via an alkylene spacer group. The synthesis of appropriate monomers is necessary for the success of this project. The monomer synthesis must be general enough to allow for spacer and tail length variation. A general route for the conversion of the monomers to high molecular weight polymers is required.

The versatile synthesis of hydrocarbon monomers and twin-like model compounds containing biphenyl mesogens will be described in this dissertation. The mesomorphic properties will be studied as a function of the size of alkyl substituents on the biphenyl core. Ziegler-Natta catalysis is the method of choice for the polymerization of the monomers. The mesomorphic properties of the polymers as a function of spacer and tail length are to be examined. High field ^{13}C Nuclear Magnetic Resonance (NMR) experiments will be used to determine the tacticities of the polymers. Attempts will be made to prepare polymers of differing tacticities so that the effect of tacticity on liquid crystalline polymer properties may be studied.

Topic Background

Three subjects of interest will be discussed in this review: Liquid Crystals, Side Chain Polymers and Ziegler-Natta Catalysis. Many books and review articles are available on these subjects and reference is made to them at appropriate places in the text. Those subtopics which have a more direct bearing on this dissertation are discussed below.

Liquid Crystals

Cholesteryl benzoate was the first compound to be recognized as a liquid crystal. In 1888 the Austrian botanist Reinitzer¹ reported that it displayed two distinct melting points, at 145 °C and 179 °C. The crystalline solid transformed into a turbid liquid at 145 °C which persisted until the transition to an isotropic melt at 179 °C. The intermediate phase between the liquid and crystal phases was given the name "liquid crystal" by Lehmann² in 1904. The state of order present in this middle phase is less than the highly ordered crystal but more than the isotropic melt. Liquid crystals are frequently called "mesomorphic", from the Greek "mesos" meaning middle, and "morphe" meaning form.³ The mesomorphic state of matter is one in which the orientational order of the molecules comprising the system is present, but the positional order relative to the crystalline state is absent. This state can be attained either in a solution or on heating. Substances which form liquid crystalline solutions are known as lyotropic and those which exhibit mesomorphic behavior on heating or cooling are known as thermotropic.

The principal factor that determines whether or not a material will exhibit liquid crystallinity is asymmetry of molecular shape. Calculations by Onsager⁴, Isahara⁵⁻⁶ and Flory⁷ predicted the formation of an anisotropic phase in solutions of rodlike molecules. It is important to note that the predictions were based on a consideration of the length to breadth ratio, or axial ratio, of the rodlike molecules. Flory found that when the axial ratio reached a critical value of 6.7, phase separation into an isotropic phase and an anisotropic phase was predicted to occur. No intermolecular attractive forces were required to bring about this phase separation.

Flory states⁸ in 1982 that "the principle molecular feature responsible for liquid crystallinity invariably is asymmetry of molecular shape...". In fact nearly all known liquid crystalline molecules have anisotropic rod or disc shapes. Figure 1.1 is a schematic diagram showing some of the various types of liquid crystalline order. Nematic liquid crystals are aligned roughly parallel to one another. The order is essentially one dimensional and the centers of gravity show no long range order. Correlations exist only along the axes of the molecular groups.⁹

Smectic liquid crystals form layered structures as seen in Figure 1.1. There are seven basic polymorphs corresponding to different types of order within the layers. In addition to correlations along the axes of the molecular groups, correlations exist in a plane that is at some angle to the axes. The order is essentially two dimensional. Smectic liquid crystals are more ordered than nematic liquid crystals but less ordered than crystalline solids.

Nematic

Cholesteric

Smectic A

Smectic B

Discotic

Figure 1.1
Liquid Crystalline Order

Cholesteric liquid crystals form layered structures in which nematic order exists within each layer with the molecular axes parallel to the plane of the layers. The axis that describes the average direction of the molecular axes, called the director axis or director, changes in a regular way on going from one layer to the next. A helix is traced out perpendicular to the layer planes by the director. The molecules must be chiral to form a cholesteric phase, named for the cholesteryl moiety, which was present in the first cholesteric liquid crystals discovered.

Discotic liquid crystals are planar molecules that can exhibit nematic or smectic liquid crystalline order. The smectic phases favor columnar arrangements as shown in Figure 1.1. For a detailed description of the structures of the known liquid crystalline phases, see the book by Demus and Richter.¹⁰

Liquid crystals are characterized by three main methods: Differential Scanning Calorimetry (DSC)¹¹, Polarized Light Optical Microscopy (POM), and X-ray diffraction. DSC measures the heat of fusion of the liquid crystal as a phase transition occurs. The change in enthalpy is a function of the change in degree of order. Nematic liquid crystals typically show a larger enthalpy change on going from the crystalline to nematic state than from the nematic to isotropic state. This is because most of the order is lost at the crystalline-nematic transition. Smectic liquid crystals usually show a smaller enthalpy change on going from the crystalline state to the smectic state than from the smectic state to the isotropic state. Most of the order is lost at the smectic-isotropic transition.

When liquid crystals are viewed by POM, the birefringent liquid crystals exhibit textures that are characteristic of the type of mesophase. Transitions from one type of liquid crystal to another can be clearly seen and correlated with the DSC

results. Books authored by Demus and Richter¹² and by Gray¹³ both contain many color photomicrographs that are very helpful when trying to identify a mesophase.

X-ray diffraction is a technique which provides information on structural regularities in crystalline and liquid crystalline compounds. X-ray diffraction patterns of smectic liquid crystals show the presence of low-angle reflections corresponding to the layer spacing. A wide-angle spacing is also observed that corresponds to the intermolecular spacing. Nematic liquid crystals show only a wide-angle spacing because there are no layers present.¹⁴⁻¹⁵

Typical structural elements common to most rod-like liquid crystals can be seen in Figure 1.2. The molecules derive their rod-like nature from the inclusion of rigid units like benzene or cyclohexane rings. Sometimes a rigid or semi-rigid linking group is used to connect the rigid units. This usually increases the axial ratio of the rod. Twin-like mesogens¹⁶ have a flexible unit in the center of the molecule that connects two rigid units.

Tails or terminal groups are frequently necessary to stabilize the mesophase. Proper choice of terminal groups can increase the polarizability of the molecule and provide further stability. For instance, if an electron-donating group such as alkoxy is placed on one end of the molecule and an electron-withdrawing group such as nitrile is attached at the other end, the electron distribution becomes highly anisotropic, thus increasing intermolecular attractive forces (dipole-dipole type) and increasing the stability of the mesophase. For a detailed discussion of the effects of various structural elements on liquid crystalline properties, see the review by Gray.¹⁷

Rigid Unit: Typically benzene or cyclohexane

Linking group: Typically ester, azomethine or alkene

Terminal group or tail: Typically alkyl, alkoxy or nitrile

Figure 1.2

Structural Elements Common to Most Rod-like Liquid Crystals

As mentioned previously, however, intermolecular attractive forces are believed to be unnecessary for the formation of the mesophase. By concentrating on rod-like molecules which do not contain heteroatoms such as N or O, a number of workers have prepared hydrocarbon liquid crystals. Table 1.1 contains a list of these molecules taken from the literature. Although intermolecular attractive forces are still present in these molecules¹⁸⁻¹⁹, the forces are weaker than those in molecules containing strong dipoles or hydrogen bonds. The R groups shown in the table are generally n-alkyl with $n = 2-7$. T_{cl} is the range of clearing temperatures exhibited by members of the series. The table has been divided into three parts according to whether the mesogen is alicyclic, mixed aromatic and alicyclic, or aromatic. In Table 1.2 the transition temperatures of the di-n-pentyl derivatives of bicyclohexane, phenylcyclohexane and biphenyl are shown. The order of stability observed is alicyclic > aromatic > mixed aromatic and alicyclic. A review of the effect of various structural elements on the properties of hydrocarbon liquid crystals may be found in reference 19.

Table 1.1
Hydrocarbon Liquid Crystals

<u>Entry #</u>	<u>Structure</u>	<u>T_{cl}, °C</u>	<u>S/N</u>	<u>Reference</u>
<u>Alicyclic</u>				
1		17-114	S,N	19, 23, 25, 27, 29, 31
2		91-106	S	19,23, 25
3		57-66	S	19, 23
4		26-110	S	19, 25, 26
5		249a	S	34
6		125-141	S, N	21
7		74-99	N	40
8		209-247	S	19, 27

(continued)

Table 1.1 (continued)

<u>Entry #</u>	<u>Structure</u>	<u>T_{cl}, °C</u>	<u>S/N</u>	<u>Reference</u>
<u>Alicyclic-Aromatic</u>				
9		9-58	S,N	29, 31, 41
10		16-62	S,N	41
11		-11-92	S,N	25,28, 29
12		126-145	S,N	31, 35
13		82-144	S,N	27, 42, 46
14		107 ^b	S	25, 43
15		93-171	S,N	25, 27, 38, 39, 42, 44
16		196 ^c	S, N	20
17		155-210	S,N	33
18		25-55	N	36
19		49-61	S,N	36
20		239-274	S,N	27, 31
21		188 ^d	S	31
22		311 ^e	S,N	27, 31, 39

(continued)

Table 1.1 (continued)

<u>Entry #</u>	<u>Structure</u>	<u>T_{cl}, °C</u>	<u>S/N</u>	<u>Reference</u>
<u>Aromatic</u>				
23		80-132	N	32
24		28-84	S	25, 26, 29, 30 this work
25		185-228	S	25, 43, 45
26		352 ^c	S	19, 24
27		139-191	S	this work
28		148-164	S,N	37
29		425	S,N	47
30		565	S,N	47

- a) $R = R' = n - C_7H_{15}$
 b) $R = R' = n - C_4H_9$
 c) $R = R' = n - C_5H_{11}$
 d) $R = n - C_4H_9, R' = n - C_5H_{11}$
 e) $R = n - C_3H_7, R' = n - C_5H_{11}$

Table 1.2
Transition Temperatures of Dipentyl Mesogens

<u>Structure</u>	<u>Transition Temperatures</u>
K 40 S 110.4 I
K -0.8 S(-8) N (-5) I
K 26 S _E 47.6 S _B 52.2 I

Side Chain Polymers

A review of side chain polymers and particularly poly(1-alkene)s is presented. A discussion of side chain liquid crystalline polymers follows. An excellent review of both topics may be found in the book by Shibaev and Plate⁴⁸.

Side chain, or comb, polymers are linear polymers with relatively long, closely spaced side chains. Long side branches often mean that the molecular weight of the side chains is much greater than the molecular weight of the main chain. The physical properties of comb polymers are thus strongly dependent on the length and the chemical nature of the side chains. In the majority of the systems studied thus far, the side chains are n-alkyl groups. Poly(1-alkene)s, poly(alkyl acrylate)s, poly(alkyl methacrylate)s, poly(alkyl vinyl ether)s, poly(alkyl styrene)s, and poly(alkyl siloxane)s⁴⁹⁻⁵⁰ have been prepared. Side chain crystallization is usually noted when the side chain lengths reach 8-10 carbon atoms. Poly(1-alkene)s are probably the most intensively studied of this group. Because of structural similarities between the polymers prepared for this dissertation and the poly(1-alkene)s, the properties of the poly(1-alkene)s will be examined in more detail.

Poly(1-alkene)s are prepared by the polymerization of 1-alkenes with transition metal (Ziegler-Natta) catalysts. The lowest homologue of this series, poly(1-propene), or poly(propylene), was first prepared in this fashion by Natta himself. Isotactic poly(propylene) has a crystalline melting point of about 180 °C. As the length of the side chains is lengthened, the melting point observed for the isotactic polymer decreases regularly. Poly(1-hexene) and poly(1-octene) are very difficult to crystallize even by cooling and stretching. As the side chains become

longer than six carbon atoms, crystallinity is again observed and an increasing trend in melting points is reported. Two melting points are reported for polymers with side chains eleven carbon atoms or longer. Table 1.3 contains data on the melting points in this series reported by Porter, Wang and Knox.⁵¹

Reding⁵² and Turner-Jones⁵³⁻⁵⁴ performed X-ray studies on a series of isotactic poly(1-alkenes). Turner-Jones has correlated the crystal structure with the observed trend in melting points. She pointed out that the helical main chains are able to crystallize with one another in the case of poly(propylene), but this type of crystallization becomes increasingly difficult as the length of the side chain increases. For poly(1-hexene) and poly(1-octene), the main chains can no longer contact one another and crystallization is effectively prevented. As the side chains become longer they develop a tendency to crystallize independently of the backbone, distorting the helical conformation of the main chain. The rising trend in melting points results from the crystallization of increasingly lengthy side chains. Porter, Knox and Wang⁵¹ have extrapolated the side chain length to infinity and found a value which compares favorably with the melting point reported for polyethylene. The X-ray results reported by Turner-Jones show that the side chains pack parallel to each other in layers whose thickness corresponds to a structure in which the side chains are arranged on both sides of the main chain. Depending on thermal treatment, the angle at which the side chains are oriented with respect to the main chain can assume two different values. In the more crystalline, more stable Type II structure, the side chains are packed into an orthorhombic lattice at an angle of 131° to the axis of the main chain. In the type I structure, the side chains are oriented at right angles to the main chain.

Table 1.3
Melting Points of Isotactic Poly(1-olefin)s

<u>Poly(1-olefin)</u>	<u>Melting point, °C</u>
Poly(1-butene)	126-128
Poly(1-pentene)	70
Poly(1-hexene)	-
Poly(1-heptene)	37-38
Poly(1-octene)	-
Poly(1-nonene)	30-32
Poly(1-decene)	35
Poly(1-undecene)	39-40
Poly(1-dodecene)	44
Poly(1-tridecene)	55 39
Poly(1-tetradecene)	54 3
Poly(1-pentadecene)	59 13
Poly(1-hexadecene)	70 41
Poly(1-octadecene)	68-75 42

Turner-Jones' experiments were done on isotactic polymers. Tacticity has an enormous effect on the physical properties of polymers. Isotactic poly(propylene) has a melting point of 180 °C whereas atactic poly(propylene) is completely amorphous. In 1968 Aubrey and Barnatt⁵⁵ prepared a sample of poly(1-octadecene) which displayed two melting points when examined by differential scanning calorimetry (DSC). The polymer was prepared in bulk with a $\text{Et}_3\text{Al} / \text{TiCl}_4$ catalyst. Fifty percent of the polymer was found to be soluble in hexane at 25 °C. The hexane soluble portion of the polymer was found to display only one melting point by DSC, corresponding to the lower melting transition of the unextracted polymer. The hexane insoluble portion of the polymer exhibited the melting point of the upper transition of the unextracted polymer. The conclusion drawn by Aubrey and Barnatt was that the polymer obtained from the polymerization consisted of two fractions which melted at two different temperatures and could be largely separated by hexane extraction. It was postulated that the lower melting was atactic and the higher melting isotactic and that the melting behavior of both polymers was strongly influenced by side chain crystallization.

A similar study was carried out in 1981 by Magagnini and coworkers⁵⁶ using a sample of poly(1-eicosene) obtained by polymerization with $\alpha\text{-TiCl}_3 / \text{Al}(\text{i-Bu})_3$. The polymer was extracted with boiling ether and the insoluble residue recrystallized twice from heptane. DSC and ^{13}C Nuclear Magnetic Resonance (NMR) experiments were then performed on the fractionated and unfractionated polymers. The unfractionated polymer showed two peaks on the DSC scan at 54 °C and 80 °C. The fraction soluble in boiling ether had a single melting transition at 54 °C and a ^{13}C NMR spectrum consistent with an atactic polymer. The polymer recrystallized from heptane had a single melting transition at 80 °C and a ^{13}C NMR spectrum consistent

with an isotactic structure. The results clearly show that the polymer obtained from the polymerization was composed of a mixture of atactic and isotactic polymers which independently exhibited their individual melting points.

The thermal transitions and packing arrangements of the side chains of poly(1-eicosene) were clarified in a series of papers by Magagnini et al.⁵⁷⁻⁵⁹ By studying the splitting of the 720 cm^{-1} infrared band, Magagnini was able to show that the side chains of the atactic and isotactic polymers had different crystal structures. These structures were confirmed by X-ray diffraction studies. Isotactic polymer that had been cooled slowly from the melt (Type II) gave a split 720 cm^{-1} infrared peak at $25\text{ }^{\circ}\text{C}$, indicating orthorhombic packing. The side chains of the atactic fraction, however, showed a single 720 cm^{-1} peak at room temperature, indicative of hexagonal packing. As the temperature of the atactic polymer was lowered, the peak began to split into a doublet, demonstrating that a hexagonal-orthorhombic packing transition was taking place. The transition took place over a broad temperature range and was not detectable by DSC. The isotactic fraction underwent an orthorhombic-hexagonal transition on heating to $75\text{ }^{\circ}\text{C}$. Thus, it was shown that the side chains of both polymers pack into an orthorhombic lattice at low temperatures and into a hexagonal lattice at higher temperatures. At any given temperature, a greater fraction of the atactic polymer is in a hexagonal arrangement than the isotactic polymer.

In summary, Magagnini has shown that poly(1-eicosene) can be polymerized to yield a mixture of atactic and isotactic polymers. The fractions can be easily separated by solvent extraction. The long alkyl side chains can crystallize into hexagonal or orthorhombic packings, depending on thermal history. The two fractions independently exhibit their melting points in the unextracted polymer. When the polymers are separated, the lower melting is the atactic and the higher

melting is the isotactic. The orthorhombic-hexagonal transition takes place on heating in both polymers over a broad temperature range. The transition range is different in size and location for each polymer. The transition is undetectable by normal DSC methods.

Side Chain Liquid Crystalline Polymers (SCLCP) result from the incorporation of a mesogenic moiety into the side chain of a polymer. Several good reviews⁶⁰⁻⁶⁵ are available. Intense research activity began in this area in the early 1970's when the technological and commercial success of low molecular weight liquid crystals for electrooptical displays became apparent. Workers reasoned that the optical properties of the mesogenic molecules could be combined with the attractive mechanical properties of polymers by including the mesogen in a polymer side chain.

The synthetic strategy taken by early workers was to place a polymerizable group on one end of a known liquid crystal. These monomers were frequently styrene, acryloyl or methacryloyl derivatives. Hsu and Blumstein⁶¹ list over 100 such monomers in their 1978 review. Although the monomers were almost always liquid crystalline, most of the resulting polymers were not. In the late 1970's it was realized that the direct attachment of the mesogen to the polymer backbone could be preventing the formation of a mesophase. It was reasoned that the tendency for the polymer backbone to assume a statistical conformation in the melt did not allow the mesogens to orient properly. In 1978 Ringsdorf and coworkers⁶⁶ showed that a flexible spacer between the main chain and the mesogen decoupled the conflicting tendencies of the main chain toward disorder and the mesogen toward order. Following this insight, a large number of SCLCP's have been prepared in the last ten years.

Figure 1.3 is a schematic showing the main structural features of SCLCP's. The mesogen does not have to be rod-shaped as shown. Discotic and cholesteric SCLCP's have also been successfully prepared. The vast majority of SCLCP's prepared thus far are poly(acrylate), poly(methacrylate), poly(acrylamide), poly(methacrylamide), poly(phosphazene) and poly(siloxane) derivatives. Mesogens such as biphenyl, phenylbenzoate and benzalaniline are usually connected to the polymer backbone via alkylene or oxyalkylene spacers. Tail units are typically alkyl, alkoxy or nitrile.

SCLCP's have been prepared by two main routes. In the first, a monomer is prepared which contains a polymerizable group and a mesogen, usually separated by a flexible spacer. The monomer is frequently, though not always, itself a liquid crystal. Polymerization of the monomer yields the corresponding polymer. This is the preferred route for the preparation of acrylate and methacrylate derivatives. The second method involves the addition of a mesogenic group to a functionalized polymer. The most common example is the reaction of poly(methylhydrosiloxane) with a mesogen containing a terminal olefin in the presence of a catalyst. This hydrosilation route is the usual method for the preparation of poly(siloxane) derivatives.

SCLCP's are characterized by the same methods used to characterize low molecular weight liquid crystals. Nematic, smectic, cholesteric and discotic phases are known. In addition, the molecular weight and molecular weight distribution must be determined for complete characterization.

Figure 1.3
Main Structural Features of
Side Chain Liquid Crystalline Polymers

The transition temperatures of SCLCP's have been found to be strongly dependent on the degree of polymerization (DP) when the DP is fairly low. Data from Shibaev and Plate⁶⁷ for a series of poly(acrylate) and poly(methacrylate) derivatives show that a DP of approximately 200 is required before a plateau is reached in a plot of transition temperatures versus DP. In contrast, Finkelmann and coworkers⁶⁸ report that a poly(siloxane) derivative with a DP of 10 exhibits transition temperatures that are only 5% lower than polymers of extrapolated infinite molecular weight. The data show that it is possible for two different fractions of the same polymer to show different liquid crystalline phases at the same temperature if their degrees of polymerization are below a critical value. This critical value is different for different polymers and for different members of a homologous series with different side chain lengths. Comparative studies of SCLCP's should only be done when the DP of the polymers are above their respective critical values.

Only a few isolated studies on the effect of tacticity on the properties of SCLCP's have been published. In 1978 the properties of poly(p-biphenyl acrylate) (PPBA) and poly(p-biphenyl methacrylate) (PPBMA) of differing tacticities were studied⁶⁹ by Newman, Frosini and Magagnini. ¹H NMR was used to determine the tacticities of five samples of PPBA. Two of the samples were mostly syndiotactic, whereas the other three were predominately isotactic. The molecular weights and molecular weight distributions were not determined. The measured tacticities and equilibrium melting points are tabulated in Table 1.4. Despite the differences observed in the melting temperatures, no significant differences between the isotactic and syndiotactic samples were seen by X-ray diffraction. All of the samples exhibited a low angle diffraction pattern consistent with a layer spacing of 21.0 Å - 23.2 Å, depending on thermal history. The authors concluded that the

Table 1.4
Tacticities and Melting Points of PPBA Samples

<u>Polymerization Method</u>	<u>Tacticity</u>	<u>Melting Point, °C</u>
n-BuLi / toluene / -78 °C	90 % isotactic	238
Bz ₂ O ₂ / bulk / 65-70 °C	55% syndiotactic	277
UV irradiation/ toluene / -78 °C	65% syndiotactic	305

tacticity differences did not affect the observed smectic structure. None of the PPBMA samples, regardless of tacticity, were liquid crystalline. Unfortunately, because of a lack of molecular weight characterization and incomplete tacticity and thermal data, it is difficult to draw significant conclusions from this work.

In 1981, Ringsdorf, Wendorff, Hahn and Portugall⁷⁰ studied the effect of tacticity on the transitions of the polymer shown in Figure 1.4. A sample A was prepared by anionic initiation and a sample R by radical initiation. The tacticity and thermal characterization data are summarized in Table 1.5. No significant differences between the samples were observed by X-ray diffraction. Both were crystalline at room temperature and showed a broad halo by wide angle X-ray diffraction when heated above their transition temperatures. Although the X-ray results indicated a nematic structure for both polymers, a smectic texture was observed by POM. The authors were unable to draw firm conclusions about the nature of the mesophase exhibited by either sample A or sample R. Molecular weight and molecular weight distribution data were not reported.

Figure 1.4

SCLCP Studied by Ringsdorf, Wendorff, Hahn and Portugall.

Table 1.5

SCLCP Tacticities and Melting Points

	<u>% iso.</u>	Triad Tacticity <u>% syn.</u>	<u>% hetero</u>	Transition Temp., °C <u>K - LC</u>	<u>LC - I</u>
Sample R	2	63	35	117	127-131
Sample A	68	25	7	131	135

One paper has appeared on SCLCP tacticity as a function of spacer length. In 1987, Duran and Gramain⁷¹ reported the tacticities of a series of polymers and copolymers with the structure shown in Figure 1.5. Free radical initiation was used to prepare polymers with varying n . Molecular weights determined by Gel Permeation Chromatography (GPC) were found to be high. ^1H NMR was used to measure the tacticities of the polymers. These values were expressed as a percentage of the number of syndiotactic, heterotactic or isotactic triads. As n was varied from zero to four, a decrease in isotacticity from 20% to 10% was seen, with a concomitant increase in syndiotactic triads. The number of heterotactic sequences remained constant. The authors suggested that biphenyl-biphenyl attractions between the growing chain end and the incoming monomer were stronger in monomers with short spacers, leading to greater isotacticity. No thermal or X-ray data were reported.

Figure 1.5

SCLCP Studied by Duran and Gramain.

Ziegler-Natta Catalysis

Ziegler-Natta catalysts make possible the polymerization of ethylene and 1-alkenes to high molecular weight at low pressures and temperatures. They are the catalysts of choice for the polymerization of the monomers prepared in this dissertation. They were discovered by Professors K. Ziegler and G. Natta, who were awarded the 1963 Nobel Prize for Chemistry for their work. The literature available on the subject is vast, but the book by J. Boor, Jr.⁷² was found to be particularly helpful.

Ziegler-Natta catalysts are a mixture of a metal alkyl of Group I to III and a salt of transition metals of Group IV to VIII. A very large number of combinations are possible, some of which are polymerization catalysts for certain monomers. Most of the catalysts are insoluble in the solvents in which they are employed, so polymerization must take place at the surface of the catalyst. Almost all of the heterogeneous catalysts produce polymer that is mostly isotactic. Soluble catalysts are necessary for the preparation of syndiotactic polymers. Completely atactic polymer has also been produced with soluble catalysts.⁷³ The sensitivity of the catalyst components to variables such as catalyst ratio, order of mixing, moisture, air, temperature, method of catalyst preparation and presence of promoters has made it difficult to obtain consistent results. The heterogeneous nature of the catalyst further complicates mechanistic and kinetic studies and the conclusions drawn in many experiments are specific to the particular system studied.

The literature contains literally dozens of suggested polymerization mechanisms. It is quite likely that "the mechanism" is actually a combination of several mechanistic pathways that operate at different rates depending on the specific

polymerization conditions employed. Nevertheless, the proposed mechanisms generally have two steps in common. The first is the complexation of the monomer to the catalyst, and the second is insertion of the monomer into the catalyst-polymer bond. One mechanism that has achieved broad acceptance is that of Green, Ivin and coworkers,⁷⁴⁻⁷⁵ shown in Figure 1.6. The catalyst is bound to the polymer by a transition metal-carbon bond. This bond undergoes α -elimination to produce a carbene and a metal hydride. A metallocyclobutane forms between the carbene and complexed monomer. A hydride shift to the tertiary carbon completes the cycle.

The most common Ziegler-Natta catalysts are based on TiCl_3 and trialkylaluminums. Both the nature of the alkyl substituent on Al and the crystal structure of the TiCl_3 have been found to influence tacticity. When used to prepare poly(propylene), the various Ti/Al catalysts gave polymer that ranged from 40% to 90% isotactic.⁷⁶ The high degrees of isotacticity found for most of the polymers were believed to be the result of steric restrictions imposed by the catalyst surface.

Soluble catalyst systems based on vanadium have been found to produce syndiotactic polymer.⁷⁷⁻⁷⁹ The rate of polymerization of 1-propene is much higher than 1-butene, and higher 1-olefins do not polymerize at all.⁸⁰ Recent evidence⁸¹ suggests that secondary insertion of the monomer into the metal carbon bond occurs instead of primary insertion as seen in Figure 1.6. Steric interactions between the last added and incoming monomer are thought to be responsible for the syndiotactic configuration of poly(propylene). These same interactions are believed to be too large in the case of the more bulky 1-olefins to allow the polymerization to proceed.

Kaminsky and coworkers⁸²⁻⁸⁵ have recently developed a series of soluble catalysts that have very high activities. The catalysts are based on combinations of Hf, Zr or Ti metallocenes with methalumoxane. Poly(propylene) produced with

these catalysts is completely atactic. Attempts to polymerize higher 1-olefins have resulted in low molecular weight polymers. Mechanistic studies are not yet available on these systems.

Figure 1.6

Proposed Mechanism of Ziegler-Natta Polymerization

Rationale for Thermotropic Hydrocarbon Side Chain Liquid Crystalline Polymers

Almost all of the thermotropic side chain liquid crystalline polymers that have been reported in the literature contain heteroatoms such as N or O. The heteroatoms can cause hydrogen bonds and/or strong dipoles to be present in the polymers. These attractive forces probably stabilize the mesophase, but should not be necessary for its formation.

Thermotropic hydrocarbon side chain liquid crystalline polymers are prepared in this dissertation to demonstrate that strong intermolecular forces are not required for the formation of a mesophase. Low molecular weight hydrocarbon liquid crystals have been known for some time, but this is believed to be the first report in which hydrocarbon mesogens have been incorporated into the side chain of a polymer to form hydrocarbon side chain liquid crystalline polymers. The strongest intermolecular forces in this system are the relatively weak induced dipole - induced dipole forces existing between the polarizable electrons of the biphenyl rings.

The use of Ziegler-Natta catalysts to initiate polymerization results in the formation of polymer with particular tacticity. The tacticities of the polymers prepared in this work are determined by ^{13}C NMR. Attempts are made to prepare polymers with different tacticities so that the effect of tacticity on liquid crystalline properties may be studied.

References

1. Reinitzer, F.; Wilnez, J.; *Monatsh Chem* **1888**, 85, 421.
2. Kelker, H.; *Mol. Cryst. Liq. Cryst.* **1973**, 21, 1.
3. Wunderlich, B.; Grebowicz, J. In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; p. 1.
4. Onsager, L. *Ann. N. Y. Acad. Sci.* **1949**, 51, 627.
5. Isahara, A. *J. Chem. Phys.* **1950**, 18, 1446.
6. Isahara, A. *J. Chem. Phys.* **1951**, 19, 1142.
7. Flory, P. J. *Proc. R. Soc. London Ser. A.* **1956**, 234, 73.
8. Flory, P. J. In "Polymer Liquid Crystals" Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B. Academic Press: New York, 1982; p. 103.
9. Reference 3, p. 19.
10. Demus, D.; Richter, L.; "Textures of Liquid Crystals" Verlag Chemie: New York, 1978.
11. See Reference 3 for a detailed discussion.
12. See Reference 10 for a detailed discussion.
13. Gray, G. W.; Goodby, J. W. G.; "Smectic Liquid Crystals", Philadelphia: Heyden & Son, 1984.
14. de Vries, A.; *Mol. Cryst. Liq. Cryst.* **1985**, 131, 125.
15. Azaroff, L. V.; *Mol. Cryst. Liq. Cryst.* **1980**, 60, 73.
16. Griffin, A. C.; Britt, T. R.; *J. Am. Chem. Soc.* **1981**, 103, 4957.
17. Gray, G. W.; In "Polymer Liquid Crystals" Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B. Academic Press: New York, 1982; Chap. 2.
18. See Samulski, E. T.; Toriumi, H.; *Mol. Cryst. Liq. Cryst.* **1983**, 101, 163, and references therein.

19. Toyne, K. J.; In "Thermotropic Liquid Crystals" Gray, G. W. John Wiley and Sons: New York, 1987, Chapter 2.4.
20. Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, 128, 45.
21. Petrzilka, M.; Schleich, Kuno; *Helvetica Chimica Acta* **1982**, 65, 1242.
22. Reiffenrath, V.; Schneider, F.; *Z. Naturforsch.*, **1981**, 36a, 1006.
23. Praefcke, K.; Schmidt, D.; Heppke, G.; *Chem. Ztg.* **1980**, 104, 269.
24. Demus, D.; Demus, H.; Zashke, H.; In "Flussige Kristalle in Tabellen" VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, German Democratic Republic, 1974, p. 230.
25. Osman, M. A.; *Z. Naturforsch* **1983**, 38a, 693.
26. Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, 131, 353.
27. Eidenschink, R.; *Mol. Cryst. Liq. Cryst.* **1985**, 123, 57.
28. Takatsu, H.; Takeuchi, K.; *Mol. Cryst. Liq. Cryst.* **1986**, 138, 231.
29. Petrzilka, M.; *Mol. Cryst. Liq. Cryst.* **1984**, 111, 347.
30. Dabrowski, R.; Zytinski, E.; *Mol. Cryst. Liq. Cryst.* **1982**, 87, 109.
31. Petrzilka, M.; Schadt, M.; Gerber, P. R.; Villiger, A.; Tricke, G.; *Mol. Cryst. Liq. Cryst.* **1983**, 94, 139.
32. Grant, B.; *Mol. Cryst. Liq. Cryst.* **1978**, 48, 175.
33. Carr, N.; Gray, G. W.; Kelley, S. M.; *Mol. Cryst. Liq. Cryst.* **1985**, 129, 301.
34. Billard, J.; Mamlok, L.; *Mol. Cryst. Liq. Cryst., Letters* **1978** 41, 217.
35. Takatsu, H.; Takeuchi, K.; Sato, H.; *Mol. Cryst. Liq. Cryst.* **1984**, 111, 311.
36. Cereghetti, M.; Marbet, R.; Schleich, K.; *Helv. Chim. Acta* **1982**, 65, 1318.
37. Lauk, Urs H.; Skrabal, P.; Zollinger, H.; *Helv. Chim. Acta* **1985**, 68, 1406.
38. Ullrich, K.; Wendorff, J. H.; *Mol. Cryst. Liq. Cryst.* **1985**, 131, 376.

39. Eidenschink, R.; *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 119.
40. Varech, D.; Jacques, J.; *Mol. Cryst. Liq. Cryst., Letters* **1983**, *92*, 141.
41. Carr, N.; Gray, G. W.; *Mol. Cryst. Liq. Cryst.* **1985**, *124*, 27.
42. Balkwill, P.; Bishop, D.; Pearson, A.; Sage, I.; *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 1.
43. Karamysheva, L. A.; Kovshev, E. I.; Pavluchenko, A. I.; Roitman, K. V.; Titov, V. V.; Torgova, S. I.; Grebenkin, M. F.; *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 241.
44. Haase, W.; Paulus, H.; Muller, H. T.; *Mol. Cryst. Liq. Cryst.* **1983**, *97*, 131.
45. Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, *128*, 45.
46. Takatsu, H.; Takeuchi, K.; Sato, H.; *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 345.
47. Irvine, P. A.; Wu, D. C.; Flory, P. J.; *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 1795.
48. Plate, N. A.; Shibaev, V. P.; "Comb Shaped Polymers and Liquid Crystals" Plenum Press: New York, 1987.
49. Plate, N. A.; Shibaev, V. P.; *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.
50. Wunderlich, B.; "Macromolecular Physics Volume 3", Academic Press: New York, 1980; pp. 326-327.
51. Porter, R. S.; Wang, J.; Knox, J. R.; *Polym. J.* **1978**, *10*, 619, and references therein.
52. Reding, F. P.; *J. Polym. Sci.* **1956**, *21*, 547.
53. Clark, K. J.; Turner-Jones, A.; Sandiford, D. J. H.; *Chem. Ind. (London)* **1962**, 2010.
54. Turner-Jones, A.; *Makromol. Chem.* **1964**, *71*, 1.
55. Aubrey, D. W.; Barnatt, A.; *J. Polym. Sci., Part A-2* **1968**, *6*, 241.
56. Magagnini, P. L.; Segre, A. L.; Andruzzi, F.; Lupinacci, D.; *Macromolecules* **1981**, *14*, 1845.

57. Magagnini, P. L.; Andruzzi, F.; Vergamini, P.; Benedetti, E. *Polym. Bull.* **1980**, *2*, 241.
58. Magagnini, P. L.; Andruzzi, F.; Benetti, G. F.; *Macromolecules* **1980**, *13*, 12.
59. Magagnini, P. L.; Andruzzi, F.; Lupinacci, D.; Paci, M.; *Polymer* **1982**, *23*, 277.
60. Finkelmann, H.; In "Polymer Liquid Crystals", Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B.; Academic Press: New York, 1982; Chapter 2.
61. Blumstein, A.; Hsu, E. C.; In "Liquid Crystalline Order in Polymers", Blumstein, A.; Academic Press: New York, 1978; Chapter 3.
62. Shibaev, V. P.; Plate, N. A.; *Polym. Sci. USSR*, **1977**, *19*, 1065.
63. Hardy, Gy.; Cser, F.; Horvath, J.; Nyitrai, K.; *Israel J. Chem.* **1985**, *25*, 252.
64. Finkelmann, H.; Rehage, G.; In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; p.99.
65. Shibaev, V. P.; Plate, N. A.; In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; p.173.
66. Ringsdorf, H.; Portugal, M.; Happ, M.; Finkelmann, H.; *Makromol. Chem.* **1978**, *179*, 2541.
67. Shibaev, V.P.; Kostromin, S. G.; Plate, N. A.; *Eur. Polym. J.* **1982**, *18*, 651.
68. Stevens, H.; Rehage, G.; Finkelmann, H.; *Macromolecules* **1984**, *17*, 851.
69. Newman, B. A.; Frosini, V.; Magagnini, P. L.; In " Mesomorphic Order in Polymers", Blumstein, A.; ACS Symposium Series No. 74, American Chemical Society: Washington D. C. 1978; p. 71.
70. Hahn, B.; Wendorff, J. H.; Portugall, M.; and Ringsdorf, H.; *Coll. Polym. Sci.* **1981**, *259*, 875.
71. Duran, R.; Gramain, P.; *Makromol. Chem.* **1987**, *188*, 2001.
72. Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979.

73. Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J.; In "Comprehensive Organometallic Chemistry" Wilkinson, Sir G.; New York: Pergamon Press, 1982; Chapter 22.5.
74. Green, M. L. H.; *Pure Appl. Chem.* **1978**, *30*, 27.
75. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. J. *Chem. Soc., Chem Commun.* **1978**, 604.
76. Reference 72, pp. 88 and 96.
77. Zambelli, A.; Allegra, G.; *Macromolecules* **1980**, *13*, 42.
78. Zambelli, A.; Tosi, C.; Sacchi, C.; *Macromolecules* **1972**, *5*(5), 649.
79. Doi, Y.; Ueki, S.; Keii, T.; *Macromolecules* **1979**, *12*, 314.
80. Reference 72, p. 91.
81. Reference 72, p. 10.
82. Kaminsky, W.; Sinn, H.; In "Advances in Organometallic Chemistry Volume 18", Academic Press: New York, 1980; pp. 99-149.
83. Kaminsky, W.; Schlobohm, M.; *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 103.
84. Kaminsky, W.; Herwig, J.; *Polym. Bull.* **1983**, *9*, 464.
85. Kaminsky, W.; Luker, H.; *Makromol. Chem. R. C.* **1984**, *5*, 275.

CHAPTER II

SYNTHESIS OF THERMOTROPIC HYDROCARBON LIQUID CRYSTALLINE MONOMERS AND MODEL COMPOUNDS

Introduction

The general structures of the target monomer and polymer selected for this dissertation are shown in Figure 2.1. The combination of spacer and tail length necessary for liquid crystallinity was not known at the outset of this investigation. The ideal synthesis will be versatile enough to allow the spacer and tail length to be easily varied. Specific monomer and polymer targets were chosen on a trial and error basis.

The general synthetic route to the monomers required for this dissertation is illustrated in Figure 2.2 for 8-[4-(4'-ethylbiphenyl)]-1-octene (abbreviated as MEBP26), a monomer that will give a polymer with a six carbon spacer and a two carbon tail. The first step of the synthesis is a Friedel-Crafts acylation of 4-bromobiphenyl with acetyl chloride in CH_2Cl_2 . Wolff-Kishner reduction of the ketone follows to yield 4-ethyl-4'-bromobiphenyl in 50% overall yield, based on 4-bromobiphenyl. The synthetic strategy is nearly identical to that used by Gray¹ to prepare several 4-alkyl-4'-bromobiphenyl derivatives. Control over the tail length may be exercised by choice of the appropriate acid chloride.

Figure 2.1
Target Monomer and Polymer

Figure 2.2

The general synthetic scheme for the monomer synthesis is illustrated for 8-[4-(4'-ethylbiphenyl)]-1-octene (MEBP26).

$\text{AlCl}_3 / \text{CH}_2\text{Cl}_2$

$\text{HOCH}_2\text{CH}_2\text{OH} \quad \text{KOH} / \text{H}_2\text{NNH}_2$

THF

1. Mg
2. $\text{Br}(\text{CH}_2)_8\text{Br}$
3. 3% Li_2CuBr_4

1. $\text{N}(\text{CH}_3)_3$
2. Ag_2O
3. Δ

The third step of the scheme shown in Figure 2.2 is a coupling reaction between 4-ethyl-4'-biphenylmagnesium bromide and one end of 1,8-dibromooctane.^{2,3} The reaction is performed in tetrahydrofuran (THF) in the presence of a Li_2CuBr_4 catalyst. The spacer length of the monomer may be controlled by selecting the appropriate dibromoalkane. An excess of dibromoalkane is used to limit coupling with both ends of the dibromoalkane. The excess is removed by distillation during the work up. After removal of the dibromoalkane, the product consists of a yellow oil containing a white precipitate.

The white precipitate may be removed by filtering the yellow oil. After purification, the white precipitate is found to be the product of coupling with both ends of the dibromoalkane, illustrated for 1,8 bis [4-(4'-ethylbiphenyl)]octane (abbreviated as 2BP8BP2) in Figure 2.3. Different structures, useful as main chain model compounds, may be prepared by varying the acid chloride and dibromoalkane employed. The yellow oil may be distilled or used directly in the fourth step of the reaction sequence.

The elimination of HBr in the final step is accomplished with a Hoffman elimination⁴. The oil obtained from the previous step is treated with $\text{N}(\text{CH}_3)_3$ to form a trimethylammonium bromide salt. This product is water soluble and filtration of the aqueous solution removes organic impurities. Reaction with Ag_2O and evaporation results in a brown paste of the trimethylammonium hydroxide. Heating under vacuum eliminates $\text{N}(\text{CH}_3)_3$ and H_2O to form the 1-alkene in 20-50% yield.

Figure 2.3

Reaction Pathway for Model Compound Formation, Illustrated for 2BP8BP2

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 from Aldrich Chemical Co. as a "Gold Label" product and used without further purification. 4-Bromobiphenyl was purchased from Aldrich Chemical Co., recrystallized from isopropanol and dried under vacuum before use. 1,4-Dibromobutane, 1,6-dibromohexane and 1,8-dibromooctane were purchased from Aldrich and vacuum distilled from CaH_2 before use. Magnesium metal and 1,2 dibromoethane were obtained from Aldrich Chemical Co. as "Gold Label" products and used without further purification. LiBr and CuBr_2 were obtained from Aldrich Chemical Co. 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 Chemical Co. 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.

Preparations

4-acetyl-4'-bromobiphenyl. A clean, dry 2000 mL 3-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 mole, 96.0 g) was added to the flask with a powder funnel. Acetyl chloride (51.8 g, 0.66 mole) was slowly added to the stirred mixture. After the contents of the flask had again cooled to 5 °C, 140 g (0.6 mole) of 4-bromobiphenyl was added with a powder funnel over the course of 10 minutes. The resulting red suspension was allowed to warm to room temperature and stirred overnight.

The contents of the flask were poured into 1000 g ice/60 mL conc. HCl in a large beaker. The beaker contents were stirred and heated to drive off CH_2Cl_2 . After cooling, the crystalline solid was removed by filtration. The solid was recrystallized from 50/50 isopropanol/ CHCl_3 to yield, after drying, 127.3 g of white crystals, mp 130-131 °C. Literature mp: 131-133 °C⁵, 131 °C⁶ 129-130 °C⁷. Yield: 77%, based on 4-bromobiphenyl.

4-ethyl-4'-bromobiphenyl. 4-Acetyl-4'-bromobiphenyl, (123.8 g, 0.45 mole), 500 mL of ethylene glycol, 66 g (1.0 mole) of 85% potassium hydroxide, and 95 mL (1.35 mole) of hydrazine hydrate were placed into a one liter 3-neck round-bottom flask with stir bar. A still head was attached and the flask was heated and stirred at 110 °C for one hour. 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 hours, 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 crystalline 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 of product with a mp of 128-129 °C, yield 40%. Literature mp: 125-126 °C.⁸

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 with a mp of 104-105 °C. Literature mp: 104-104.5 °C.¹

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 three times from ethanol to yield 71.3 g (64% yield) of 4-butyl-4'-bromobiphenyl, mp 104-105 °C. Literature mp: 102-102.5 °C.¹

0.1 M Li_2CuBr_4 / THF solution. 0.17 g (0.002 mole) of LiBr and 0.22 g (0.001 mole) CuBr_2 were placed into a dry 50 mL single neck round-bottom flask. The flask was septa-capped, 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 mole) were placed into an oven-dried 250 mL 3-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 minutes. A solution of 23.33 g (0.1 mole) of 4-bromobiphenyl in 50 mL of THF was prepared under Ar in a 100 mL round-bottom flask. Fifty mL of THF were 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 round-bottom flask to activate the magnesium. After activation was complete (about 30 minutes), 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 one hour. The resulting orange solution was stirred for an additional hour.

1,6-Dibromohexane (73.19 g, 0.30 mole) was placed into a 500 mL 3-neck round-bottom flask with a stir bar. The flask was fitted with a reflux condenser and an adapter containing a coarse fritted disc (Aldrich adapter, catalog Z10,747-6). The system was septa-capped and Ar was bubbled through the liquid for at least one hour. The Grignard reagent previously prepared was transferred via cannula to the adapter. The solution flowed through the coarse fritted disc into the 1,6-dibromohexane. The resulting yellow solution was heated to gentle reflux and 3 mL of previously prepared 0.1M Li_2CuBr_4 / THF solution were added via syringe. After about 10 minutes of gentle reflux, the solution turned dark green over the course of about one minute. The dark green solution was refluxed for two hours, then allowed to cool to room temperature.

The reaction mixture was poured into a beaker containing 50 g ice / 10 mL conc. 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 washed with ether. The

ethers 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 millitorr) was excess 1,6-dibromohexane. The second fraction boiling 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. 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 mole) of 1,8-dibromooctane was used in place of 1,6-dibromohexane. The white precipitate insoluble in ether was filtered 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). Analysis, calculated for $\text{C}_{32}\text{H}_{34}$: C: 91.81%, H: 8.19% Found: C: 92.03%, H: 8.00%. The melting behavior will be discussed in the next chapter. After distilling the excess 1,8-dibromooctane, the major product was vacuum distilled at 600 millitorr and 190-200 °C to yield 21.6 g (62%) of a yellow oil that crystallized on cooling, mp 34-35 °C.

6-(4-biphenyl)-1-hexene (MEBP04). 20.6 g (0.06 mole) of 1-(4-biphenyl)-6-bromohexane was mixed at room temperature with 50 mL of 25% $\text{N}(\text{CH}_3)_3$ in methanol. The flask was heated slightly to produce a clear solution, which was allowed to stir overnight at room temperature. 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. Ag_2O (3.9 g, 0.06 mole) 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 necked 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 $\text{N}(\text{CH}_3)_3$ 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 millitorr yielded 7.4 g of clear oil, 31% yield based on 1-(4-biphenyl)-6-bromohexane. Analysis: Calculated for $\text{C}_{18}\text{H}_{20}$: C: 91.47 %. H: 8.53%. Found: C: 91.51%. H: 8.50%.

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). Vacuum distillation from CaH_2 at 500 millitorr and 160-170 °C gave 7.9 g of clear oil, 50% yield based on 1-(4-biphenyl)-8-bromooctane. Analysis: Calculated for $\text{C}_{20}\text{H}_{24}$: C: 90.85%. H: 9.15%. Found: C: 91.00%. H: 8.91%.

1-[4-(4'-ethylbiphenyl)]-6-bromohexane. This compound was prepared from 4-ethyl-4'-bromobiphenyl in a manner similar to 1-(4-biphenyl)-6-bromohexane. The white precipitate insoluble in ether was filtered and dissolved in CHCl_3 . Ethanol was added to the solution 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). The melting behavior will be discussed in the next chapter. Analysis: Calculated for $\text{C}_{34}\text{H}_{38}$: C: 91.43%. H: 8.57%. Found: C: 91.30%. H: 8.60%. 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 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 is consistent with 1,8-bis-[4-(4'-ethylbiphenyl)]octane (2BP8BP2). The melting behavior will be discussed in the next chapter. Analysis: Calculated for $\text{C}_{36}\text{H}_{42}$: C: 91.08%. H: 8.92%. Found: C: 91.25%. H: 8.73%. After 1,8-dibromooctane was removed by vacuum distillation, the yellow residue was recrystallized from ethanol and dried under vacuum 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 6-(4-biphenyl)-

1-hexene (MEBP04). Vacuum distillation from CaH_2 yielded 3.2 g (27% yield) of a waxy white solid. The melting behavior will be discussed in the next chapter.

Analysis: Calculated for $\text{C}_{20}\text{H}_{24}$: C: 90.85%. H: 9.15%. Found: C: 90.80% H: 9.12%.

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 6-(4-biphenyl)-1-hexene (MEBP04). Vacuum distillation from CaH_2 yielded 7.0 g (48% yield) of a waxy white solid. The melting behavior will be discussed in the next chapter. Analysis: Calculated for $\text{C}_{22}\text{H}_{28}$: C: 90.35%. H: 9.65%. Found: C: 90.29%. H: 9.52%.

1-[4-(4'-butylbiphenyl)]-6-bromohexane. This compound was prepared from 4-butyl-4'-bromobiphenyl in a manner similar to 1-(4-biphenyl)-6-bromohexane. After vacuum distillation of excess 1,6-dibromohexane, the yellow residue was recrystallized from ethanol by placing its 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 formed in the reaction was dissolved in CHCl_3 and filtered. Ethanol was added to the filtrate and the resulting precipitate was recrystallized from 50/50 CHCl_3 /ethanol and dried in vacuum to give 500 mg of white crystalline solid. The melting behavior will be discussed in the next chapter. The ^1H NMR spectrum was consistent with 1,8-bis-[4-(4'-butylbiphenyl)]octane (4BP8BP4). Analysis: Calculated for $\text{C}_{40}\text{H}_{50}$: C: 90.51%. H: 9.49%. Found: C: 90.43% H: 9.41%.

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. The melting behavior will be discussed in the next chapter. Analysis: Calculated for $C_{22}H_{28}$: C: 90.35%. H: 9.65%. Found: C: 90.22%. H: 9.45%.

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. The melting behavior will be discussed in the next chapter. Analysis: Calculated for $C_{24}H_{32}$: C: 89.94%. H: 10.06%. Found: C: 90.02%. H: 10.11%.

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 mole) of 4-ethyl-4'-bromobiphenyl and 0.36 g (0.015 mole) of Mg in 10 mL 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 mole) 1,4-dibromobutane. The resulting solution was heated to reflux and stirred under Ar. Using a syringe, 0.3 mL of 0.1M Li_2CuBr_4 solution was added to the flask. Within 15 minutes, a precipitate had formed, making stirring impractical. The flask was cooled and 10 g ice/1ml conc. 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 melting behavior will be discussed in the next chapter. The ^1H NMR spectrum is consistent with 1,4-bis-[4-(4'-ethylbiphenyl)]butane (2BP4BP2). Analysis: Calculated for $\text{C}_{32}\text{H}_{34}$: C: 91.81%. H: 8.19%. Found: C: 91.54%. H: 7.98%.

1,4-bis-[4-(4'-butylbiphenyl)]butane (4BP4BP4). This compound was prepared from 4-butyl-4'-bromobiphenyl and 1,4-dibromobutane analogously to the preparation of 1,4-bis-[4-(4'-ethylbiphenyl)]butane. After recrystallization from 50/50 CHCl_3 /ethanol, 710 mg (42% yield) of vacuum dried white crystalline solid was obtained. The melting behavior of this compound will be discussed in the next chapter. The ^1H NMR spectrum is consistent with 1,4-bis-[4-(4'-butylbiphenyl)]butane (4BP4BP4). Analysis: Calculated for $\text{C}_{36}\text{H}_{42}$: C: 91.08%. H: 8.92%. Found: C: 91.05%. H: 8.89%.

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 for the monomers and model compounds are reported in Tables 2.1 and 2.2, respectively. Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet) and integration.

Table 2.1
¹H NMR Data for Monomers

<u>Code</u>	<u>n</u>	<u>m</u>	<u>Chemical Shift</u>
MEBP04	0	4	7.0 - 7.6 (m, 9H), 5.6-5.9 (m, 1H), 5.0 (m, 2H), 2.5 (t, 2H), 2.0 (m, 2H) 1.5 (m, 2H), 1.3 (m, 2H)
MEBP06	0	6	7.2-7.7 (m, 9H), 5.8 (m, 1H), 5.0 (m, 2H), 2.6 (t, 2H), 2.1 (m, 2H), 1.6-1.7 (m, 2H), 1.2 -1.5 (m, 6H)
MEBP24	2	4	7.1-7.6 (m, 8H), 5.5-6.0 (m, 1H), 5.0 (m, 2H), 2.6 (m, 4H), 2.1 (m, 2H), 1.5 (m, 2H), 1.3 (m, 5H)
MEBP26	2	6	7.0-7.5 (m, 8H), 5.5 -6.0 (m, 1H), 4.8-5.1 (m, 2H), 2.5-2.9 (m, 4H), 2.0-2.1 (m, 2H), 1.2-1.9 (m, 11H)
MEBP44	4	4	7.1-7.6 (m, 8H), 5.8 (m, 1H), 5.0 (m, 2H), 2.6 (m, 4H), 2.1 (m, 2H), 1.2-1.8 (m, 8H), 1.0 (t, 3H)
MEBP46	4	6	7.2-7.6 (m, 8H), 5.8 (m, 1H), 5.0 (m, 2H), 2.6 (t, 4H), 2.0 (m, 2H), 1.2-1.8 (m, 12H), 0.9 (t, 3H)

Table 2.2
¹H NMR Data for Model Compounds

<u>Code</u>	<u>n</u>	<u>m</u>	<u>Chemical Shift</u>
BP8BP	0	8	7.2-7.7 (m, 18H), 2.5-2.8 (t, 4H), 1.3-1.8 (m, 12H)
2BP4BP2	2	4	7.0-7.6 (m, 16H), 2.4-2.7 (m, 8H), 1.2-1.8 (m, 10H)
2BP6BP2	2	6	7.1-7.7 (m, 16H), 2.5-2.8 (m, 8H), 1.2-1.8 (m, 14H)
2BP8BP2	2	8	7.1-7.6 (m, 16H), 2.4-2.8 (m, 8H), 1.1-1.8 (m, 18H)
4BP4BP4	4	4	7.1-7.7 (m, 16H), 2.2-2.6 (t, 8H), 1.2-1.8 (m, 12 H), 0.9 (t, 6H)
4BP8BP4	4	8	7.2-7.7 (m, 16H), 2.4-2.7 (m, 8H), 1.2-1.7 (m, 20H), 0.9 (t, 6H)

Results and Discussion

A versatile four step synthesis has been used to prepare six hydrocarbon monomers and six hydrocarbon model compounds. All of the new materials gave satisfactory ^1H NMR spectra and elemental analyses. Four of the model compounds were isolated as side products from the syntheses of the monomers, and two were synthesized deliberately.

The preparation of twelve low molecular weight hydrocarbon compounds for this dissertation shows that the syntheses of many other monomers and model compounds are possible. The copper catalyzed coupling reaction was found to proceed with 1,4-dibromobutane, 1,6-dibromohexane and 1,8-dibromooctane and it is expected that the reaction would proceed with other 1,n-dibromoalkanes as well. Dibromoalkanes with $n = 2-12$ are commercially available.

Gray¹ has prepared a number of 4-alkyl-4'-bromobiphenyl derivatives by varying the length of the acid chloride employed. The syntheses are straightforward and proceed in good to excellent yields. Various combinations of 4-alkyl -4'-bromobiphenyl and 1,n-dibromoalkane could be used to prepare a large number of monomers and model compounds by the general synthetic route developed in this dissertation.

References

1. Gray, G. W.; Harrison, K. J.; Nash, J. A.; Constant, J.; Hulme, D. S.; Kirton, J.; Raynes, E. P.; In "Liquid Crystals and Ordered Fluids 2" Johnson, J. F.; Porter, R.S. Plenum Press: New York, 1974; p.617.
2. Tamura, M.; Kochi, J. K.; *J. Organometal. Chem.* **1972**, *42*, 205.
3. Friedman, L.; Shani, A.; *J. Am. Chem. Soc.* **1974**, *96*, 7101.
4. Cope, Arthur C.; Trumbull, Elmer R.; In "Organic Reactions", Cope, Arthur C.; New York: John Wiley and Sons, Inc., 1960, Chapter 5.
5. Schwab, John. M.; Lin, Daniel C. T.; *J. Am. Chem. Soc.* **1985**, *107*, 6046.
6. Carpenter, B. R.; Turner, E. E.; *J. Chem. Soc.* **1934**, 869.
7. Byron, D. J.; Gray, G. W.; Wilson, R. C.; *J. Chem. Soc. C* **1966**, 840.
8. Gray, G. W.; Mosley, Alan; *J. C. S. Perkin II* **1976**, 97.

CHAPTER III

CHARACTERIZATION OF THERMOTROPIC HYDROCARBON LIQUID CRYSTALLINE MONOMERS AND MODEL COMPOUNDS

Introduction

A compilation of thermotropic hydrocarbon liquid crystals obtained in a recent search of the literature was presented in Table 1.1. In most cases, the liquid crystals listed were synthesized to compare their properties to other liquid crystals containing polar or hydrogen bonding functionalities. Few authors explicitly discuss hydrocarbon liquid crystals as a separate class of mesogenic molecules. The most notable exceptions are the works of Osman¹ and Toyne², who point out that hydrocarbon liquid crystals have very weak intermolecular attractions yet retain their liquid crystalline character because of their anisotropic shape. Samulski and Toriumi³ have suggested that 4,4'-di-n-alkyl-bibicyclo[2.2.0]octanes have especially low intermolecular attractions and would thus be useful for the comparison of various theories of the liquid crystalline phase. Others⁴⁻⁶ have expressed interest in hydrocarbon liquid crystals because of their low viscosities. Varech and Jacques⁷ have also recognized the importance of geometrical factors in the formation of the liquid crystalline phase by studying hydrocarbon systems. The inclusion of hydrocarbon mesogens in the side chain of hydrocarbon polymers to form thermotropic hydrocarbon side chain liquid crystalline polymers has not been reported.

Since the monomers and model compounds obtained in this dissertation contain the biphenyl mesogen, they are expected to display liquid crystalline behavior similar to previously synthesized liquid crystals containing the same mesogen. In this Chapter, Differential Scanning Calorimetry (DSC), Polarized Light Optical Microscopy (POM) and X-ray diffraction will be used to characterize the liquid crystalline phases exhibited by the monomers and model compounds. The influence of various substituents on the type of mesophase displayed will be examined. A comparison of the liquid crystalline properties of the new monomers and model compounds with those previously reported will be made.

Experimental Section

Measurements

DSC experiments were performed on a Perkin Elmer DSC-II at a heating rate of 20 °C per minute and a cooling rate of 10 °C per minute, 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.

POM studies were carried out on a Leitz-Wetzler microscope equipped with a Mettler hot stage at a magnification of 320X. Photomicrographs were taken at a magnification of 120X with crossed polarizers.

X-ray diffraction experiments were carried out on a Statton flat film camera using Ni filtered Cu K- α 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 thermal data obtained for the monomers from the DSC experiments is contained in Table 3.1. Also shown in Table 3.1 are the phase types exhibited by the monomers as identified by POM and X-ray diffraction.

Four of the six monomers were found to be liquid crystalline. The phase type exhibited by the liquid crystalline monomers is smectic B, which corresponds to hexagonal packing within the smectic layer planes. MEBP24 displays a smectic B phase by POM which persists even on cooling to -40 °C. A transition to the crystalline state was not observed. Lack of crystallization in disubstituted biphenyl hydrocarbon liquid crystals, even when cooled to low temperatures, has been noted previously by Petrzilka⁴.

It is interesting to note that the monomers that are disubstituted are liquid crystalline and monomers that are not disubstituted are not liquid crystalline. All of the substituted biphenyl hydrocarbon liquid crystals found in the literature are disubstituted. In Table 3.2 the transition temperatures and phase types of dialkyl substituted biphenyl liquid crystals reported in the literature are shown together with the data obtained for the monomers prepared for this work. Entry #1 is an example of a dialkyl substituted biphenyl compound that is not liquid crystalline. No examples of monoalkyl substituted biphenyl hydrocarbon liquid crystals have been found. The data obtained for this dissertation are supportive of the idea that disubstitution of the biphenyl nucleus is necessary, but not sufficient, for the formation of a liquid crystalline phase.

Table 3.1
Monomer Thermal Properties

<u>Code</u>	<u>n</u>	<u>m</u>	<u>Transition Temp., °C</u>	<u>ΔH KJ/mole</u>	<u>ΔS J/mole °K</u>
MEBP04	0	4	K 1.3 I	15.1	55.1
MEBP06	0	6	K 18.3 I	21.0	71.9
MEBP24	2	4	S _B 26.3 I	8.4	28.0
MEBP26	2	6	K 9.4 S _B S _B 28.2 I	4.8 7.9	16.8 26.3
MEBP44	4	4	K 24.4 S _B S _B 38.5 I	0.8 7.2	2.5 23.1
MEBP46	4	6	K -24.6 S _B S _B 42.4 I	2.2 9.6	9.0 30.5

Table 3.2
Dialkyl Substituted Biphenyl Compounds

<u>Entry #</u>	<u>Structure</u>	<u>Transition Temp. °C</u>	<u>Reference</u>
1		K 40 I	9
2		S 33.9 I	4
3		K -18 S 47.8 I	10
4		K 26 S _E 47 S _B 52 I	1,11
5		S _E 42 S _B 53.5 I	11
6		S _E 36 S _B 63 I	11
7		S _B 26.3 I	this work
8		K 9.4 S _B 28.2 I	this work
9		K 24.4 S _B 38.5 I	this work
10		K -24.4 S _B 42.4 I	this work

The transition temperatures and phase types of the monomers prepared for this work are similar to those of the dialkyl substituted biphenyl liquid crystals in Table 3.2. Isotropization temperatures between 26 and 63 °C and smectic phases are observed in all cases. Longer dialkyl substituents generally result in higher clearing temperatures. None of the known dialkyl substituted biphenyl liquid crystals have been reported to display a nematic phase and that observation is confirmed in this work.

The DSC scans obtained for the monomers are contained in Appendix A. A representative DSC scan, photomicrograph and wide angle X-ray pattern for MEBP46 are shown in Figures 3.1, 3.2 and 3.3, respectively. The small peak seen in the DSC scan at -24 °C represents the transition from crystalline to smectic B. The peak is small compared to the melting peak at 42 °C because the difference in order between crystal and smectic B is small compared to the difference in order between smectic B and isotropic. The photomicrograph of MEBP46 shown in Figure 3.2 shows a structured lancet texture that is typical of smectic B liquid crystals. The X-ray pattern in Figure 3.3 shows small angle spacings that correspond to the length of the molecule and a wide angle pattern that indicates an intermolecular spacing of about 4.6 Å. The X-ray diffraction results for the liquid crystalline monomers and model compounds are summarized in Table 3.3. Photomicrographs of MEBP24 and MEBP26 shown in Figure 3.4a and 3.4b, respectively, show rod-shaped grains that are also typical of the smectic B phase .

Figure 3.5 shows the DSC heating scans obtained for MEBP04 and MEBP06. A single peak is seen for both compounds that corresponds to the transition from crystalline to isotropic melt. Characteristic liquid crystalline textures were not observed for either compound by POM.

Figure 3.1

Second heating and cooling DSC scans of MEBP46.

Heating rate: 10 °C per minute

Cooling rate: 5 °C per minute

Figure 3.2

Photomicrograph of MEBP46 at 35 °C.
120X magnification with crossed polarizers

Figure 3.3
X-ray diffraction pattern of MEBP46 at 35 °C

Table 3.3
X-Ray Diffraction Results for Liquid
Crystalline Monomers and Model Compounds

<u>Compound Code</u>	<u>Intermolecular Spacing, Å</u>	<u>Observed Layer Spacing, Å</u>	<u>Calculated Length of Molecule, Å</u>
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

(a)

(b)

Figure 3.4

Photomicrographs of a) MEBP24 at 23 °C and b) MEBP26 at 25 °C.

120X magnification with crossed polarizers.

Figure 3.5

Second heating DSC scans for MEBP04 and MEBP06.

Heating rate: 20 °C per minute

Six model compounds have been prepared for this dissertation. The thermal data and phase identification obtained from DSC, POM and X-ray diffraction are shown in Table 3.4. The DSC scans of the model compounds are contained in Appendix B. Three of the compounds, 2BP4BP2, 4BP4BP4 and 4BP8BP4, were found to be liquid crystalline. 2BP4BP2 displays a monotropic smectic B phase that is observed only on cooling. Figure 3.6 shows the DSC scan obtained for 2BP4BP2. Although only one peak is seen on heating, the two peaks seen on cooling are indicative of a monotropic liquid crystalline phase. The phase was identified as smectic B by POM. 4BP4BP4 exhibits a smectic B phase and a monotropic smectic E phase (orthorhombic packing within the smectic layers), whereas 4BP8BP4 shows a smectic B phase. The X-ray diffraction data for 4BP4BP4 and 4BP8BP4 are contained in Table 3.3.

BP8BP displays a single melting point with no evidence of liquid crystallinity. 2BP6BP2 and 2BP8BP2 both have two melting points by DSC, but characteristic liquid crystalline textures were not observed by POM. The DSC scan shown in Figure 3.7 was obtained for 2BP8BP2. Although the DSC data appear to indicate the presence of a liquid crystalline phase between 129 °C and 140 °C, the X-ray data shown in Figure 3.8 indicate that a change in crystal structure occurs at 129 °C. The crystalline diffraction pattern in Figure 3.8a, taken at room temperature, is different from the crystalline pattern obtained at 132 °C that is shown in Figure 3.8b. The most likely explanation for the data is that a crystal-crystal transition takes place at 129 °C. The small peak at lower temperature may also be due to the melting of small crystallites or impurities, but the data are not sufficient to distinguish between these possibilities. Regardless of the nature of the transition, it is important to note that neither 2BP6BP2 nor 2BP8BP2 show evidence of liquid crystallinity.

Table 3.4
Model Compound Thermal Properties

<u>Code</u>	<u>n</u>	<u>m</u>	<u>Transition Temp., °C</u>	<u>ΔH KJ/mole</u>	<u>ΔS J/mole °K</u>
BP8BP	0	8	K 142 I	56	135
2BP4BP2	2	4	K 181 I (174 S _B 152 K)	46	101
2BP6BP2	2	6	K ₁ 120 K ₂ K ₂ 149 I	3.9 35	10 84
2BP8BP2	2	8	K ₁ 129 K ₂ K ₂ 140 I	8.4 42	21 101
4BP4BP4	4	4	K 131 S _B S _B 191 I (94 S _E 106 S _B)	12 24	31 52
4BP8BP4	4	8	K 125 S _B S _B 141 I	13 27	31 66

Figure 3.6
Second heating and cooling DSC scans of 2BP4BP2.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 3.7

Second heating and cooling DSC scans of 2BP8BP2.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

(a)

(b)

Figure 3.8

X-ray diffraction patterns of 2BP8BP2 at a) 25 °C and b) 132 °C

Figure 3.9 shows the DSC scan for 4BP4BP4. The three peaks seen on cooling show that a monotropic smectic E phase is present between 106 °C and 94 °C, an observation confirmed by POM. Figure 3.10a is a photomicrograph of the smectic B phase, which transforms to the smectic E phase shown in Figure 3.10b on cooling. Figure 3.11 shows the smectic B X-ray diffraction pattern seen for 4BP4BP4 at 140 °C on heating. The inner rings correspond to the length of the molecule and the outer ring corresponds to an intermolecular spacing of 4.6 Å.

Model compounds with four carbon terminal groups or tails display the most stable liquid crystalline phases. Structures with two carbon tails are sometimes weakly liquid crystalline (2BP4BP2) or display crystal-crystal transitions. The one compound that lacks tails is definitely not liquid crystalline. Thus, for a given length of the flexible core, it seems that longer tails stabilize the formation of the mesophase. This is expected as the tail acts to increase the axial ratio of the mesogen. Shorter lengths of the flexible core stabilize the mesophase, as 4BP4BP4 has a broader mesogenic range than 4BP8BP4. For model compounds with two carbon tails, the one with the shortest flexible core, 2BP4BP2, is the only one to display a mesophase. Since only six compounds were prepared, it is difficult to draw definitive conclusions from the limited data. Given that limitation, however, it appears that shorter flexible cores and longer tails confer the most mesophase stability. No other hydrocarbon twin-like mesogens have been reported in the literature, so comparisons of the results obtained in this work with previous work are difficult. Nevertheless, it has been previously noted⁸ that shorter flexible cores lead to greater mesophase stability at constant tail length in twin-like ester liquid crystals.

Figure 3.9

Second heating and cooling DSC scans of 4BP4BP4.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

(a)

(b)

Figure 3.10

Photomicrographs (120X, crossed polarizers) of the
 a) smectic B texture at 140 °C and b) monotropic smectic E
 texture at 100 °C exhibited by 4BP4BP4 on cooling.

Figure 3.11
X-ray diffraction pattern of 4BP4BP4 at 140 °C

References

1. Osman, M. A.; *Z. Naturforsch* **1983**, *38a*, 693.
2. Toyne, K. J.; In "Thermotropic Liquid Crystals" Gray, G. W. John Wiley and Sons: New York, 1987, Chapter 2.4.
3. Samulski, E. T.; Toriumi, H.; *Mol. Cryst. Liq. Cryst.* **1983**, *101*, 163.
4. Petrzilka, M.; *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 347.
5. Takatsu, H.; Takeuchi, K.; Sato, H.; *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 311.
6. Eidenschink, R.; *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 119.
7. Varech, D.; Jacques, J.; *Mol. Cryst. Liq. Cryst., Letters* **1983**, *92*, 141.
8. Buglione, J. A.; Roviello, A.; Sirigu, A.; *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 169.
9. Baeyens-Volant, D.; David, C.; *Mol. Cryst. Liq. Cryst.* **1985**, *116*, 217.
10. Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 353.
11. Dabrowski, R.; Zytynski, E.; *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 109.

CHAPTER IV

SYNTHESIS OF THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Introduction

The preparation of the monomers required for this dissertation was described in Chapter II. The Ziegler-Natta catalyst chosen for the polymerization of the monomers is $\text{Et}_3\text{Al/TiCl}_4$, a catalyst that has been reported to yield a 50/50 mixture of atactic and isotactic polymer when used to polymerize 1-octadecene¹ or 1-propene². At the outset of this work, it was thought that a similar tactic mixture would result when the catalyst was used to polymerize the monomers prepared for this work. A solvent extraction of the resulting polymer was planned to separate the atactic and isotactic fractions. Solvent extractions have been used previously to separate atactic and isotactic fractions of poly(1-octadecene)¹ and poly(1-eicosene)³.

As discussed in Chapter I, atactic and isotactic poly(1-alkenes) with long (>10 carbon atoms) side chains have been shown⁴ to exhibit two distinct melting points. Magagnini and coworkers⁵⁻⁷ have shown that poly(1-eicosene) can be polymerized to yield a mixture of atactic and isotactic polymers. The two fractions independently exhibit their melting points in the unextracted polymer. The fractions can be readily separated by solvent extraction. The long alkyl side chains can crystallize into hexagonal or orthorhombic packings, depending on thermal history. When the polymers are separated, the lower melting is the atactic and the higher melting is the isotactic. An orthorhombic-hexagonal transition takes place on heating

in both polymers over a broad temperature range. The transition range is different in size and location for each polymer and is undetectable by normal DSC methods.

It is reasonable to expect that tacticity may have a similar effect on the polymers prepared for this dissertation. The synthesis, GPC molecular weight and tacticity of the polymers will be discussed in this Chapter. Six polymers will be prepared using the $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst and one will be prepared with a catalyst that has been reported⁸ to yield highly isotactic polymer when used to polymerize 1-propene. The tacticity of the polymers will be determined by high field ^{13}C NMR and attempts will be made to separate the isotactic and atactic fractions. The mesomorphic properties of the polymers will be examined by DSC, POM and X-ray diffraction and will be reported in Chapter V.

Experimental Section

Materials

Chlorobenzene was purchased from Aldrich Chemical Co. and freshly distilled under an Ar atmosphere from LiAlH_4 before use. Triethylaluminum was obtained from Aldrich Chemical Co. as a 1.0M solution in hexanes and was used without further purification. Titanium tetrachloride was obtained from Aldrich Chemical Co. and was used as received.

A catalyst slurry consisting of MgCl_2 , ethyl benzoate, p-cresol, triethylaluminum and titanium tetrachloride was kindly provided by Professor J. C. W. Chien at the University of Massachusetts. The slurry will be referred to as the "Chien catalyst". The preparation of the Chien catalyst has been previously described.⁸ Methyl 4-methylbenzoate was purchased from Aldrich Chemical Co. as a "Gold Label" product and was dried under vacuum before use.

Preparations

Poly[6-(4-biphenyl)-1-hexene] (PEBP04). 6-(4-Biphenyl)-1-hexene (MEBP04) (2.36g, 0.01 mole) was placed into a 25 mL single-neck round-bottom flask with a Teflon[®] coated stir bar. The flask was attached to a vacuum line, degassed, backflushed with Ar several times and capped with a septa. Ten mL of dry chlorobenzene was added via syringe to produce a clear monomer solution.. One mL (0.001 mole) of a 1.0M Et_3Al solution in hexanes was added via syringe to produce a clear solution. Six drops of TiCl_4 from a #16 syringe needle (about 60

mg, 3×10^{-4} mole) were added to the flask, immediately producing a dark red suspension. The suspension was stirred at room temperature for 24 hours.

The contents of the flask were poured into 250 mL of ethanol. The white product that precipitated was allowed to coagulate for several hours before removal by filtration. The polymer, which was soluble in hot benzene, was extracted from the precipitate by stirring the precipitate in hot benzene, centrifuging, and decanting the warm, clear benzene solution into 250 mL of ethanol to precipitate the polymer. The process was repeated twice with the newly precipitated polymer to completely remove the hot benzene insoluble material. The polymer was collected by filtration and dried under vacuum to yield 240 mg of white, fibrous product. Yield, based on monomer weight, was 10%. The melting behavior will be discussed in the next Chapter. Elemental analysis: Calculated for $C_{18}H_{20}$: C: 91.47%, H: 8.53%. Found: C: 91.18%, H: 8.69%. The analysis of the product that was insoluble in hot benzene was variable, but a typical elemental analysis was C: 29.14%, H: 6.04%.

Poly[8-(4-biphenyl)-1-octene] (PEBP06). The preparation of this polymer from MEBP06 is similar to that described for poly[6-(4-biphenyl)-1-hexene] (PEBP04). Analysis: Calculated for $C_{20}H_{24}$: C: 90.85%, H: 9.15%. Found: C: 90.63%, H: 9.21%. The melting behavior will be discussed in the next Chapter. Yield, 12%.

Poly{6-[4-(4'-ethylbiphenyl)]-1-hexene} (PEBP24). The preparation of this polymer from MEBP24 is similar to that described for poly[6-(4-biphenyl)-1-hexene] (PEBP04). Analysis: Calculated for $C_{20}H_{24}$: C: 90.85%, H: 9.15%. Found: C: 90.80%, H: 9.29%. The melting behavior will be discussed in the next Chapter. Yield, 5%.

Poly{8-[4-(4'-ethylbiphenyl)]-1-octene}(PEBP26 #1). The preparation of this polymer from MEBP26 is similar to that described for poly[6-(4-biphenyl)-1-hexene) (PEBP04). Analysis: Calculated for $C_{22}H_{28}$: C: 90.35%. H: 9.65%. Found: C: 90.13%, H: 9.63%. The melting behavior will be discussed in the next Chapter. Yield, 15%.

Poly{6-[4-(4'-butylbiphenyl)]-1-hexene}(PEBP44). The preparation of this polymer from MEBP44 is similar to that described for poly[6-(4-biphenyl)-1-hexene) (PEBP04). Analysis: Calculated for $C_{22}H_{28}$: C: 90.35%. H: 9.65%. Found: C: 90.23%, H: 9.74%. The melting behavior will be discussed in the next Chapter. Yield, 12%.

Poly{8-[4-(4'-butylbiphenyl)]-1-octene}(PEBP46). The preparation of this polymer from MEBP46 is similar to that described for poly[6-(4-biphenyl)-1-hexene) (PEBP04). Analysis: Calculated for $C_{24}H_{32}$: C: 89.94%. H: 10.06%. Found: C: 89.97%, H: 9.91%. The melting behavior will be discussed in the next Chapter. Yield, 8%.

Poly{8-[4-(4'-ethylbiphenyl)]-1-octene}(PEBP26 #2). In addition to the polymer prepared above, MEBP26 was also polymerized using the Chien catalyst. The catalyst slurry concentration was 39.5 mg of solids per mL of heptane. Titanium comprised 3.5% of the weight of the solids. 8-[4-(4'-ethylbiphenyl)]-1-octene ((MEBP26) (0.585 g., 2×10^{-3} mole) was placed into a 10 mL single-neck round-bottom flask with a stir bar. The monomer was dried for 24 hours under vacuum. The flask was septa-capped and flushed with Ar. Two mL of chlorobenzene was added via syringe to produce a clear monomer solution. 3.34 mL (3.34×10^{-3} mole) of 1.0M Et_3Al in hexanes was added to the flask via syringe. A solution of 167 mg (1.11×10^{-3} mole) of methyl 4-methylbenzoate in 1 mL of

chlorobenzene was added to the flask via syringe. Within two minutes, 0.7 mL (0.96 mg Ti, 2×10^{-5} mole) of the vigorously stirred Chien catalyst was added to the flask via syringe. The resulting brown suspension was stirred at room temperature for 16 hours. The Ti/monomer ratio was 1/100, the $\text{Et}_3\text{Al}/\text{Ti}$ ratio was 167/1 and the $\text{Et}_3\text{Al}/$ methyl 4-methylbenzoate ratio was 3/1.

The suspension was poured into 50 mL of ethanol, producing a white precipitate. The precipitate was collected by filtration, stirred in hot benzene, centrifuged and the clear supernatant precipitated into ethanol. The process was repeated 3 times, until all of the precipitate was soluble in hot benzene. After vacuum drying, the yield of fibrous white product was 210 mg, 36%. Analysis: Calculated for $\text{C}_{22}\text{H}_{28}$: C: 90.35%. H: 9.65%. Found: C: 90.08%, H: 9.92%. The melting behavior will be discussed in the next Chapter.

Polymer fractionation. Attempts were made to separate the atactic and isotactic fractions assumed to be present in each polymer by extraction with boiling hexane, boiling cyclohexane, boiling diethyl ether and room temperature benzene and toluene. The technique employed was to stir the polymers with the solvent for several hours, then draw off some solvent with a pipette and add it to an excess of ethanol. No polymers were observed to precipitate by this technique. Recrystallization from benzene was also attempted, but it was also unsuccessful in fractionating the polymer samples.

Measurements

Elemental analyses were performed at the Microanalytical Laboratory at the University of Massachusetts. Tacticities were determined by ^{13}C NMR in CDCl_3 solvent using tetramethylsilane (0.00 ppm) as an internal standard. A Varian XL-300 instrument operating at 75.43 MHz was used for all of the experiments. The percent of isotactic polymer in each sample was estimated by measuring peak areas and by comparing the spectra to that of poly(1-eicosene) in the literature.³ A spin inversion recovery experiment was performed to measure T_1 for the peaks used to determine tacticity and T_1 was found to be less than 200 milliseconds. Since the time between pulses should be at least ten times larger than T_1 , an acquisition time of 0.8 seconds and a delay time of 2.2 seconds was used to acquire the spectra. An inverse gated decoupling technique (decoupled only during the acquisition phase) was used to suppress Nuclear Overhauser Effect (NOE) enhancement. It was found that 5000-10,000 scans of a sample consisting of 150 mg of polymer in 2.35 g of CDCl_3 gave the best spectra.

The molecular weights of the polymers were determined using Gel Permeation Chromatography (GPC). A Waters 201 Liquid Chromatograph with ultrastyrigel columns was employed and the molecular weights reported are relative to polystyrene standards.

Results and Discussion

Six polymers were prepared using a $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst and one with the Chien catalyst. The GPC molecular weights of these seven polymers, relative to polystyrene standards, are shown in Table 4.1. The molecular weights are generally high with broad molecular weight distributions, normal characteristics for polymers prepared with Ziegler-Natta catalysts.⁹

The yields obtained in the preparation of the polymers were rather low, ranging from 5% to 15%, when $\text{Et}_3\text{Al}/\text{TiCl}_4$ was used as the catalyst. This is rather unusual, because control experiments were performed using the same catalyst with 1-octadecene monomer and yields of 60-70% were obtained. When the Chien catalyst was used to polymerize MEBP26, however, a yield of 36% was obtained. The reason for the large variations in yield is unknown.

The ^{13}C NMR spectra for all seven polymers are displayed in Figures 4.1 to 4.7. The peak assignments, shown in Table 4.2, were determined by comparison with known spectra and by calculation using standard additivity relationships.¹⁰ The aromatic regions of the spectra have been omitted for clarity. The backbone methylene resonance occurs at about 40 ppm in all of the polymers. This peak is particularly useful for the assignment of dyad tacticity because of its relative isolation in the spectra. In Figure 4.8 this region is highlighted for all seven polymers by placing them on the same scale as a series of poly(1-eicosene) spectra taken from the literature. The poly(1-eicosene) spectra were obtained by Magagnini³ and consist of five samples with tacticities ranging from 100% isotactic to 100% atactic. The tacticities assigned to each of the polymer samples are shown next to the respective spectra.

Table 4.1

GPC Molecular Weight

<u>Code</u>	<u>n</u>	<u>m</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w / M_n</u>
PEBP04	0	4	49,000	450,000	9
PEBP06	0	6	43,000	660,000	15
PEBP24	2	4	26,000	250,000	10
PEBP26 #1	2	6	90,000	850,000	9
PEBP26 #2	2	6	80,000	380,000	5
PEBP44	4	4	14,000	330,000	24
PEBP46	4	6	70,000	710,000	10

Figure 4.1
 ^{13}C NMR spectrum of PEBP04

Figure 4.2
 ^{13}C NMR spectrum of PEBP06

Figure 4.3
¹³C NMR spectrum of PEBP24

Figure 4.4

^{13}C NMR spectrum of PEBP26 #1.

Polymer was prepared with $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst.

Figure 4.5

^{13}C NMR spectrum of PEBP26 #2.

Polymer was prepared with Chien catalyst.

Figure 4.6
 ^{13}C NMR spectrum of PEBP44

Figure 4.7
 ^{13}C NMR spectrum of PEBP46

Table 4.2
¹³C NMR Aliphatic Carbon Peak Assignments for Polymers

Carbon ^a Number	Chemical Shift, ppm					
	<u>PEBP04</u>	<u>PEBP06</u>	<u>PEBP24</u>	<u>PEBP26</u>	<u>PEBP44</u>	<u>PEBP46</u>
1	39.9	40.0	39.9	40.0	39.9	40.0
2	32.0	32.2	32.0	32.2	32.0	32.2
3	34.5	34.9	34.5	34.9	34.5	34.8
4	26.3	26.5	26.3	26.5	26.3	26.5
5	32.0	29.7	32.0	29.7	32.0	29.8
6	35.6	30.0	35.7	30.0	35.6	30.2
7		31.6	28.4	31.6	35.3	31.7
8		35.7	15.5	35.7	33.6	35.7
9				28.4	22.4	35.3
10				15.5	14.0	33.6
11						22.4
12						14.0

a) The numbering system is shown in Figures 4.1-4.7.

Figure 4.8

At the top of the Figure, the ^{13}C NMR spectra of the seven polymers prepared in this work are shown. In the lower part of the Figure, the ^{13}C NMR spectra published by Magagnini for five samples of poly(1-eicosene) are shown. The percent isotactic content of each polymer is shown next to the respective spectrum. All twelve ^{13}C NMR spectra have been placed on the same horizontal scale.

Poly(1-eicosene)

The isotactic content of the polymers prepared for this dissertation ranges from $65\% \pm 10\%$ to $90\% \pm 10\%$. The reason for the variation is unknown. Previous studies¹¹ on the polymerization of 1-butene have indicated that the ratio of Et_3Al to TiCl_4 strongly influences the tacticity of the resulting polymer, but work by Aubrey and Barnatt¹ on the polymerization of 1-octadecene shows that the ratio is not an important factor. It should be noted that problems with reproducibility in the area of Ziegler-Natta polymerizations are well known.¹² The isotactic content was higher than the 50/50 ratio of isotactic to atactic polymer reported by Aubrey and Barnatt for poly(1-octadecene), but their polymerizations were carried out in bulk instead of the chlorobenzene solvent employed in this work.

Another explanation for the high isotactic content of some of the polymers, particularly PEBP26 #1, is that specific interactions between the monomers or between the monomers and catalyst surface act to increase the isotactic content of the resulting polymer. Duran and Gramain have proposed¹³ (see Chapter I, p. 24) that biphenyl-biphenyl attractions between the growing chain end and the incoming monomer are responsible for changes in tacticity in the liquid crystalline poly(acrylate) derivative shown in Figure 1.5.

Attempts to separate the polymers prepared in this work into atactic and isotactic fractions by solvent extraction were unsuccessful. One of the goals of this project is to compare the properties of atactic and isotactic side chain liquid crystalline polymers. An obvious solution to this dilemma is to deliberately synthesize atactic polymer using a catalyst other than $\text{Et}_3\text{Al}/\text{TiCl}_4$. The solubility properties of the atactic material could then be easily determined and a judgement made as to whether a solvent extraction is possible. In Chapter VI this possibility will be explored by attempting to prepare atactic polymers using soluble Ziegler-Natta catalysts.

References

1. Aubrey, D. W.; Barnatt, A.; *J. Polym. Sci., Part A-2* **1968**, *6*, 241.
2. Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979, p.86.
3. Magagnini, P. L.; Segre, A. L.; Andruzzi, F.; Lupinacci, D.; *Macromolecules* **1981**, *14*, 1845.
4. Porter, R. S.; Wang, J.; Knox, J. R.; *Polym. J.* **1978**, *10*, 619.
5. Magagnini, P. L.; Andruzzi, F.; Vergamini, P.; Benedetti, E. *Polym. Bull.* **1980**, *2*, 241.
6. Magagnini, P. L.; Andruzzi, F.; Benetti, G. F.; *Macromolecules* **1980**, *13*, 12.
7. Magagnini, P. L.; Andruzzi, F.; Lupinacci, D.; Paci, M.; *Polymer* **1982**, *23*, 277.
8. Chien, J. C. W.; Kuo, C. I.; Ang, T.; *J. Polym. Sci. Polym. Chem. Ed.* **1985** *23*, 723.
9. Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979, Chapter 10.
10. Breitmaier, E.; Voelter, W. "¹³C NMR Spectroscopy", Verlag Chemie, New York, 1978, Chapter 4.
11. Medalia, A. I.; Orzechowski, J. A. Trinchera; Morley, J. P.; *J. Polym. Sci.* **1959**, *41*, 241.
12. Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979, p. 480.
13. Duran, R.; Gramain, P.; *Makromol. Chem.* **1987**, *188*, 2001.

CHAPTER V

CHARACTERIZATION OF THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Introduction

Side Chain Liquid Crystalline Polymers (SCLCP) are generally characterized by the same techniques used to characterize low molecular weight liquid crystals. Differential Scanning Calorimetry (DSC) is used to measure the enthalpy change associated with thermal transitions in the polymers. The transition from a polymer glass or crystal to polymer liquid crystal is accompanied by a decrease in order and enthalpy and is recorded as an endothermic DSC peak. A further loss of order and enthalpy occurs when the transition of a polymer liquid crystal into an isotropic polymer melt occurs and another endothermic peak is seen in the DSC scan. Exothermic DSC peaks are observed on cooling as the isotropic polymer recrystallizes and regains the order and internal energy lost on melting.

Polarized Light Optical Microscopy (POM) is used to observe the birefringent state of a polymer liquid crystal. Textures similar to those seen for low molecular weight liquid crystals are often observed. Another texture that is sometimes seen is referred to as a "fine grain" texture¹⁻². Fine grain textures are most frequently observed in smectic polymer liquid crystals because the high viscosities present in the smectic state hinder the formation of large, micron sized domains. Annealing times of several weeks are often necessary to develop more recognizable textures.

X-ray diffraction of side chain polymer liquid crystals is used to characterize the intermolecular and, for smectic polymers, the interlayer spacings formed by the liquid crystalline phase³⁻⁶. Using a flat film camera, a broad halo corresponding to the intermolecular spacing is observed for nematic polymers. A second ring corresponding to the layer thickness is also observed for smectic polymers. When the polymers are oriented fibers and the fiber axis is vertical, equatorial arcs are seen on the X-ray film corresponding to the interlayer spacing. The interlayer spacing may correspond to single layer or double layer packing, as seen in Figure 5.1. Other types of packing have been reported but are less common⁷⁻⁸.

In this Chapter, the results obtained from DSC, POM and X-ray studies on the polymers prepared in Chapter IV are presented. The effect of the variation of spacer and tail lengths on polymer liquid crystal properties will be examined.

Single Layer Packing

Double Layer Packing

Figure 5.1

Single Layer and Double Layer Packing of
Side Chain Liquid Crystalline Polymers

Experimental Section

Measurements

DSC experiments were performed on a Perkin Elmer DSC-II at a heating rate of 20 °C per minute and a cooling rate of 10 °C per minute, 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.

POM studies were carried out on a Leitz-Wetzler microscope equipped with a Mettler hot stage at a magnification of 320X. Photomicrographs were taken at a magnification of 120X with crossed polarizers.

X-ray diffraction experiments were carried out on a Statton flat film camera using Ni filtered Cu K- α 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 data obtained from the results of the DSC experiments are summarized in Table 5.1. The second heating and cooling DSC scans for the seven polymers are shown in Figures 5.2 to 5.8. The transition temperatures reported are for the peak maximums of the second heating scans. The transition enthalpies were calculated by measuring the area under the respective peaks and are expressed in kilojoules per mole of repeat unit. The transition entropies were calculated by assuming equilibrium and dividing the transition enthalpies by the absolute temperatures of the respective transitions and are expressed in joules per mole degree Kelvin. Since the heating rate used was 20 °C per minute, it is unlikely that equilibrium was established in the experiment. The absolute values of the transition entropies are probably incorrect, but they are useful for comparison because all of the experiments were performed at the same heating rate.

All of the polymers are brittle at room temperature and visibly soften when heated on a Fisher-Johns melting point apparatus at a temperature of $60 \pm 5^\circ \text{C}$. No clear evidence of a glass transition temperature is observed by DSC. It is likely that the amount of glassy material in the polymers is too small to be detectable by the DSC techniques used for this work.

Table 5.1
Polymer Thermal Properties

Code	n	m	Transition Temp., °C	ΔH KJ / mole	ΔS J / mole °K
PEBP04	0	4	K 151 I	3.0	7.1
PEBP06	0	6	K 126 I	7.2	18.1
PEBP24	2	4	S _E 140 S _B S _B 197 I	11.0	23.4
PEBP26 #1	2	6	S _E 110 S _B S _B 176 I	9.7	21.6
PEBP26 #2	2	6	S _E 110 S _B S _B 176 I	11.4	25.4
PEBP44	4	4	S _E 158 S _B S _B 206 I	2.1 3.3	4.8 6.7
PEBP46	4	6	S _E 145 S _B S _B 181 I	1.4 4.3	3.3 9.5

Figure 5.2
Second heating and cooling DSC scans for PEBP04.
Heating rate: 20 °C per minute
Cooling rate: 10 °C per minute

Figure 5.3

Second heating and cooling DSC scans for PEBP06.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 5.4

Second heating and cooling DSC scans for PEBP24.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 5.5

Second heating and cooling DSC scans for PEBP26 #1.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 5.6

Second heating and cooling DSC scans for PEBP26 #2.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 5.7

Second heating and cooling DSC scans for PEBP44.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure 5.8

Second heating and cooling DSC scans for PEBP46.

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

The DSC scans for PEBP04 and PEBP06 show a single broad transition on heating or cooling. The polymers are not liquid crystalline as evidenced by X-ray diffraction and POM data. The POM and X-ray diffraction results will be discussed in detail later.

The DSC scans of PEBP24, PEBP26 #1 (prepared with $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst) and PEBP26 #2 (prepared with the Chien catalyst) show three distinct regions on heating. The first region is a flat baseline which extends from low temperatures up to a second region in which the baseline has a positive slope. The third region contains a definite peak which coincides with the transformation of the polymer to an isotropic melt as evidenced by POM. Based on X-ray evidence, the polymers are smectic E liquid crystals in the first region and smectic B liquid crystals in the second region. Transition enthalpies were not calculated for the smectic E liquid crystal polymer to smectic B liquid crystal polymer transition because of the lack of a true peak in the second region. The first transition temperature listed in Table 5.1 for the three polymers with two carbon tails is the onset of the second region and the second transition temperature is the peak maximum in the third region. The transition enthalpies and entropies were calculated from the combined area under the second and third regions. The enthalpies and entropies obtained in this way represent the total change on going from the smectic E liquid crystalline state to the isotropic state.

The DSC scans obtained for PEBP44 and PEBP46 clearly show the presence of two peaks. The data in Table 5.1 for these two polymers were obtained by measuring the areas under the respective peaks. The lower temperature peak represents the transition from smectic E to smectic B and the higher temperature peak is the clearing temperature. The X-ray diffraction and POM evidence discussed below is supportive of this conclusion.

The X-ray diffraction experiments were carried out on fiber samples of the polymers at multiple temperatures. A typical experiment consisted of heating the polymer sample above its clearing temperature on a Fisher-Johns melting point apparatus and pulling a fiber from the melt with tweezers. The fibers prepared in this way generally had very small diameters, about the thickness of a human hair. The fibers were cut into lengths of about one centimeter and placed into an X-ray capillary with a diameter of one and a half millimeters. Ten to fifteen short fibers were typically placed into the capillary. The capillary was sealed with a flame and placed into the hot stage, which was then inserted into the X-ray apparatus. At least three exposures of about one hour each were made for each polymer. The first exposure was done at room temperature, the second at a temperature about 10 °C below the clearing temperature, and the third at room temperature again.

Table 5.2 contains the data obtained from the second and third exposures of the X-ray experiments. PEBP26 #1 and PEBP26 #2 gave identical results so their X-ray data have been combined. The d-spacings are given in angstroms and the letters in parentheses after the values are the intensities and the positions of the reflections. The abbreviations vs = very strong, s = strong, m = medium, w = weak and vw = very weak describe the intensities. All of the reflections could be described as equatorial or halo, as the layer spacings were generally equatorial and the intermolecular spacings were broad halos. The positions are described by the abbreviations h = halo or e = equatorial.

Representative pairs of X-ray diffraction patterns for PEBP04, PEBP26 and PEBP46 are given in Figures 5.9 to 5.11. The upper pattern in each pair is the second (high temperature) exposure and the lower pattern is the third (room temperature) exposure.

Table 5.2
Results of X-ray Fiber Diffraction Experiments

The X-ray data in Table 5.2 have been arranged so that the small angle and higher order reflections are in the first row of each set corresponding to a particular temperature. The first order reflections were not observed in the patterns used to compile the data because the scattering angles were too small. The first order data were obtained by moving the film further from the sample and increasing the exposure time, but this data is not included in Table 5.2. The first value in the first row of each temperature set is actually a second order reflection. The layer spacings may be obtained from the data by multiplying the first number in the first row by two, the second number by three, etc. Fourth order reflections were not observed for PEBP24 and PEBP26, and the last number in the first row for these two polymers is the value obtained for the fifth order reflection. The second row contains the wide angle data corresponding to the same temperature. Gaps are found in the second row for the last four polymers in the table because reflections corresponding to the $6.0\text{\AA}$ and $4.0\text{\AA}$ reflections in PEBP04 and PEBP06 were not observed for the polymers which had two or four carbon tails. See Table 5.3 for a summary of the results obtained for the liquid crystalline polymers.

<u>Code</u>	<u>Temp., °C</u>	<u>d-spacing, Å</u>			
PEBP04	145	14.0(vs, e) 6.3(w, e)	9.3(vs, e) 4.7(vs, h)	4.0(m, e)	
	27	13.9(vs, e) 6.0(w, e)	9.2(vs, e) 4.7(vs, h)	4.0(m, e)	3.2(vw, h)
PEBP06	120	16.8(m, e)	11.2(vs, e) 4.7(vs, h)	4.2(m, e)	
	27	16.6(m, e)	11.0(vs, e) 4.7(vs, h)	4.2(m, e)	6.7(vw, e) 3.3(w, h)
PEBP24	185	16.0(vs, e)	10.6(vs, e) 4.6(vs, h)		6.4(vw, e)
	27	16.0(vs, e)	10.6(vs, e) 4.6(vs, h)		6.4(vw, e) 3.3(vw, h)
PEBP26	165	18.8(vs, e)	12.6(vs, e) 4.6(vs, h)		7.4(w, e)
	27	18.8(vs, e)	12.6(vs, e) 4.6(vs, h)		7.4(w, e) 3.3(vw, h)
PEBP44	195	17.9(vs, e)	11.9(vs, e) 4.6(vs, h)	8.9(vw, e)	7.1(w, e)
	27	18.0(vs, e)	11.9(vs, e) 4.6(vs, h)	9.0(w, e)	7.1(w, e) 3.3(vw, h)
PEBP46	175	19.9(vs, e)	13.3(vs, e) 4.6(vs, h)	10.0(vw, e)	7.9(vw, e)
	27	20.0(vs, e)	13.3(vs, e) 4.6(vs, h)	10.0(vw, e)	7.9(vw, e) 3.3(vw, h)

Figure 5.9
X-ray fiber diffraction patterns of PEBP04 at a) 145 °C and b) 27 °C.
Fiber axis vertical

(a)

(b)

Figure 5.10

X-ray fiber diffraction patterns of PEBP26 at a) 165 °C and b) 27 °C.

Fiber axis vertical

(a)

(b)

Figure 5.11

X-ray fiber diffraction patterns of PEBP46 at a) 175 °C and b) 27 °C.

Fiber axis vertical

As mentioned previously, smectic side chain liquid crystalline polymers are distinguished by two types of d-spacings, interlayer and intermolecular. PEBP24, PEBP26, PEBP44 and PEBP46 all show these types of spacings by fiber X-ray diffraction. The X-ray diffraction data for the four polymers have been summarized in Table 5.3. In each case, the layer spacings correspond to a double layer type of packing as seen in Figure 5.12. As many as four higher order reflections are observed for the interlayer spacings, indicating that a high degree of smectic order exists. The conformation of the backbone is not known because no meridional arcs were present in the X-ray diffraction results that could be used to calculate a helix repeat distance. A helical or distorted helical structure is expected, as Turner-Jones⁹ has suggested a distorted 3/1 or 4/1 helical structure for other long side chain poly(1-alkene)s. The intermolecular spacings were found to be about 4.6Å, the same intermolecular spacing observed for the monomers.

The four polymers with tails appear to exhibit the smectic B mesophase at temperatures just below their respective clearing points. The smectic B mesophase is characterized by hexagonal packing of the mesogens within the smectic layers, so only one intermolecular spacing, in this case 4.6Å, is observed. On cooling, a transition to smectic E takes place, as evidenced by the appearance of a wide angle reflection corresponding to a d-spacing of 3.3Å. The ratio of 4.6 to 3.3 is approximately the square root of two, indicating that the packing is orthorhombic (smectic E) at room temperature. The monomers and model compounds previously discussed in Chapters II and III also exhibit smectic B and smectic E mesophases, giving further support to the conclusion that the mesophase is smectic B at higher temperatures and smectic E at lower temperatures.

Table 5.3
Summary of X-Ray Diffraction Results for Liquid Crystalline Polymers

<u>Polymer Code</u>	<u>Intermolecular Spacing, Å</u>	<u>Observed Layer Spacing, Å</u>	<u>Calculated^a Spacing for Double Layer Packing, Å</u>
PEBP24	4.6	32.0	29.0
PEBP26	4.6	37.0	33.0
PEBP44	4.6	36.0	33.0
PEBP46	4.6	40.0	37.0

- a) The difference between the calculated and observed layer spacings is about $3.5 \pm 0.5 \text{ Å}$. The difference is attributed to the uncertain nature of the backbone conformation (a 2/1 helix is assumed) and to the space between chain ends. Turner-Jones has reported⁹ a value of 3.3 Å for the space between chain ends in long side chain poly(1-alkenes).

Figure 5.12

The double layer packing and calculated layer thickness of PEBP46 is illustrated. The actual layer spacing derived from X-ray diffraction measurements is 40 Å.

Since the polymers are brittle and inflexible at room temperature, the smectic E phase is probably "frozen in" when the polymers are cooled below the glass transition temperature. The state of the polymer at room temperature is therefore not crystalline, but a liquid crystalline glass¹⁰. The 4.6Å halo appears broad and no higher order reflections are observed even at room temperature, observations consistent with a liquid crystalline glass. The 4.6Å reflection would be expected to become sharp and give higher order reflections if crystallization had occurred on cooling. As previously mentioned, the transition from a smectic E polymer liquid crystal glass to a smectic E polymer liquid crystal was not detectable by DSC, but a visually observed softening temperature was observed for all polymers at about 60 ± 5 °C.

The X-ray fiber diffraction patterns of PEBP04 and PEBP06 are similar to the X-ray diffraction patterns obtained for the other polymers except that wide angle equatorial reflections are observed. Because the reflections are equatorial, a structural regularity in a direction perpendicular to the fiber axis must be present. The polymer backbone itself is an obvious candidate, and it is possible that the main chains are crystallizing with one another. The spacings derived from small angle X-ray measurements indicate double layer packing. The conformation of the backbone is unknown, as meridional arcs in the X-ray diffraction pattern necessary for the calculation of a helix repeat distance were not observed. Two equatorial spacings, 6.0Å and 4.0Å, are observed in the X-ray fiber diffraction pattern for PEBP04 while only the 4.0Å equatorial reflection is observed for PEBP06. All of the reflections are visibly sharper at room temperature than at high temperature, an indication that crystallization is taking place. The appearance of the wide angle equatorial reflections is not consistent with the presence of a liquid crystalline phase.

The POM evidence supports the conclusion that the polymers with tails are liquid crystalline and the polymers that do not have tails are not liquid crystalline. Figure 5.13 is a photomicrograph of the fine grain texture displayed by PEBP46 under crossed polarizers. Similar textures have been observed for PEBP44, PEBP26 and PEBP24. The fine grain texture is a characteristic of smectic side chain liquid crystalline polymers. The smectic polymers were annealed in a vacuum oven at temperatures 5-10 °C below the clearing temperature for periods as long as a week, but the fine grain textures remained. The polymers may be too viscous to allow more recognizable smectic textures to develop. Characteristic textures were not observed by POM for PEBP04 or PEBP06.

The weight of the evidence is supportive of the conclusion that the side chain polymers prepared in this study must have a tail to exhibit liquid crystalline phases. It may be argued that the side chains of the polymers without tails are too short to allow for liquid crystallinity and that the short length of the side chain, not the absence of a tail, is responsible for the lack of liquid crystallinity. However, PEBP24 and PEBP06 have essentially the same side chain lengths and PEBP24 is liquid crystalline while PEBP06 is not. It also appears that four carbon tails promote liquid crystallinity better than two carbon tails. The polymers with four carbon tails gave two distinguishable peaks when examined by DSC, while the polymers with two carbon tails gave rather ambiguous DSC results.

For polymers with the same length tails, lower clearing temperatures were found for polymers with longer spacers. The trend toward lower clearing temperatures with increasing spacer length has also been observed in other side chain liquid crystalline systems¹¹⁻¹³. Since PEBP24 and PEBP44 have clearing temperatures near 200 °C, no attempts were made to prepare polymers with shorter

spacers because of the possibility of polymer degradation while performing POM studies at high temperatures. Longer spacer lengths typically result in smectic phases, while shorter spacers increase the tendency to display nematic phases.

Figure 5.13

Photomicrograph (120X, crossed polarizers) of fine grain texture exhibited by PEBP46 at 160 °C on cooling.

References

1. Finkelmann, H.; Rehage, G.; In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; pp.148-149.
2. Shibaev, V. P.; Plate, N. A.; In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; p.147.
3. de Vries, A.; *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 125.
4. Azaroff, L. V.; *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 73.
5. Plate, N. A.; Shibaev, V. P.; "Comb Shaped Polymers and Liquid Crystals" Plenum Press: New York, 1987, pp. 267-295.
6. Richardson, R. M.; Herring, N. J.; *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 143.
7. Reference 1, p.147.
8. Reference 2, p.193.
9. Turner-Jones, A.; *Makromol. Chem.* **1964**, *71*, 1.
10. Wunderlich, B.; Grebowicz, J. In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; pp. 25-30.
11. Reference 1, p.145.
12. Finkelmann, H.; In "Polymer Liquid Crystals", Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B.; Academic Press: New York, 1982; Chapter 2.
13. Reference 5, Tables 4.10 and 4.11, pp. 274-278.

CHAPTER VI

ATTEMPTS TO PREPARE ATACTIC THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Introduction

The use of a $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst to polymerize the monomers prepared for this dissertation has resulted in the preparation of predominantly isotactic thermotropic hydrocarbon side chain liquid crystalline polymers. The percentage of each polymer that is isotactic has been determined by ^{13}C NMR and the results given in Figure 4.8. Since attempts to separate the tactic fractions by solvent extraction were unsuccessful, the results of experiments designed to test the feasibility of synthesizing completely atactic poly(1-alkene)s will be discussed in this Chapter. Because of the known differences in physical properties of atactic and isotactic poly(1-eicosene)s detailed in Chapter I, it is reasonable to expect that tacticity will affect the properties of the polymers prepared in this work.

Soluble catalysts based on vanadium derivatives are well known for the preparation of syndiotactic poly(1-propene)¹⁻². Previous attempts to prepare syndiotactic poly(1-butene) have been unsuccessful, however. It has been proposed that steric interactions between the last monomer added to the growing polymer chain and the incoming monomer are too great to allow the polymerization of 1-olefins higher than 1-propene³. This view is supported by the observation that 1-butene and ethylene may be copolymerized with syndiotactic specific catalysts. One attempt to prepare a syndiotactic poly(1-alkene) will be described below.

Since it appeared unlikely that syndiotactic polymers could be made from the monomers prepared for this dissertation, attention has been focused on the synthesis of atactic poly(1-alkenes). Soluble catalysts for the preparation of atactic poly(1-propene) have been recently described by Kaminsky⁴⁻⁷ and coworkers. Catalysts based on dicyclopentadienyl complexes of titanium, zirconium or hafnium in combination with methalumoxane have been found to polymerize 1-propene to 100% atactic polymers with high molecular weights. Very little work has been reported on attempts to prepare higher poly(1-alkene)s with these catalysts.

Because only limited amounts of the monomers prepared for this dissertation are available, 1-octadecene is used as a model monomer. Aubrey and Barnatt have shown⁸ that poly(1-octadecene) polymerized with $\text{Et}_3\text{Al}/\text{TiCl}_4$ may be separated into two fractions via hexane extraction. The lower melting, hexane soluble fraction was thought to be atactic polymer and the higher melting, hexane insoluble fraction was thought to be isotactic polymer. The preparation and separation of poly(1-octadecene) are reproduced in this work and the tacticity investigated with ^{13}C NMR. Once the solubility and thermal properties of atactic poly(1-octadecene) are firmly established, various catalysts are used to attempt to polymerize 1-octadecene. It was hoped at the outset of this investigation that the tacticities of the resulting polymers could be quickly determined by examination of their thermal or solubility properties. The proper catalyst could then be used to polymerize the monomers prepared for this dissertation and the resulting polymers investigated by DSC, POM and X-ray diffraction. The success of this approach will be discussed in this Chapter.

Experimental Section

Materials

1-Octadecene was obtained from Aldrich Chemical Co., vacuum distilled (96 °C, 700 millitorr) from CaH_2 and stored under dry argon before use. Chlorobenzene was purchased from Aldrich Chemical Co. and freshly distilled from LiAlH_4 under an Ar atmosphere before use. Triethylaluminum was obtained from Aldrich Chemical Co. as a 1.0M solution in hexanes and was used without further purification. Trimethylaluminum was obtained from Aldrich Chemical Co. as a 2.0M solution in hexanes and was used as received. Diethyl aluminum chloride was obtained as a 1.8M solution in toluene from Aldrich Chemical Co. and was used as received. Titanium tetrachloride was obtained from Aldrich Chemical Co. and was used as received. Titanocene dichloride, zirconocene dichloride, hafnocene dichloride and vanadium(III) acetylacetonate were obtained from Aldrich Chemical Co. and were used as received. Magnesium chloride was obtained from Aldrich Chemical Co. as a "Gold Label" product and dried azeotropically with benzene on a vacuum line before use. Aluminum sulfate hexadecahydrate was purchased from Aldrich Chemical Co. and dried azeotropically with benzene on a vacuum line prior to use.

Preparations

Preparation of poly(1-octadecene) with $\text{Et}_3\text{Al}/\text{TiCl}_4$. 2.52 g (0.01 mole) of 1-octadecene was added via syringe to a 25 mL, septa-capped, Ar flushed round-bottom flask containing a Teflon[®] coated stir bar. One mL (0.001 mole) of a 1.0M Et_3Al solution in hexanes was added via syringe to produce a clear solution. Six drops of TiCl_4 from a #16 syringe needle (about 60 mg, 3×10^{-4} mole) were added to the flask, immediately producing a dark red suspension. The suspension was stirred at room temperature for 24 hours.

The contents of the flask were poured into 250 mL of ethanol. The white product that precipitated was allowed to coagulate for several hours before removal by filtration. The precipitate was stirred in hot hexane and centrifuged. The warm, clear hexane supernatant was poured into 250 mL of ethanol, resulting in the precipitation of a white polymer. The polymer was filtered and twice again stirred in hot hexane, centrifuged and the clear supernatant poured into ethanol to precipitate the polymer. The polymer was filtered and dried under vacuum to yield 1.54 g of white, fibrous product. The yield was 61%. This sample is designated POCT2.

One gram of POCT2 were placed into a centrifuge tube and stirred with 10 mL of hexane at room temperature. After several hours, the mixture was centrifuged and the clear supernatant poured into 100 mL of ethanol, producing a white precipitate. More hexane was added to the polymer remaining in the centrifuge tube and the process was repeated until no precipitate was observed when the supernatant was decanted into ethanol. The hexane soluble polymer was removed by filtration from the ethanol, dried under vacuum and weighed to give 290 mg of white polymer, designated POCT2S. The hexane insoluble portion was precipitated into

ethanol, filtered, dried under vacuum and weighed to give 690 mg of white polymer, designated POCT2I. The w/w ratio of hexane insoluble polymer to hexane soluble polymer was 70 to 30. The melting behavior of the polymers will be discussed later.

Attempted polymerization of 1-octadecene with $V(acac)_3/AlEt_2Cl$. A 0.046M solution of $V(acac)_3$ in chlorobenzene was prepared by transferring 160 mg of $V(acac)_3$ to a 25 mL round-bottom flask in a glove bag under an Ar atmosphere, capping the flask with a septa and adding 10 mL of chlorobenzene via syringe.

A Teflon[®] coated stir bar was placed into a separate 25 mL round-bottom flask and the flask was septa-capped and Ar flushed. 1-Octadecene (2.52 g, 0.01 mole) was added via syringe. Ten milliliters of chlorobenzene were added to the flask via syringe to produce a clear solution. The solution was cooled under flowing Ar in a $MgCl_2$ / ice bath to about -15 °C. Fifty-six μ l of 1.8M $AlEt_2Cl$ in toluene (1×10^{-4} moles) added to the flask via syringe to produce a clear solution. The previously prepared 0.46M $V(acac)_3$ solution (0.22 mL, 1×10^{-5} moles) was added to the flask via syringe. The resulting clear solution was stirred at about -15 °C for 3 hours, then poured into 200 mL of ethanol. No polymer was observed to precipitate.

Polymerization of 1-octadecene with $MgCl_2/TiCl_4/Et_3Al$. $MgCl_2$ (0.85 g) and 0.15 g of $TiCl_4$ were ground together with an agate mortar and pestle in a glove box under a nitrogen atmosphere. Twenty mg of the ground mixture was transferred to a 25 mL round-bottom flask containing a Teflon[®] coated stir bar and the flask capped with a septa. 1.0 mL of 1.0M Et_3Al solution in hexanes (0.001 mole) was added to the flask via syringe, resulting in the immediate formation of a dark red suspension. 1-Octadecene (2.52g, 0.01 moles) was added to the red suspension via syringe and the resulting mixture was stirred at 50 °C for 3 hours, during which time it became very viscous.

The contents of the flask were precipitated into acetone, filtered, stirred in hot hexane, centrifuged and the supernatant precipitated into acetone. The process of stirring the precipitate in hot hexane, centrifugation and precipitation of the supernatant was repeated twice. After precipitation, filtration and vacuum drying, 0.40 g of white polymer product was obtained, a yield of about 16%. The polymer is designated as POCT1.

POCT1 was fractionated in room temperature hexane in a manner analogous to POCT2 above. Two fractions, one hexane soluble and one hexane insoluble, were obtained. 78% of POCT1 was insoluble and is designated as POCT1I. 22% of POCT1 was soluble and is designated as POCT1S.

Attempted polymerization of 1-octadecene with Cp_2TiCl_2 /methalumoxane, Cp_2ZrCl_2 /methalumoxane and Cp_2HfCl_2 /methalumoxane. A methalumoxane solution was prepared by the reaction of trimethylaluminum and aluminum sulfate hexadecahydrate. 3.94 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (0.10 mole of H_2O) was placed into a 3-necked 250 mL round-bottom flask with a Teflon[®] coated stir bar. The flask was septa capped and flushed with Ar., with provision made for efficient exhaust of gas. Twenty-five mL of dry chlorobenzene was added via syringe. The flask was cooled in ice under Ar and 100 mL of 2.0M Me_3Al in hexanes (0.20 moles) was added cautiously via cannula over the course of 30 minutes. The ice was allowed to melt and the suspension slowly warmed to room temperature with the evolution of gas. The mixture of clear liquid and white solid was stirred for 48 hours until all gas evolution had ceased. Stirring was halted and the white solid was allowed to settle to the bottom of the flask overnight.

The following amounts of catalyst were transferred to separate 100 mL round-bottom flasks containing Teflon[®] coated stir bars in a glove bag under Ar: 10 mg of

Cp_2TiCl_2 (4×10^{-5} moles), 20 mg of Cp_2ZrCl_2 (1×10^{-4} moles) and 10 mg of Cp_2HfCl_2 (2.6×10^{-5} moles). The flasks were capped with septa and flushed with Ar. Twelve and one-half mL of the methalumoxane solution previously prepared was added to each of the flasks via syringe. The metallocene catalysts dissolved as the Cp_2TiCl_2 solution turned orange, the Cp_2ZrCl_2 solution turned pale green and the Cp_2HfCl_2 solution remained clear. 1-Octadecene (2.52 g, 0.01 mole) was added to each flask via syringe. The Cp_2TiCl_2 solution turned green over the course of about 5 minutes. The colors of the other solutions remained the same. The solutions were allowed to stir for 24 hours at room temperature, then for 48 hours at 50°C .

The contents of the flasks were poured into separate beakers, each containing 250 mL of ethanol. The only flask which gave a precipitate corresponded to the Cp_2ZrCl_2 catalyst. The precipitate was filtered, washed with dilute sulfuric acid and recrystallized from ethanol. The white, crystalline product was dried under vacuum to yield 300 mg of a product melting at $44\text{--}45^\circ\text{C}$. Elemental analysis: C: 85.70, H: 14.52. This product is designated as OCTZr.

Attempted polymerization of 1-octadecene with Cp_2ZrCl_2 and in situ methalumoxane. Cp_2ZrCl_2 (51 mg, 1.74×10^{-4} mole) was transferred to a 10 mL round-bottom flask in a glove bag flushed with Ar. The flask was septa-capped and 5.8 mL of chlorobenzene was added to give a 0.03 M solution.

Five mL of chlorobenzene and 0.018 g of water (0.001 mole) were added via syringe to a 25 mL round-bottom flask with a Teflon[®] coated stir bar. The flask was chilled in ice water and 1.5 mL of 2.0M Me_3Al solution in hexanes (0.003 moles) was added slowly via syringe. The flask was stirred and gas was evolved. After about 30 minutes, 2.52 g (0.01 mole) of 1-octadecene were added via syringe to give

a clear solution. Seven drops from a #16 syringe needle, about 0.1 mL (1×10^{-6} mole), of the previously prepared 0.03M Cp_2ZrCl_2 solution were added via syringe to give a clear solution. The flask was stirred for one day at room temperature. An additional 3 drops of 0.03M Cp_2ZrCl_2 solution and 0.5 mL of 2.0M Me_3Al solution in hexanes was added via syringe. The temperature of the solution was raised to 50 °C and the solution was stirred for four days.

The solution was poured into 250 mL of ethanol, producing a white precipitate. The precipitate was stirred in hot hexane, centrifuged and the supernatant decanted into ethanol to produce a white precipitate. The precipitate was filtered and dried under vacuum to yield 200 mg of white product. The precipitate was soluble in hot hexane and room temperature hexane. This product is designated POCTZr.

Attempted polymerization of 8-(4,4'-ethylbiphenyl)-1-octene (MEBP26) with Cp_2ZrCl_2 and in situ methalumoxane. 0.013g (7.2×10^{-4} mole) of water was added via syringe to 2.19 g of MEBP26 (0.0075 mole) in a 25 mL round-bottom flask containing a Teflon® coated stir bar. The flask was flushed with Ar and 5 mL of chlorobenzene was added via syringe to give a clear solution. 2.0M Me_3Al solution in hexanes (1.1 mL) was added via syringe, resulting in the formation of a small amount of a white precipitate, a yellow color and the evolution of gas. Five drops from a #16 syringe needle of 0.03M Cp_2ZrCl_2 solution in chlorobenzene were added via syringe. The resulting solution was stirred at 50 °C for 115 hours. After cooling, the clear reaction mixture was poured into 250 mL of ethanol. The white precipitate was stirred in hot benzene, centrifuged and reprecipitated into ethanol. The process was repeated and the precipitate dried under vacuum to yield 318 mg of white product. This product is designated PEBP26-A. Elemental analysis: Calculated for polymer: C: 90.35%, H: 9.65%. Found: C: 90.33%, H: 9.64%.

The residue insoluble in hot benzene was washed with ethanol, filtered and dried under vacuum to yield 45 mg of slightly brown product. The elemental analysis of the residue was C: 19.37%, H: 4.67% with a 53.8% ash content.

Measurements

Elemental analyses were performed at the Microanalytical Laboratory at the University of Massachusetts. DSC experiments were performed on a Perkin Elmer DSC-II at a heating rate of 20 °C per minute and a cooling rate of 10 °C per minute, 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. ^1H NMR experiments were performed on a 200 MHz Varian XL-200 instrument in CDCl_3 solvent with tetramethylsilane as an internal standard (0.00 ppm). ^{13}C NMR measurements were made on a Varian XL-300 instrument operating at 75.43 MHz using CDCl_3 as solvent and tetramethylsilane (0.00 ppm) as an internal standard.

Results and Discussion

A sample of poly(1-octadecene) designated as POCT2 has been prepared in bulk with $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst. POCT2 was extracted with hexane to give 70% of a hexane insoluble fraction, designated POCT2I, and 30% of a hexane soluble fraction, designated POCT2S. The DSC scans of POCT2, POCT2I and POCT2S are shown on the same scale in Figure 6.1. The DSC scan of POCT2 clearly shows two melting endotherms at 36 °C and 65 °C. The DSC scans of POCT2S and POCT2I show only one melting endotherm, at 42 °C for POCT2S and at 68 °C for POCT2I. Thus, the DSC and solubility behavior of POCT2 found in this work are in general agreement with the results reported by Aubrey and Barnatt. The only major difference is the ratio of hexane insoluble material to hexane soluble material, found to be 50 / 50 by Aubrey and Barnatt and 70 / 30 in this work. The reason for the difference is not known.

Figure 6.2 shows the ^{13}C NMR data obtained for POCT2, POCT2I and POCT2S. The peak at 40.4 ppm is due to the backbone methylene carbon atoms. An isotactic polymer is expected to display one peak in this region because the magnetic environments of all of the backbone methylene carbons are the same. An atactic polymer is expected to show two main peaks in this region, because there are basically two different environments in which the backbone methylene carbons can exist. The first is the situation in which the two adjacent side groups are on the same side of the chain, a meso dyad, and the second is one in which the side groups are on opposite sides of the chain, a racemic dyad. The two types of tacticity are clearly illustrated in the ^{13}C NMR data of Magagnini for poly(1-eicosene) shown previously in Figure 4.8.

Figure 6.1
DSC second heating scans for POCT2S (hexane soluble),
POCT2I (hexane insoluble), and POCT2 (unfractionated) .
Heating rate: 10 °C per minute

Figure 6.2

^{13}C NMR spectra of POCT2S (hexane soluble), POCT2I (hexane insoluble) and POCT2 (unfractionated), shown on the same horizontal scale.

The ^{13}C NMR data in Figure 6.2 and the DSC data in Figure 6.1 clearly shows that poly(1-octadecene) polymerized with $\text{Et}_3\text{Al}/\text{TiCl}_4$ displays two melting points, one due to an atactic fraction and the other to the isotactic fraction. The two fractions can be separated by a simple hexane extraction and the hexane insoluble, higher melting POCT2I is isotactic whereas the hexane soluble, lower melting POCT2S is atactic. These conclusions are consistent with those drawn by Magagnini for poly(1-eicosene) except that different solvents were used for the extraction. 1-Octadecene and 1-eicosene are excellent monomers to use for catalyst studies because the tacticities of the resulting polymers may be determined quickly and simply from DSC and solubility measurements. The use of ^{13}C NMR to determine tacticity, a more time consuming and costly technique, may thus be avoided.

Various catalysts have been used in this work to attempt to synthesize atactic or syndiotactic poly(1-octadecene). The hexane solubilities of the products of these reactions are shown in Table 6.1. The use of $\text{V}(\text{acac})_3 / \text{AlEt}_2\text{Cl}$, $\text{Cp}_2\text{TiCl}_2 /$ methalumoxane, or $\text{Cp}_2\text{HfCl}_2 /$ methalumoxane as catalysts for the polymerization of 1-octadecene was unsuccessful. The catalyst $\text{MgCl}_2 / \text{TiCl}_4 / \text{Et}_3\text{Al}$ was found to give a lower yield of hexane soluble polymer than $\text{Et}_3\text{Al} / \text{TiCl}_4$. $\text{Cp}_2\text{ZrCl}_2 /$ in situ methalumoxane gave a white solid (designated POCTZr) that was completely soluble in hexane. The use of $\text{Cp}_2\text{ZrCl}_2 /$ methalumoxane also gave a product completely soluble in hexane (designated OCTZr). These results identified Cp_2ZrCl_2 and some form of methalumoxane as the best catalyst candidate for the successful polymerization of the monomers prepared in this work.

Table 6.1
Hexane Solubility of Reaction Products
of 1-Octadecene with Various Catalysts

<u>Catalyst</u>	Hexane solubility at 25 °C	
	<u>% insoluble</u>	<u>% soluble</u>
Et ₃ Al/TiCl ₄	70	30
V(acac) ₃ / AlEt ₂ Cl	No ethanol insoluble products	
MgCl ₂ / TiCl ₄ / Et ₃ Al	78	22
Cp ₂ TiCl ₂ / methalumoxane	No ethanol insoluble products	
Cp ₂ HfCl ₂ / methalumoxane	No ethanol insoluble products	
Cp ₂ ZrCl ₂ / methalumoxane	0	100
Cp ₂ ZrCl ₂ / in situ methalumoxane	0	100

The attempt to polymerize MEBP26 with Cp_2ZrCl_2 / in situ methalumoxane resulted in the formation of a white solid, designated PEBP26-A, that was insoluble in ethanol. The elemental analysis of PEBP26-A is consistent with that expected for the polymer. However, the ^{13}C NMR data shown in Figure 6.3 shows the presence of a peak at 150.3 ppm and another at 108.4 ppm that are not expected for the polymer. Furthermore, no peaks are seen that correspond to the backbone methylene carbon atoms at about 40.4 ppm. The ^1H NMR spectrum of PEBP26-A shown in Figure 6.4 shows a peak at 4.7 ppm that corresponds to vinylic protons that are not expected to be present in the polymer. The ^{13}C NMR peaks at 150.3 ppm and 108.4 ppm are consistent with a 1,1-dialkylsubstituted double bond. The structure that seems most consistent with these spectra is shown in Figure 6.5. The degree of polymerization of about three is based on the integration of the ^1H NMR spectrum shown in Figure 6.4, which shows that there are about 12 aromatic protons for each vinyl proton. The peak at 1.99 ppm is due to the allylic protons, which are in a 2/1 ratio to the vinylic protons. The benzylic protons at 2.6 ppm are in a ratio of 6/1 to the vinylic protons, again indicating that the product is a trimer. The peak at 0.9 ppm is due to the "backbone" methyl group. The peaks from 1.9 to 1.2 ppm are due to the other 41 protons in the structure and the integration is supportive of the trimer structure shown in Figure 6.5.

The product of the reaction of Cp_2ZrCl_2 / methalumoxane with 1-octadecene has been designated OCTZr. The ^{13}C and ^1H NMR spectra of OCTZr are shown in Figures 6.6 and 6.7, respectively. Once again, the presence of peaks at 150.4 and 108.3 ppm in the ^{13}C NMR spectrum and 4.7 ppm in the ^1H NMR spectrum are indicative of a 1,1-dialkylsubstituted double bond. In this case, the integration of the ^1H NMR spectrum indicates that the product is a dimer as shown in Figure 6.8.

Figure 6.3
 ^{13}C NMR spectrum of PEBP26-A

Figure 6.4
 ^1H NMR spectrum of PEBP26-A

Figure 6.5

Proposed structure of PEBP26-A

Figure 6.6
 ^{13}C NMR spectrum of OCTZr

Figure 6.7
 ^1H NMR spectrum of OCTZr

Figure 6.8

Proposed structure of OCTZr

The NMR spectra obtained for PEBP26-A and OCTZr indicate that only very low degrees of polymerization have been achieved. Under the conditions used in these experiments, neither Cp_2ZrCl_2 / in situ methalumoxane nor Cp_2ZrCl_2 / methalumoxane were found to be effective polymerization catalysts. These results were not entirely unexpected, as Kaminsky has reported that poly(1-hexene)s prepared at 20 °C, 40 °C and 60 °C with zirconocene catalysts "show much lower formation rates and extremely small molecular weights."⁵ In the present work very long reaction times at 50 °C were used unsuccessfully to try to increase the reaction rate. It is possible that the steric hindrance between the last added monomer and incoming monomer prevents the polymerization from proceeding, as has been postulated for vanadium based catalysts.

References

1. Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979, Chapter 15, Section IV.
2. Doi, Y.; Ueki, S.; Keii, Tominaga; *Macromolecules* **1979**, *12*, 814.
3. Reference 1, page 414.
4. Kaminsky, W.; Sinn, H.; In "Advances in Organometallic Chemistry Volume 18", Academic Press: New York, 1980; pp. 99-149.
5. Kaminsky, W.; Schlobohm, M.; *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 103.
6. Kaminsky, W.; Herwig, J.; *Polym. Bull.* **1983**, *9*, 464.
7. Kaminsky, W.; Luker, H.; *Makromol. Chem. R. C.* **1984**, *5*, 275.
8. Aubrey, D. W.; Barnatt, A.; *J. Polym. Sci., Part A-2* **1968**, *6*, 241.

CHAPTER VII

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

Conclusion

A versatile synthetic pathway has been developed to synthesize a new series of hydrocarbon monomers and model compounds containing the biphenyl mesogen. The synthesis allows the spacer and tail length of the monomers and model compounds to be varied in a simple and systematic fashion. Six new monomers have been prepared using the new synthesis and their liquid crystalline properties have been investigated via differential scanning calorimetry (DSC), polarized light optical microscopy (POM) and X-ray diffraction. Four of the monomers were discovered to be liquid crystalline. The influence of the tail and spacer length was found to have a critical effect on the transition temperatures. The two monomers that did not have tails were not liquid crystalline. Monomers with two and four carbon tails were liquid crystalline, and the isotropization temperatures of the monomers increased with increasing tail and spacer length. All of the liquid crystalline monomers displayed the smectic B mesophase.

Comparison of the properties of the liquid crystalline monomers synthesized for this work with dialkyl substituted biphenyl liquid crystals confirmed three trends. The first is that dialkyl substitution of the biphenyl mesogen is necessary for the attainment of a liquid crystalline phase. No monoalkyl substituted biphenyl liquid crystals have been found in the literature and no liquid crystalline phases were seen in the monoalkyl substituted biphenyl compounds prepared for this work. The second

trend is that only smectic phases have been observed in the dialkyl substituted biphenyl liquid crystals previously reported and in the liquid crystalline monomers prepared for this dissertation. Only smectic B and/or smectic E phases were observed for the monomers and previously reported liquid crystals. The third trend is the general increase in clearing point (isotropization temperature) observed with increasing length of dialkyl substituent. This trend was observed in both the monomers and the previously reported liquid crystals.

Dialkyl substitution of biphenyl seems to be necessary because biphenyl itself is too short to be mesogenic and the dialkyl substituents act to increase the effective axial ratio. Smectic phases probably result from the attractive forces that exist between the polarizable electron clouds of the aromatic biphenyl rings. The most surprising trend is the increase in clearing temperature with increasing length of substituents, even up 4-pentyl-4'-heptylbiphenyl (entry #5 in Table 3.2) and MEBP46, which has a four carbon substituent on one side and an eight carbon substituent on the other side. The usual trend observed is a decrease in clearing temperature with increasing substituent length, subject to the usual odd-even effect.¹ However, many exceptions to the usual trend have been reported² and only a few dialkyl substituted biphenyl liquid crystals have been investigated thus far.

Six new twin-like model compounds have been prepared for this work. Four of the model compounds have been isolated as side products of the monomer synthesis and two were synthesized deliberately by modifying monomer synthetic conditions. Three of the model compounds were found to display liquid crystalline phases. Two of the remaining three exhibited crystal-crystal transitions and the other model compound was not liquid crystalline. As with the monomers, the spacer and tail lengths were discovered to substantially affect the transition temperatures.

Longer tails and shorter spacers were found to impart greater mesophase stability to the model compounds. The one model compound without tails exhibited neither liquid crystallinity nor crystal-crystal transitions. Model compounds with two carbon tails displayed a monotropic smectic B phase with a four carbon spacer and crystal-crystal transitions with six or eight carbon spacers. When the tail length was four carbons, model compounds with four or six carbon spacers were clearly smectic B liquid crystals.

The three trends observed for the model compounds are similar to those seen for the monomers. An alkyl tail seems to be necessary for liquid crystallinity and the model compounds with the longest tails were the most stable. Only smectic B and/or smectic E phases were observed for the liquid crystalline materials. Shorter spacers led to more stable liquid crystalline phases, an apparent violation of the trends noted above, but the longer spacers probably lead to greater flexibility and thus to lower clearing temperatures.

Six new polymers have been prepared for this work by polymerizing the monomers described herein with a Ziegler-Natta catalyst, $\text{Et}_3\text{Al}/\text{TiCl}_4$. Yields were generally low, and it is suspected that the catalyst became coated with the polymer during polymerization and prohibited monomer from diffusing to the catalyst surface. The tacticity of the polymers was determined via ^{13}C NMR and found to range from $65\% \pm 10\%$ to $90\% \pm 10\%$. Attempts to separate the isotactic and atactic fractions by solvent extraction were unsuccessful. A sample of polymer with a two carbon tail and six carbon spacer, designated PEBP26 #2, was prepared in 36% yield with a different catalyst that was reported to yield 96% isotactic polymer when used to polymerize 1-propene. PEBP26 #2 was found by ^{13}C NMR to be about 90% isotactic, the same tacticity as the PEBP26 prepared with $\text{Et}_3\text{Al}/\text{TiCl}_4$ catalyst.

DSC, POM and X-ray diffraction were employed to investigate the liquid crystalline properties of the six new polymers. The six polymers could be grouped into three classes. In the first class are PEBP44 and PEBP46, which gave DSC scans which clearly showed two peaks, a smaller one at lower temperatures and a larger one at higher temperatures. X-ray diffraction was used to determine that the smaller peak represents the transition from smectic E to smectic B liquid crystal. The larger peak represents the transition from smectic B to isotropic. A fine grain texture, indicative of smectic liquid crystallinity, was observed by POM for both polymers. In the second class are PEBP24 and PEBP26, which gave DSC scans showing three regions. In the first region the baseline was flat and horizontal, in the second region the baseline was flat but with a positive slope, and the third region contained a large peak that corresponded to the isotropization temperature as observed by POM. X-ray diffraction showed that the polymer was a smectic E liquid crystal in the first region and a smectic B liquid crystal in the second region. It is thought that the transition from smectic E to smectic B occurs over a broad temperature range, so that a sharp peak is not seen in the DSC scan. It has been noted previously³ that transitions from orthorhombic to hexagonal packing in the side chains of poly(1-eicosene) occur over a broad temperature range and are undetectable by normal DSC methods.

The members of the third class are PEBP04 and PEBP06, the two polymers that do not have tails. Both polymers showed a single peak by DSC and no evidence of liquid crystallinity by POM. X-ray diffraction experiments performed on polymer fibers revealed the presence of sharp equatorial reflections at wide angles that could be indicative of main chain crystallization. PEBP04 and PEBP06 are not believed to be liquid crystalline.

X-ray diffraction of the four liquid crystalline polymers showed that the side groups were arranged on both sides of the main chain, an arrangement commonly referred to as double layer packing. The conformation of the main chain is unknown, as no reflections along the fiber axis were present to determine a repeat distance. Turner-Jones⁴ has suggested that the main chains of long side chain isotactic poly(1-alkenes) pack into a distorted ternary or quaternary helix. A 3/1 or 4/1 helical structure may also be present in the polymers described herein, as they are structurally similar to those investigated by Turner-Jones.

As was the case with the monomers and model compounds, the tail length once again plays a critical role in determining the liquid crystalline properties of the polymers prepared for this dissertation. The polymers that do not have tails are not liquid crystalline and the polymers that have four carbon tails gave liquid crystalline phases that were detectable by DSC. Polymers with two carbon tails gave DSC results that were somewhat ambiguous, although X-ray diffraction and POM experiments confirmed that they were also liquid crystalline. At constant spacer length, the effect of increasing the tail length was to increase the clearing temperature of the polymers, although the difference in clearing temperatures between the polymers with two and four carbon tails was small. At constant tail length, the effect of increasing the spacer length was to decrease the clearing temperatures. Since only six polymers were prepared, it is difficult to draw definitive conclusions from these trends. However, based on the experience derived from the monomers and model compounds, it is clear that presence of a tail on the biphenyl mesogen increases the likelihood that the polymer will display liquid crystalline phases.

It has been noted that side chain liquid crystalline polymers usually show more ordered phases than the monomers from which they are derived.⁵ This effect is attributed to the fact that the monomers lose some mobility when they become "anchored" to the polymer chain. The monomers prepared for this work display the smectic B phase whereas the polymers display both smectic B and the more highly ordered smectic E phase, thus confirming the aforementioned trend.

A procedure has been developed to screen catalysts for their ability to polymerize 1-octadecene to atactic polymer. Using ^{13}C NMR and DSC, it has been shown that atactic poly(1-octadecene) is soluble in hexane at room temperature and displays a lower melting point than isotactic poly(1-octadecene), which is insoluble in hexane at room temperature. Using this information, a series of catalysts were used to try to prepare atactic poly(1-octadecene). The hexane solubility of the products of the polymerization attempts were examined to determine their tacticity. The most promising catalyst, $\text{Cp}_2\text{ZrCl}_2/\text{methalumoxane}$, was selected to attempt to polymerize MEBP26, but ^{13}C and ^1H NMR investigations revealed that the polymer had a degree of polymerization of about three. Thus, attempts to prepare atactic polymers from the monomers prepared for this dissertation were unsuccessful.

Suggestions for Future Work

Preparation of Atactic Polymers

Since some atactic polymer was shown by ^{13}C NMR to be present in the polymers prepared for this dissertation with $\text{Et}_3\text{Al}/\text{TiCl}_4$, the preparation of atactic polymers is clearly possible. It is suggested that 1-octadecene be used a model monomer to screen catalysts and catalyst conditions that have not been tried thus far. Suitable catalysts could be identified by testing the hexane solubility of the polymerization products. The proper catalyst could be used to make atactic polymers from the monomers prepared in this work. The liquid crystalline properties of the polymers could then be determined by DSC, POM and X-ray diffraction and compared to the isotactic polymers already prepared.

Preparation of Copolymers

All of the liquid crystalline polymers prepared for this work were found to be smectic. Random copolymers prepared from monomers with two different spacer lengths could show nematic phases because it would be more difficult for the biphenyl mesogens to align.

Zambelli has prepared syndiotactic copolymers from 1-propene and 1-butene. Kaminsky has prepared atactic copolymers from 1-propene and 1-hexene. It should also be possible to prepare isotactic, syndiotactic and atactic copolymers with 1-propene and the monomers prepared for this dissertation using the proper catalysts. The liquid crystalline properties of the resulting polymers could then be studied as a function of tacticity and monomer ratio.

Lyotropic Hydrocarbon Liquid Crystalline Polymers

The polymers prepared for this work are soluble in hydrocarbon solvents such as hot benzene. It seems likely that lyotropic liquid crystals or liquid crystalline gels could be formed at the proper polymer concentration. Since existing lyotropic liquid crystalline polymers such as Kevlar® are formed in polar media, a comparison of the properties of lyotropic liquid crystalline polymers formed in non-polar media may be very interesting.

Preparation of Other Thermotropic Hydrocarbon SCLCP's

Table 1.1 is a list of other hydrocarbon mesogens that could be incorporated into a hydrocarbon side chain polymer. Particularly interesting are those mesogens such as bicyclohexyl and bibicyclo[2.2.2]octane that do not contain aromatic rings and would have even weaker intermolecular attractions than the polymers prepared for this dissertation. Although the syntheses would probably be more difficult than the syntheses described herein, the experience gained from this work suggests that a tail length of four carbons and a spacer length of six or eight carbons on a bicyclohexyl mesogen would yield a liquid crystalline monomer. Polymerization of the monomer is likely to yield a liquid crystalline polymer.

References

1. Gray, G. W.; In "Polymer Liquid Crystals" Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B. Academic Press: New York, 1982; Chap. 2.
2. Toyne, K. J.; In "Thermotropic Liquid Crystals" Gray, G. W. John Wiley and Sons: New York, 1987, Chapter 2.
3. Magagnini, P. L.; Andruzzi, F.; Vergamini, P.; Benedetti, E. *Polym. Bull.* **1980**, *2*, 241.
4. Turner Jones, A.; *Makromol. Chem.* **1964**, *71*, 1.
5. Finkelmann, H.; In "Polymer Liquid Crystals", Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B.; Academic Press: New York, 1982; Chapter 2.

APPENDIX A
MONOMER DSC DATA

Figure A.1

Second heating and cooling DSC scans of MEBP04

Heating rate: 10 °C per minute

Cooling rate: 5 °C per minute

Figure A.2

Second heating and cooling DSC scans of MEBP06

Heating rate: 10 °C per minute

Cooling rate: 5 °C per minute

Figure A.3

Second heating and cooling DSC scans of MEBP24

Heating rate: 20 °C per minute

Cooling rate: 5 °C per minute

Figure A.4

Second heating and cooling DSC scans of MEBP26

Heating rate: 20 °C per minute

Cooling rate: 5 °C per minute

Figure A.5

Second heating and cooling DSC scans of MEBP44

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure A.6

Second heating and cooling DSC scans of MEBP46

Heating rate: $10\text{ }^{\circ}\text{C}$ per minute

Cooling rate: $5\text{ }^{\circ}\text{C}$ per minute

APPENDIX B
MODEL COMPOUND DSC DATA

Figure B.1

Second heating and cooling DSC scans of BP8BP

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure B.2

Second heating and cooling DSC scans of 2BP4BP2

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure B.3

Second heating and cooling DSC scans of 2BP6BP2

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure B.4

Second heating and cooling DSC scans of 2BP8BP2

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure B.5

Second heating and cooling DSC scans of 4BP4BP4

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

Figure B.6

Second heating and cooling DSC scans of 4BP8BP4

Heating rate: 20 °C per minute

Cooling rate: 10 °C per minute

BIBLIOGRAPHY

- Aubrey, D. W.; Barnatt, A.; *J. Polym. Sci., Part A-2* **1968**, *6*, 241.
- Azaroff, L. V.; *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 73.
- Baeyens-Volant, D.; David, C.; *Mol. Cryst. Liq. Cryst.* **1985**, *116*, 217.
- Balkwill, P.; Bishop, D.; Pearson, A.; Sage, I.; *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 1.
- Billard, J.; Mamlok, L.; *Mol. Cryst. Liq. Cryst., Letters* **1978** *41*, 217.
- Blumstein, A.; Hsu, E. C.; In "Liquid Crystalline Order in Polymers", Blumstein, A.; Academic Press: New York, 1978; Chapter 3.
- Boor, J. Jr.: "Ziegler-Natta Catalysts and Polymerizations", Academic Press: New York, 1979.
- Breitmaier, E.; Voelter, W. "¹³C NMR Spectroscopy", Verlag Chemie, New York, 1978, Chapter 4.
- Buglione, J. A.; Roviello, A.; Sirigu, A.; *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 169.
- Byron, D. J.; Gray, G. W.; Wilson, R. C.; *J. Chem. Soc. C* **1966**, 840.
- Carpenter, B. R.; Turner, E. E.; *J. Chem. Soc.* **1934**, 869.
- Carr, N.; Gray, G. W.; Kelley, S. M.; *Mol. Cryst. Liq. Cryst.* **1985**, *129*, 301.
- Carr, N.; Gray, G. W.; *Mol. Cryst. Liq. Cryst.* **1985**, *124*, 27.
- Cereghetti, M.; Marbet, R.; Schleich, K.; *Helv. Chim. Acta* **1982**, *65*, 1318.
- Chien, J. C. W.; Kuo, C. I.; Ang, T.; *J. Polym. Sci. Polym. Chem. Ed.* **1985** *23*, 723.
- Clark, K. J.; Turner-Jones, A.; Sandiford, D. J. H.; *Chem. Ind. (London)* **1962**, 2010.
- Cope, Arthur C.; Trumbull, Elmer R.; In "Organic Reactions", Cope, Arthur C.; New York: John Wiley and Sons, Inc., 1960, Chapter 5.
- Dabrowski, R.; Zytinski, E.; *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 109.

- de Vries, A.; *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 125.
- Demus, D.; Demus, H.; Zashke, H.; In "Flussige Kristalle in Tabellen" VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, German Democratic Republic, 1974, p. 230.
- Demus, D.; Richter, L.; "Textures of Liquid Crystals" Verlag Chemie: New York, 1978.
- Doi, Y.; Ueki, S.; Keii, T.; *Macromolecules* **1979**, *12*, 314.
- Doi, Y.; Ueki, S.; Keii, Tominaga; *Macromolecules* **1979**, *12*, 814.
- Duran, R.; Gramain, P.; *Makromol. Chem.* **1987**, *188*, 2001.
- Eidenschink, R.; *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 119.
- Eidenschink, R.; *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 57.
- Finkelmann, H.; In "Polymer Liquid Crystals", Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B.; Academic Press: New York, 1982; Chapter 2.
- Finkelmann, H.; Rehage, G.; In "Advances in Polymer Science 60/61" Springer-Verlag: Berlin Heidelberg, 1984; Chapter 3.
- Flory, P. J. In "Polymer Liquid Crystals" Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B. Academic Press: New York, 1982; Chapter 4.
- Flory, P. J. *Proc. R. Soc. London Ser. A.* **1956**, *234*, 73.
- Friedman, L.; Shani, A.; *J. Am. Chem. Soc.* **1974**, *96*, 7101.
- Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J.; In "Comprehensive Organometallic Chemistry" Wilkinson, Sir G.; New York: Pergamon Press, 1982; Chapter 22.5.
- Grant, B.; *Mol. Cryst. Liq. Cryst.* **1978**, *48*, 175.
- Gray, G. W.; Harrison, K.J.; Nash, J. A.; Constant, J.; Hulme, D.S.; Kirton, J.; Raynes, E. P.; In "Liquid Crystals and Ordered Fluids 2" Johnson, J. F.; Porter, R.S. Plenum Press: New York, 1974.
- Gray, G. W.; Goodby, J. W. G.; "Smectic Liquid Crystals", Philadelphia: Heyden & Son, 1984.
- Gray, G. W.; In "Polymer Liquid Crystals" Ciferri, A.; Krigbaum, W. R.; Meyer, Robert B. Academic Press: New York, 1982; Chap. 2.

- Gray, G. W.; Mosley, Alan; *J. C. S. Perkin II* **1976**, 97.
- Green, M. L. H.; *Pure Appl. Chem.* **1978**, 30, 27.
- Griffin, A. C.; Britt, T. R.; *J. Am. Chem. Soc.* **1981**, 103, 4957.
- Haase, W.; Paulus, H.; Muller, H. T.; *Mol. Cryst. Liq. Cryst.* **1983**, 97, 131.
- Hahn, B.; Wendorff, J. H.; Portugall, M.; and Ringsdorf, H.; *Coll. Polym. Sci.* **1981**, 259, 875.
- Hardy, Gy.; Cser, F.; Horvath, J.; Nyitrai, K.; *Israel J. Chem.* **1985**, 25, 252.
- Irvine, P. A.; Wu, D. C.; Flory, P. J.; *J. Chem. Soc., Faraday Trans. I* **1984**, 80, 1795.
- Isahara, A. *J. Chem. Phys.* **1950**, 18, 1446.
- Isahara, A. *J. Chem. Phys.* **1951**, 19, 1142.
- Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem Commun.* **1978**, 604.
- Kaminsky, W.; Herwig, J.; *Polym. Bull.* **1983**, 9, 464.
- Kaminsky, W.; Luker, H.; *Makromol. Chem. R. C.* **1984**, 5, 275.
- Kaminsky, W.; Schlobohm, M.; *Makromol. Chem., Macromol. Symp.* **1986**, 4, 103.
- Kaminsky, W.; Sinn, H.; In "Advances in Organometallic Chemistry Volume 18", Academic Press: New York, 1980.
- Karamysheva, L. A.; Kovshev, E. I.; Pavluchenko, A. I.; Roitman, K. V.; Titov, V. V.; Torgova, S. I.; Grebenkin, M. F.; *Mol. Cryst. Liq. Cryst.* **1981**, 67, 241.
- Kelker, H. *Mol. Cryst. Liq. Cryst.* **1973**, 21, 1.
- Lauk, Urs H.; Skrabal, P.; Zollinger, H.; *Helv. Chim. Acta* **1985**, 68, 1406.
- Magagnini, P. L.; Andruzzi, F.; Benetti, G. F.; *Macromolecules* **1980**, 13, 12.
- Magagnini, P. L.; Andruzzi, F.; Lupinacci, D.; Paci, M.; *Polymer* **1982**, 23, 277.
- Magagnini, P. L.; Andruzzi, F.; Vergamini, P.; Benedetti, E. *Polym. Bull.* **1980**, 2, 241.

- Magagnini, P. L.; Segre, A. L.; Andruzzi, F.; Lupinacci, D.; *Macromolecules* **1981**, *14*, 1845.
- Medalia, A. I.; Orzechowski, J. A. Trinchera; Morley, J. P.; *J. Polym. Sci.* **1959**, *41*, 241.
- Newman, B. A.; Frosini, V.; Magagnini, P. L.; In " Mesomorphic Order in Polymers", Blumstein, A.; ACS Symposium Series No. 74, American Chemical Society: Washington D. C. 1978.
- Onsager, L. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 627.
- Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, *128*, 45.
- Osman, M. A.; *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 353.
- Osman, M. A.; *Z. Naturforsch* **1983**, *38a*, 693.
- Petrzilka, M.; *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 347.
- Petrzilka, M.; Schadt, M.; Gerber, P. R.; Villiger, A.; Trickes, G.; *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 139.
- Petrzilka, M.; Schleich, Kuno; *Helvetica Chimica Acta* **1982**, *65*, 1242.
- Plate, N. A.; Shibaev, V. P.; "Comb Shaped Polymers and Liquid Crystals" Plenum Press: New York, 1987.
- Plate, N. A.; Shibaev, V. P.; *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.
- Porter, R. S.; Wang, J.; Knox, J. R.; *Polym. J.* **1978**, *10*, 619.
- Praefcke, K.; Schmidt, D.; Heppke, G.; *Chem. Ztg.* **1980**, *104*, 269.
- Reding, F. P.; *J. Polym. Sci.* **1956**, *21*, 547.
- Reiffenrath, V.; Schneider, F.; *Z. Naturforsch.*, **1981**, *36a*, 1006.
- Reinitzer, F.; *Wilnez Montash Chem* **1888**, *85*, 421.
- Richardson, R. M.; Herring, N. J.; *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 143.
- Ringsdorf, H.; Portugal, M.; Happ, M.; Finkelmann, H.; *Makromol. Chem.* **1978**, *179*, 2541.
- Samulski, E. T.; Toriumi, H.; *Mol. Cryst. Liq. Cryst.* **1983**, *101*, 163.

- Schwab, John. M.; Lin, Daniel C. T.; *J. Am. Chem. Soc.* **1985**, *107*, 6046.
- Shibaev, V. P.; Plate, N. A.; In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984.
- Shibaev, V. P.; Plate, N. A.; *Polym. Sci. USSR*, **1977**, *19*, 1065.
- Shibaev, V.P.; Kostromin, S. G.; Plate, N. A.; *Eur. Polym. J.* **1982**, *18*, 651.
- Stevens, H.; Rehage, G.; Finkelmann, H.; *Macromolecules* **1984**, *17*, 851.
- Takatsu, H.; Takeuchi, K.; *Mol. Cryst. Liq. Cryst.* **1986**, *138*, 231.
- Takatsu, H.; Takeuchi, K.; Sato, H.; *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 311.
- Takatsu, H.; Takeuchi, K.; Sato, H.; *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 345.
- Tamura, M.; Kochi, J. K.; *J. Organometal. Chem.* **1972**, *42*, 205.
- Toyne, K. J.; In "Thermotropic Liquid Crystals" Gray, G. W. John Wiley and Sons: New York, 1987, Chapter 2.
- Turner Jones, A.; *Makromol. Chem.* **1964**, *71*, 1.
- Ullrich, K.; Wendorff, J. H.; *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 376.
- Varech, D.; Jacques, J.; *Mol. Cryst. Liq. Cryst., Letters* **1983**, *92*, 141.
- Wunderlich, B.; Grebowicz, J. In "Advances in Polymer Science 60/61 " Springer-Verlag: Berlin Heidelberg, 1984; p. 1.
- Wunderlich, B.; "Macromolecular Physics Volume 3", Academic Press: New York, 1980; pp. 326-327.
- Zambelli, A.; Allegra, G.; *Macromolecules* **1980**, *13*, 42.
- Zambelli, A.; Tosi, C.; Sacchi, C.; *Macromolecules* **1972**, *5*(5), 649.