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THERMOTROPIC HYDROCARBON LIQUID CRYSTALLINE MONOMERS AND MODEL COMPOUNDS

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Abstract A versatile synthesis of hydrocarbon liquid crystalline monomers and model compounds has been developed. The general formula of the monomers is $H_{2n+1}C_n$-⟨⟩-⟨⟩-$(CH_2)_m$-CH=CH_2. Some of these compounds are liquid crystalline at room temperature and generally exhibit smectic B phases. A synthetic modification allows the preparation of model compounds with the general formula $H_{2n+1}C_n$-⟨⟩-⟨⟩-$(CH_2)_m$-⟨⟩-⟨⟩-C_nH_{2n+1}. Several of these latter compounds are liquid crystalline and exhibit well defined smectic mesophases. Data obtained from differential scanning calorimetry, polarized light optical microscopy and X-ray diffraction are discussed.

INTRODUCTION

In the past ten years there has been a great deal of interest in hydrocarbon liquid crystals. Table I is a compilation of various hydrocarbon mesogenic structures cited in the recent literature. The table has been subdivided into three categories according to whether the mesogen is alicyclic, aromatic or a combination of both types. T_{cl} and S/N refer to the range of clearing temperatures and the phase type (smectic/nematic) reported, respectively. In general, R=R'= n-alkyl. Since these compounds do not contain strong dipoles or hydrogen bonds, the intermolecular attractions are due to rather weak dispersion forces.

Given favorable packing, the anisotropy of these dispersion forces and the anisotropy of molecular shape are the two factors that determine the stability of the mesophase.[1,24] The relative contribution of these two factors is difficult to determine because of their inherent inseparability. However, greater anisotropy in either category generally means enhanced stability. The relative weakness of the attractive forces in hydrocarbon mesogens is offset by their anisotropic shape. The weakness of these forces may also be responsible for the lower viscosities (relative to more polar derivatives) reported [5,11,15] for some of the entries in Table I, particularly for entry #10. On the basis of the "like dissolves like" rule of thumb, one might also expect good solubility in non-polar solvents for these hydrocarbons.

TABLE I

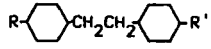
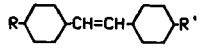
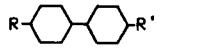
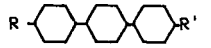
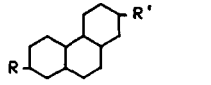
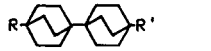
Entry #	Structure	T_{cl}, C	S/N	Reference
Alicyclic				
1		17-109	S,N	1,3,5,7
2		95[a]	S	1
3		26-110	S	1,2
4		249[b]	S	10
5		74-99	N	16
6		246[a]	S	3

TABLE I (continued)

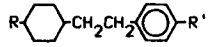
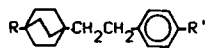
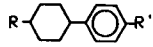
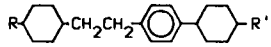
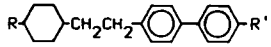
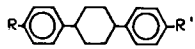
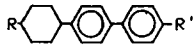
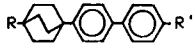
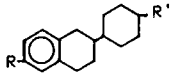
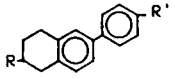
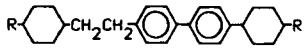
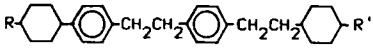
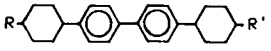
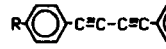
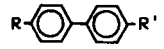
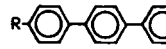
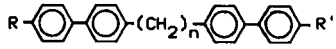
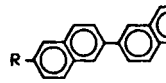
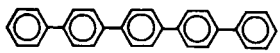
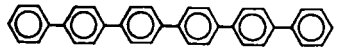
Entry #	Structure	T_{cl}, C	S/N	Reference
Alicyclic-Aromatic				
7		9-58	S,N	5,7,17
8		16-62	S,N	17
9		-11-92	S,N	1,4,5
10		126-145	S,N	7,11
11		82-144	S,N	3,18,22
12		107[c]	S	1,19
13		93-171	S,N	1,3,14,15 18,20
14		155-210	S,N	9
15		25-55	N	12
16		49-61	S,N	12
17		239-274	S,N	3,7
18		188[d]	S	7
19		311[e]	S,N	3,7,15

TABLE I (continued)

Entry #	Structure	T_{cl}, C	S/N	Reference
Aromatic				
20		80-132	N	8
21		28-84	S	1,2,5,6 this work
22		185-228	S	1,19,21
23		139-191	S	this work
24		148-164	S,N	13
25		425	S,N	23
26		565	S,N	23

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

Another area in which there has been considerable activity in recent years is the field of liquid crystalline polymers. Most, if not all, of these polymers incorporate heteroatoms such as N or O in their structures. In the main chain systems polyamides and polyesters seem to predominate, while the vast majority of side chain liquid crystalline polymers are based on polysiloxanes, poly(methacrylate)s and poly(acrylate)s. By analogy with low mole-

cular weight liquid crystals, the strong dipoles and/or hydrogen bonds in these polymers contribute to the stability of the mesophase, but should not be necessary for its formation. To our knowledge, no hydrocarbon liquid crystalline polymers have been prepared which incorporate any of the mesogens listed in Table I. In this report, a simple, versatile synthesis of hydrocarbon liquid crystalline monomers and model compounds is described. The characterization of these materials is also discussed. A future report will detail the polymer synthesis and properties.

SYNTHESIS

A side chain liquid crystalline polymer contains four elements: main chain, flexible spacer, mesogen and terminal group (tail). See Figure 1.

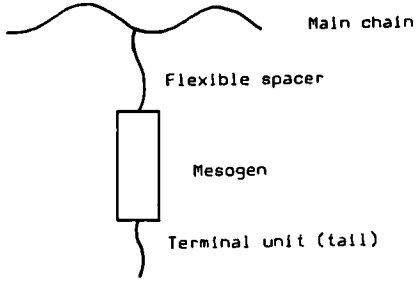


Figure 1

Elements of a side chain liquid crystal polymer

The simplest structure which incorporates these elements consists of a main chain, flexible spacer and terminal group constructed from n-alkyl groups. The biphenyl mesogen was chosen because its derivatives are the lowest melting of the aromatic mesogens and because of the availability of convenient syntheses. The target polymer is shown in Figure 2.

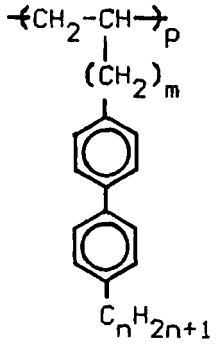
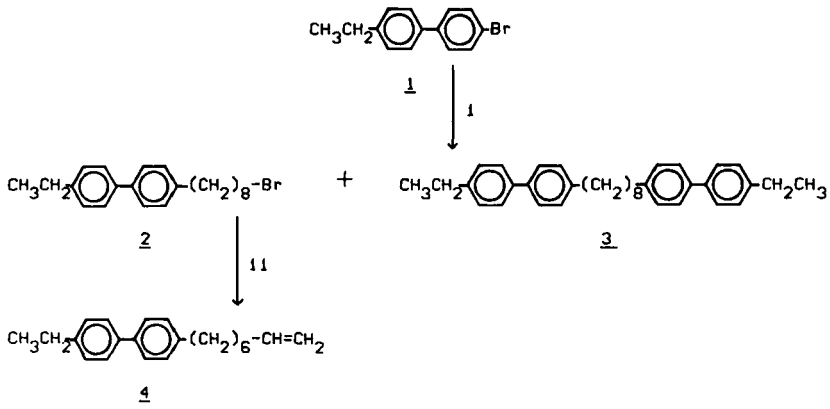


Figure 2. Target polymer structure.

The synthesis of an appropriate hydrocarbon monomer is illustrated in Scheme I. The terminal double bond may be polymerized with transition metal catalysts to give the target polymer. The use of transition metal catalysts also offers the prospect of tacticity control.

Scheme I



i) 1) Mg/THF 2) 3 Br-$(CH_2)_8$-Br / 3% Li_2CuBr_4

ii) 1) $N(CH_3)_3$ 2) Ag_2O 3)Δ

The synthesis of the starting compound 1 follows, with minor modification, from the work of Grey et al.[25,26] Refluxing the Grignard reagent formed from 1 with a 3X molar amount of 1,8 dibromooctane [27,30] produced the major product 2 and the minor product 3. The major product 2 was not isolated in a pure state because it was difficult to distill or recrystallize. High purity was not necessary because the trimethylammonium bromide salt formed in the next step was dissolved in water and the water insoluble impurities were removed by filtration. Heating the trimethylammonium hydroxide derivative (Hoffman elimination) in the final step produced the desired monomer 4.

The minor product 3 was only slightly soluble in diethyl ether, the solvent used for the workup of 2, so 3

was easily removed by filtration. Subsequent recrystallization produced pure 3, which was useful as a main chain liquid crystalline model compound.

A total of six monomers and six model compounds were synthesized. The length of the alkyl tail was varied by using starting bromobiphenyls with different alkyl substituents. The spacer length was controlled by varying the type of dibromoalkane employed. Two model compounds, 2BP4BP2 and 4BP4BP4, (Table III) were synthesized deliberately by carrying out the first step of the reaction (Scheme I, step i) with a 2:1 ratio of Grignard reagent to dibromoalkane. All of the compounds gave satisfactory elemental analyses and NMR spectra. The synthetic details and analytical data will be reported in a future communication.

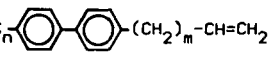
RESULTS AND DISCUSSION

The mesomorphic properties of the new monomers and model compounds are summarized in Tables II and III. Differential Scanning Calorimetry (DSC) and Polarized Light Optical Microscopy (POM) were used to characterize the liquid crystalline phases. X-ray diffraction was used in selected cases to confirm these results.

Of the six monomers prepared in this study, four were found to be liquid crystalline. The DSC trace and photomicrograph of a representative liquid crystalline monomer, MEBP46, are shown in Figures 3 and 4. Table IV compares the phase types and transition temperatures of these four liquid crystals with those of some similar hydrocarbon biphenyl liquid crystals from the literature. All of the compounds in Table IV display smectic phases.

The first two monomers in Table II do not have tails

TABLE II

Monomer 

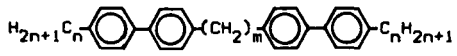
Code	n	m	Transition Temp., °C	ΔH KJ/mole	ΔS J/mole°K
MEBP04	0	4	K 1.3 I	15.1	55.1
MEBP06	0	6	K 18.3 I	21.0	71.9
MEBP24	2	4	S_B 26.3 I	8.4	28.0
MEBP26	2	6	K 9.4 S_B	4.8	16.8
			S_B 28.2 I	7.9	26.3
MEBP44	4	4	K 24.4 S_B	0.75	2.5
			S_B 38.5 I	7.2	23.1
MEBP46	4	6	K -24.6 S_B	2.2	9.0
			S_B 42.4 I	9.6	30.5

and are not liquid crystalline. The role of the tail in the formation of the mesophase will be discussed later.

Smectic phases were also exhibited by some of the model compounds shown in Table III. These are "siamese twin"[29] or gemini type liquid crystals containing a flexible core and two biphenyl groups. A DSC trace and an X-ray diffraction pattern (135°C) of a representative model compound, 4BP8BP4, are shown in Figures 5 and 6. The X-ray diffraction and POM observations (mosaic texture) prove that this model compound displays a smectic B phase. The calculated end-to-end extended chain distance of 4BP8BP4 is 34.06 Å. The layer spacing obtained from the inner rings of Figure 6

TABLE III

Model Compounds



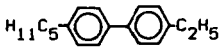
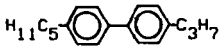
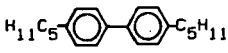
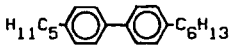
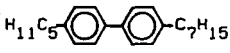
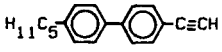
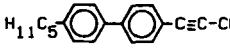
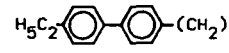
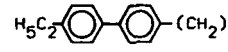
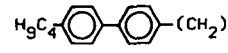
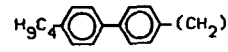
Code	n	m	Transition Temp., °C	ΔH KJ/mole	ΔS J/mole°K
8P8BP	0	8	K 142.1 I	56.2	135.0
2BP4BP2	2	4	K 181.5 I[a]	45.9	101.0
2BP6BP2	2	6	K 119.7 S	3.9	10.0
			S 149.4 I	35.4	83.7
2BP8BP2	2	8	K 128.7 S	8.4	20.9
			S 139.8 I	41.9	101.3
4BP4BP4	4	4	K 130.6 S_B	12.4	30.7
			S_B 190.7 I	24.1	52.0
4BP8BP4	4	8	K 124.5 S_B	12.5	31.4
			S_B 140.6 I	27.4	66.2

a) 2BP4BP2 displays a monotropic smectic B phase from 174.1 C to 151.7 °C.

is 37.5 Å. The difference of 3.4 Å is attributed to the space along the chain direction between the ends of the molecules. A spacing of 3.3 Å has been obtained[28] in this way for n-parrafins. The outer ring in Figure 6 corresponds to an intermolecular spacing of about 4.6 Å. BP8BP is not liquid crystalline. 2BP4BP2 displays a monotropic smectic B phase on cooling from 174.1°C to 151.7°C. Preliminary observations of 2BP6BP2 and 2BP8BP2 indicate that these compounds display a high order smectic phase. Investigations are currently in progress to ascertain their precise nature. All of the model compounds are

TABLE IV

Biphenyl Hydrocarbon Liquid Crystals

Entry #	Structure	Transition Temp., °C	Reference
1		S 33.9 I	5
2		K -18 S 47.8 I	2
3		K 26 S_E 47 S_B 52 I	1,6
4		S_E 42 S_B 53.5 I	6
5		S_E 36 S_B 63 I	6
6		K 56.4 S 82.7 I	5
7		K 60.5 S 83.4 I	5
8		S_B 26.3 I	this work
9		K 9.4 S_B 28.2 I	this work
10		K 24.4 S_B 38.5 I	this work
11		K -24.6 S_B 42.4 I	this work

soluble in benzene, toluene, cyclohexane and hexane. Increasing the length of the flexible core generally results in lower melting points and transition temperatures, as expected[29].

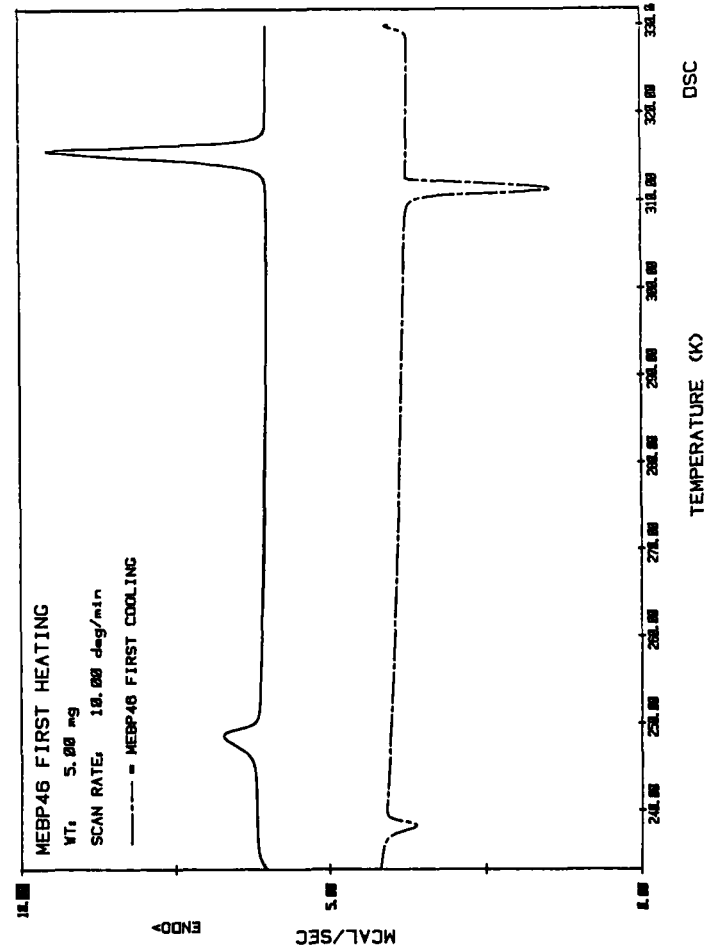


FIGURE 3. DSC heating and cooling scan for MEBP46

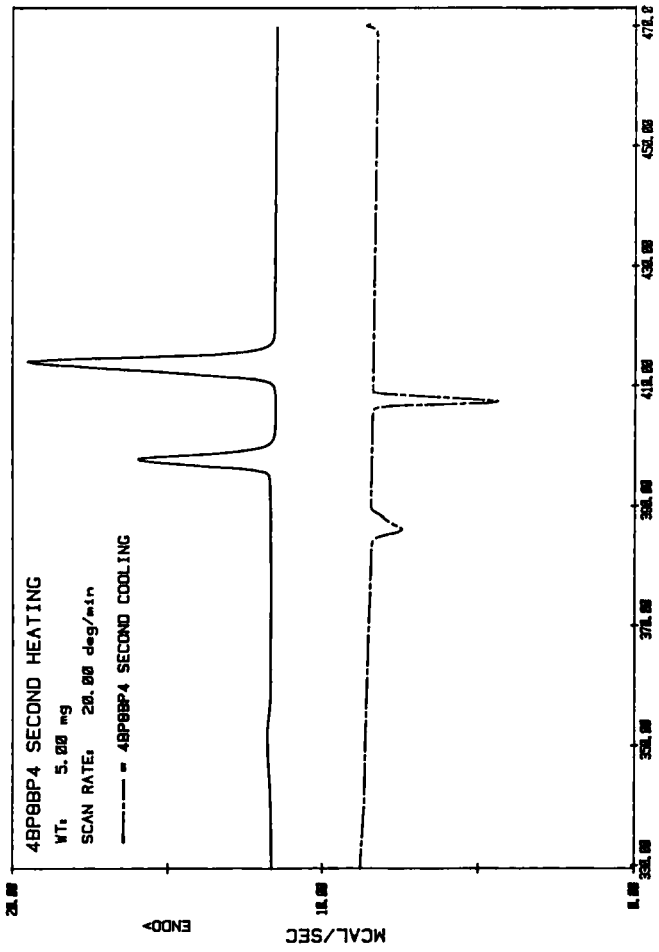


FIGURE 5. DSC heating and cooling scan for 4BP8BP4

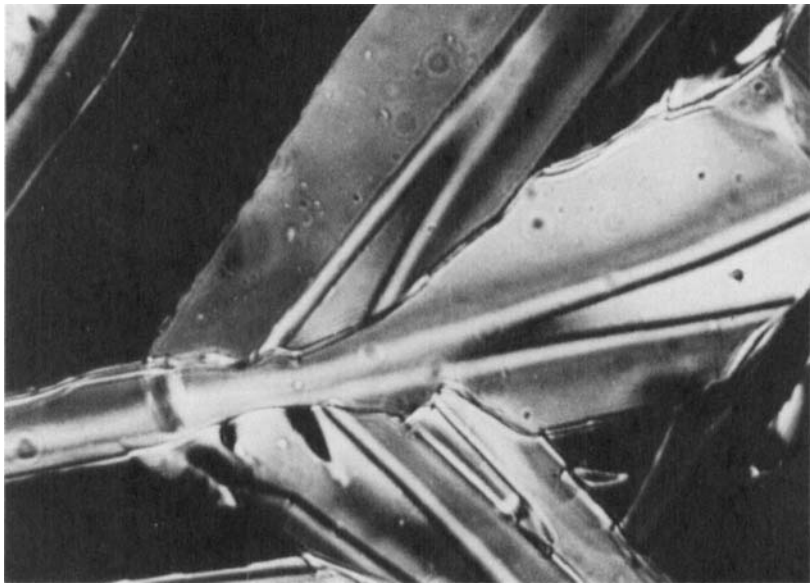


FIGURE 4

MEBP46 at 35°C with crossed polarizers
Magnification: 460X

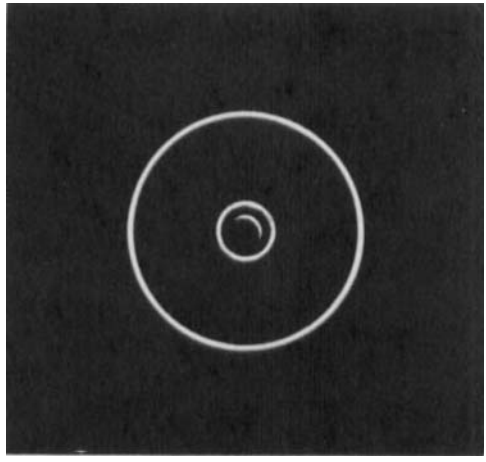


FIGURE 6

X-ray diffraction of 4BP8BP4 at 135°C

The three molecules prepared in this study that do not display liquid crystalline phases, MEBP04, MEBP06 and BP8BP, are the only three that do not have tails. All of the hydrocarbon biphenyl liquid crystals in Table IV have tails. This evidence supports the view that disubstitution of the biphenyl mesogen is a necessary (although not sufficient) condition for the formation of a liquid crystalline phase in this class of hydrocarbon liquid crystals. The tail probably increases the anisotropy of the molecule by increasing its effective axial ratio.

All of the liquid crystals characterized in this study display smectic phases; none of these display nematic phases. The compounds in Table IV also display similar phase characteristics. The K to S transition enthalpies (Tables II and III) of the compounds prepared in this study are smaller than the respective S to I transitions, indicating a highly ordered liquid crystalline phase. This order is due to the high concentration of polarizable electrons in the aromatic rings compared to the low concentration of polarizable electrons in the alkyl chains. Attractive forces between these groups of polarizable electrons are the principal source of attractive forces between the molecules, so it is not surprising that the biphenyl rings have a stronger tendency to associate which helps to stabilize the smectic phases. Apparently the terminal polarizable electrons in the double bond of the monomers do not disrupt this attraction sufficiently to induce nematic phases.

CONCLUSION

A convenient synthesis of hydrocarbon liquid crystalline monomers and model compounds has been developed.

Characterization by DSC, POM and X-ray diffraction reveals that only smectic phases are present in these compounds. The generalization has been confirmed that dialkyl substitution of the biphenyl group is necessary for these hydrocarbons to be liquid crystalline. The details of the synthesis and further X-ray and POM observations will be reported in a future communication. The properties of the polymers obtained by polymerizing the liquid crystalline monomers are included as a companion paper.

ACKNOWLEDGEMENT

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