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Liquid Crystals

Thermotropic Liquid Crystalline Polyesters Containing Naphthalenic Mesogenic Groups

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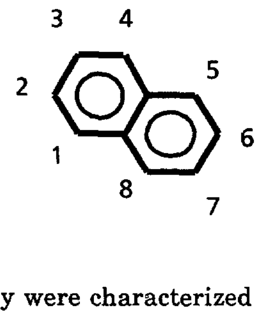
SUMMARY

Recently, the use of naphthalene in liquid crystalline compounds has become more commonplace primarily in the industrial research into LC polymers with wholly aromatic structures. A large number of compositions have appeared in the patent literature, and have been well summarized in several recent articles. Even though a large number of LC naphthalene-containing copolyesters have been prepared and reported, much of this work deals with wholly aromatic systems which include no flexible spacers. In order to investigate the effects that the naphthalene structure has on liquid crystalline behaviour, a series of low molecular weight model compounds and polymers with flexible spacers were synthesized and characterized.

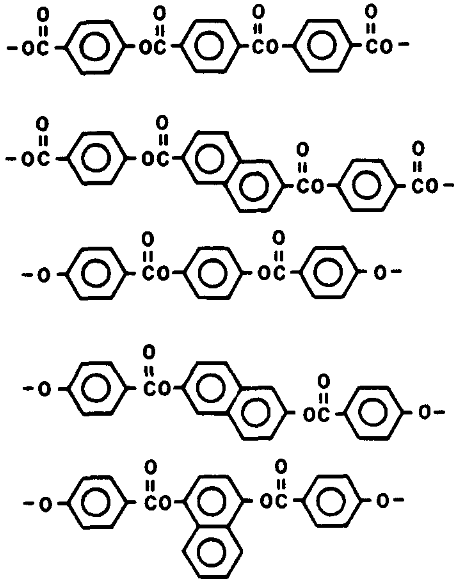
INTRODUCTION

The geometry of the naphthalene group is such that it has many of the structural features associated with the phenylene ring usually used in the mesogenic component of liquid crystalline compounds. Very few liquid crystals, however, have actually been prepared that incorporate the naphthalene residue either in the polymer or in low molecular weight mesogens outside of those copolymers appearing in the patent literature.

In a direct analogy with the phenylene group, 1,4-substitution of naphthalene would produce *para* functionality with an aromatic ring as side group, while both 1,5- and 2,6-substitution would give parallel but slightly offset structures. Compounds with functional groups in the 2,6-position have been used to a greater extent than the others in LC structures and are believed to lead to 'frustrated' chain packing in the solid state thereby resulting in reduce melting temperatures (1,2,3). Some of these aromatic copolymers have been described in the scientific literature and references to the original patents can be found in these reports. (4,5)



The liquid crystalline materials made for this study were characterized by microscopy, thermal analysis and x-ray diffraction. The structures of the mesogenic groups are shown in Figure 1 along with the reference numbers by which they are referred. Polymers 1- 5 have spacers that are 12 methylene groups in length while model compounds 6 and 7 have ethyl end groups and model compounds 8 through 10 have *n*-butyl end groups.



POLYMER	MODEL	(L/D)
1	6	2.9
2	7	2.8
3	8	2.8
4	9	2.7
5	10	2.0

FIGURE 1: Mesogenic structures of polymers and model compounds

EXPERIMENTAL

1) Synthesis of Polymers 1 and 2 from 4,4'-Dihydroxy-α,ω-Dibenzoyloxydodecane (I)

The synthesis of the dihydroxy compound and its polymerization were carried out as described elsewhere(6). The 2,6-naphthalene diacid chloride was prepared by first acidifying the potassium salt, and reacting the diacid with thionyl chloride. The terephthaloyl chloride was used as obtained. The appropriate diacid chloride was dissolved in 1,1,1- trichloroethane and to this was added an equimolar amount of the dihydroxy compound with a ten-fold excess of pyridine as proton acceptor. The reaction mixture was heated to 50°C and stirred for 24 hours. The resulting product was then added to methanol, filtered, washed with aqueous sodium bicarbonate and then washed with aqueous HCl solution. After a final washing with water, the product was finally dried under vacuum. Polymer yield, 95%.

2) Synthesis of Polymers 3 - 5 from 4,4'-Dicarboxy-α,ω- Diphenoxydodecane

a) 4,4'-Dicarbethoxy-α,ω- Diphenoxydodecane (II)

The synthesis of the diester compound was carried out as reported by Griffin and Havens(7). The 4-hydroxyethylbenzoate (33.2g, 0.20 mol) was dissolved in 250 ml anhydrous DMF, and to this was added 1,12-dibromododecane (32.8g, 0.10 mol) and sodium bicarbonate (26.8g, 0.25 mol). This mixture was heated for 4 hr at 150°C. After cooling, the slurry was filtered and recrystallized in 95% ethanol. Yield,21g (42%), T_m = 86°C.

b) 4,4'-Dicarboxy-α,ω- Diphenoxydodecane(III)

The diester (II) (10g, 0.02 mol) was dissolved in 250 mL, 95% ethanol, and to this was added 5g of potassium hydroxide dissolved in 10 mL water. The mixture was refluxed for 5 hr and after cooling, the product was acidified with 1N HCl. The resulting paste was filtered and recrystallized in 2-methoxyethanol. Yield, 7.5g (85%), T_m=248°C.

c) Polymerization

In a typical polymerization, the diacid (II) (15g, 0.034 mol) was refluxed in 100 mL thionyl chloride for 1 hr and then the thionyl chloride was removed by distillation. The resulting diacid chloride was dissolved in 100 mL 1,1,1-trichloroethane and divided into three portions. To each portion was added a solution consisting of an equimolar portion of the appropriate diphenol dissolved in a 5-fold excess of pyridine. The reaction mixtures were heated to 50°C, and stirred for 24 hours under nitrogen atmosphere. The resulting polymers were precipitated with methanol, filtered, washed with aqueous sodium bicarbonate solution and then washed with aqueous HCl and finally washed with water. The product was dried under vacuum. Yield, 95%.

3) Synthesis of Model Componds

a) Model Compounds 6 and 7 (8)

The diacid chloride (0.02 mol) was dissolved in pyridine (100 mL) and to this was added 4-hydroxyethyl benzoate (10g, 0.06 mol). After stirring for 24 hr, the resulting mixture was poured into 500 mL, 1N aqueous HCl. The precipitate was filtered, and the solid was washed with water (1x), aqueous sodium bicarbonate (3x), and water (3x). The resulting compounds were recrystallized in ethyl acetate. Yield, 85%.

b) Model Compounds 8 - 10

A quantity of 30g, 0.154 mol of 4-butoxybenzoic acid was refluxed in 100 mL thionyl chloride for one hour. After removal of the thionyl chloride by vacuum distillation, the acid chloride was dissolved in pyridine (100 mL). To this solution was added a second solution of the appropriate phenol (0.05 mol) dissolved in 50 mL pyridine. This mixture was stirred under nitrogen atmosphere for 24 hours at 40°C. After isolating the product from pyridine as described above, the model compounds were recrystallized in ethanol (1,4-naphthalene), or ethyl acetate (2,6-naphthalene, and 1,4-phenylene). Yield, 90%.

4) Physical Characterization

X-ray diagrams were recorded on Kodak DEF-5 film in a Warhus flat-film camera at a sample to film distance of 5.0 cm. The sample was sealed in a beryllium glass capillary and placed in a heating block fitted with a thermocouple and connected to a Variac. Temperature stability was approximately ±3°C. X-rays of the CuKα wavelength (λ=0.15418 nm) produced by a Philips model 1730 x-ray generator were used. Collimation was accomplished using a pair of 0.025 inch pinholes and the generator was operated typically at 40 KV and 30 MA with exposure times of 24 to 48 hours. DSC thermograms were recorded on a Perkin-Elmer DSC-IIC with sample weights from 10 to 20 milligrams and a scan rate of 20 degrees per minute. The instrument was first calibrated using an Indium standard. Liquid crystalline textures were observed under a Reichert Zetopan polarized light microscope equipped with a hotstage capable of reaching 350^{0}C.

RESULTS AND DISCUSSION

The series of model compounds and polymers that were investigated, contained mesogenic structures having three aromatic units linked internally by ester groups. Their mesogenic groups were in turn linked to either to end groups or polymethylene spacers by ester or ether linkages. The structures of the mesogenic groups under investigation are shown in Figure 1. As seen in the figure, the mesogenic groups in polymers 1 and 2 are identical except that the central terephthaloyl group has been replaced by a 2,6-dicarboxynaphthalene structure. Likewise polymers 3, 4 and 5 are similar except that the 1,4-dihydroxyphenylene residue has been replaced with a 2,6-dihydroxynaphthalene group in polymer 4 and a 1,4-dihydroxynaphthalene group in polymer 5. Polymers 1 and 3 with phenylene groups differ in the direction of the ester linkages inside their mesogenic groups, and by the fact that polymer 1 has the mesogenic group and spacers linked by an ester whereas polymer 3 has an ether group in the same position.

The melting temperature of polymers having ether linkages between the spacer and mesogenic group are typically lower than those with esters. This is probably due in part to the fact that the ether linked polymers have a spacer 2 atoms shorter, with the absence of 2 carbonyl groups. The relationship followed by the clearing transition for the ether and ester linked polymers is rather variable, but typically the clearing transition of the ether linked polymer occurs at higher temperatures.

Polymers with spacers 2 to 11 methylene groups in length and the same mesogenic group as polymer 3 were reported by Strzelecki and Van Luyen (9), and the polymer with a spacer containing 12 methylene groups was synthesized for our study. It was reported that polymers with 2 to 5 methylene groups had a single nematic mesophase. Upon reaching spacers with 6 to 9 carbon atoms, the polymers displayed 2 phases - one smectic and one nematic - and above 10 carbon atoms, two smectic phases and a single nematic phase were reported. In polymer 3, a single smectic phase followed by a single nematic phase was observed.

It seems unlikely that the melting transition should increase in going from 10 to 12 methylene units and so the reported melt transition may have instead been a crystal-crystal transition. Considerable debate surrounds the true character of the polymers with 10 methylene groups since a number of researchers have synthesized this compound and observed only a single nematic mesophase (9-11). Based on texture observation, polymer 3 appeared to go from the crystalline solid to a nematic state at 137°C, but when observed by x-ray diffraction at the lower temperature range, there was in fact a change from the crystal to a smectic phase. We have also observed nematic - like textures and smectic - like x-ray diagrams coinciding in other LC polymers. The cause of these somewhat contradictory observations remains unexplained.

The thermal transitions themselves were much sharper for polymer 1 than for polymer 3 which showed weaker and broader transitions. The results of characterization by DSC are given in Table 1.Also shown in the table are compounds 2 and 4, both polymers containing 2,6-naphthalene groups, and polymer 5 with a central 1,4-naphthalene group. These polymers were prepared to determine what effect an aromatic group that was more rigid or larger than the 1,4-phenylene group would have on polymer properties. Earlier use of such naphthalene groups has been reported to lower transition temperatures due to "frustrated" chain packing (12). However, as shown in Table 1 , the melting and clearing transition temperature of the naphthalene containing polymer, 2 was clearly higher than that of the related phenylene containing polymer. The cause of this transition temperature increase appeared not to be related to the geometry of the resulting mesogenic structures since both structures have similar L/D ratios as shown in Figure 1. When the 2,6-dihydroxynaphthalene group was added to the structure 3 in place of the 1,4-phenylene group, the polymer melting temperature increased and surprisingly the isotropization temperature decreased to produce a very narrow range of mesophase stability. This was in contrast to the behaviour of model compounds with the same mesogenic group and hexyl end groups (3) or with butyl end groups described below. The model compounds with 2,6 - naphthalene groups showed little increase in the melting temperature and an increased clearing temperature.

Table 1

Polymer	**Transition Temperatures** (°C)	**Entropy of Isotropization** (cal/mol-K) ΔS_i	$[\eta]$ (dL/g)
1*	214 233 k → s → i	3.22	0.42
2	312 361 k → s → i	0.58	---
3	137 221 271 k → s → n → i	2.32	0.20
4	200 235 k → s → i	9.20	---
5	113 145 203 k → k → s → i	2.72	---

*previously reported in reference 6.

If the 1,4-dihydroxynaphthalene group was used as in polymer 5, both the melting and clearing temperatures were decreased with respect to polymer 3. These observations were more consistent with the results obtained from model compounds made with the same mesogenic groups. Those polymers containing naphthalene, polymers 2, 4 and 5, did not display any distinct textures using polarized light hotstage microscopy, but appeared to be smectic based on wide angle x-ray diffraction analysis. The entropy of clearing transitions listed in Table 1 for polymers 1 - 3 and 5 were in the range typically observed for most LC polymers with polymethylene spacers. The value reported for polymer 4, however, is rather large, and is probably due to overlap of the melting and clearing transitions when observed by DSC.

Employing molecular models, the length to diameter ratio (L/D) for mesogenic groups containing 2,6-naphthalene was determined to be about the same as for phenylene containing structures under the assumption that the length of the mesogenic group was that of the aromatic component. The presence of the naphthalene residue produced slightly wider and longer mesogenic groups as shown by the L/D values listed in Figure 1. The molecular models also showed that there are at least two conformations about the internal ester linkages that maintain the coplanarity of the three sets of rings in the mesogenic structures. One conformation was linear, while the other was slightly offset. It is not known which, if either, of these arrangements is preferred. The mesogenic group with a 1,4-naphthalene structure was clearly much wider due to the lateral placement of the aromatic component. This produced a lower L/D value and was clearly reflected in the narrower range of mesophase stability of the model compound 10 described below, but was not as influential on the properties of polymer 5.

Low molecular weight compounds having those mesogenic structures of polymers 1 to 5 were synthesized in order to better understand the effects that naphthalene groups have on the liquid crystallinity of structures of this type. The properties of these mesogens are listed in Table 2 which reports the transition temperatures, heats of transition and the change in the entropy of the clearing transition (ΔS_i). The models 8 to 10 had ΔS_i values higher than models 6 and 7, probably due to larger end groups stabilizing the mesophase to a greater degree.

Table 2

Polymer	**Transition Temperatures** (°C)	**Heats of Transition** (cal/g)		**Change in Entropy of Isotropization** (cal/mol-K)
		ΔH_m	ΔH_i	
6**	196 205 238 k → s → n → i	20.7	0.25	0.24
7	221 295 k → n → i	21.8	0.36	0.34
8	158 243 k → n → i	17.6	1.41	1.26
9	163 302 k → n → i	14.6	1.21	1.52
10	165 197 k → n → i	14.6	1.35	1.47

**reported previously in reference 13.

Differences in the end groups make direct comparison between the two groups of mesogens difficult. Those structures with 2,6- naphthalene groups were found to exhibit somewhat higher melting and clearing transitions. Compound 5 with 1,4-naphthalene, however, had a lower range of mesophase stability than the 1,4-phenylene mesogen. All model compounds possessed a simple nematic phase with the exception of compound 6 which had an additional smectic phase. Observations made with the model compounds and polymers did not agree well as to the type of mesophase formed.

CONCLUSIONS

In a comparison of phenylene and naphthalene containing mesogens it was found that the use of 2,6-naphthalenic mesogens may not reduce transition temperatures by "frustrated" chain packing as observed in LC polymers without flexible spacers. For instance, in Table 1 polymer 2 has higher transition temperatures than polymer 1 contradictory to what one would expect if "frustrated" chain packing were operative in polymer 2. The broad, more rigid and polarizable 2,6 substituted naphthalene groups may be stabilizing the ordered structures present in the solid and mesophase to a greater degree than the 1,4 phenylene group. Transition temperatures for polymers 3, 4 and 5 indicate that for 1,4-naphthalenic mesogens the temperatures are evidently lowered. Observations of mesophase type have shown that extrapolation of results from model compounds to polymers cannot be made reliably. In this study the model compounds exhibited predominantly nematic mesophases while the polymers containing the mesogenic groups of the models exhibited predominantly smectic mesophases. It is also clear from Tables 1 and 2 that transition temperatures cannot be readily predicted from models.

REFERENCES

1. B. P. Griffin and M. K. Cox, Brit. Polym. J., 13, 147 (1980)
2. J. I. Jin, S. Antoun, C. K. Ober and R. W. Lenz, Brit. Polym. J., 13, 132 (1980)
3. W.J. Jackson, Macromolecules, 16, 1027 (1983)
4. G.W. Calundann and M. Jaffe, Proc. Robert A. Welch Conf. Chem. Res., XXVI. Synth. Polym., Houston, TX, Nov. 1982
5. A. Ciferri, W.R. Krigbaum and R.B. Meyer, eds., *Polymer Liquid Crystals,* Academic Press, N.Y. (1982)
6. C. K. Ober, J.-I. Jin and R. W. Lenz, Makromol. Chem. Rapid Commun., 4, 49(1983)
7. A. C. Griffin and S. J. Havens, J. Polym. Sci.: Polym. Phys. Ed., 19, 951(1981)
8. M.J.S. Dewar and R.S. Goldberg, J. Org. Chem., 35, 2711 (1970)
9. L.Strzelecki and D. Van Luyen, Eur. Polym. J., 16, 299(1980)
10. S. Antoun, J.-I. Jin and R. W. Lenz, J. Polym. Sci., Polym. Chem. Ed., 19, 1901(1981)
11. C. Noel, J. Billard and B. Fayolle, Preprints Macro. IUPAC, Florence, 3, 286(1981)
12. W. J. Jackson, Brit. Polym. J., 13, 154 (1981)
13. G.Galli, E.Chiellini, C.K.Ober, and R.W.Lenz, Makromol.Chem., 183, 2693 (1982)

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