Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Dr. R. W. Lenz [a] & Guerry L. Grune [b]

[a] Department of Chemical Engineering, University of Massachusetts, Amherst, MA, 01003

[b] IBM Corporation Polymers Group, Dept. E79 Research Triangle Park, NC, 27709

To cite this article: Dr. R. W. Lenz & Guerry L. Grune (1984): The Synthesis and Characterization of Thermotropic Liquid Crystal Model Compounds, Molecular Crystals and Liquid Crystals, 106:3-4, 383-399

To link to this article: http://dx.doi.org/10.1080/00268948408071455

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 383-399
0026-8941/84/1064-0383/$18.50/0

Printed in the United States of America

THE SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC LIQUID CRYSTAL MODEL COMPOUNDS

DR. R. W. LENZ
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003

GUERRY L. GRUNE
IBM Corporation
Polymers Group - Dept. E79
Research Triangle Park, NC 27709

ABSTRACT

Recently, the unique morphological classification of the "liquid crystal" state has simultaneously aroused the interest of the industrial and scientific community. With this renewed interest has come a need for better understanding and characterization of the liquid crystal transitions which occur within the many polymeric systems exhibiting this morphological phenomenon. Of the seven newly synthesized thermotropic materials for this study which are p-hydroxybenzoic acid modified compounds, six were of the rod-like geometry typically associated with mesogens. The seventh compound, a derivative of pentaerythritol, was cross-shaped and had a crystalline morphology. All compounds, including the p-hydroxybenzoic acid modified mesogenic precursor, were subjected to various characterization techniques such as proton Nuclear Magnetic Resonance (NMR), infrared spectroscopy (IR), and elemental analysis for structure determination, as well as differential scanning calorimetry (DSC), polarising microscopy equipped with a hot stage, and Fischer-Johns apparatus for thermal analysis.

Results of this study reconfirms previous investigations of similar low molecular oligomers with mesogenic forming ability both in terms of the predictable and of the actual range of the thermotropic and thermodynamic transitions. A different morphological state exists for at least two of the compounds which seemed to exhibit both crystalline and liquid crystalline states. The existence of this morphology created the opportunity for comparison of model compounds of this study with that of polyurethanes.

INTRODUCTION

The concepts of the syntheses of liquid crystalline low molecular weight compounds and of polymers containing mesogenic units in either the main or side chain are now well known. The synthesis of liquid crystal compounds has been extensively studied over the last twenty years, but only recently have investigators emphasized the need for a systematic study of the thermotropic liquid crystalline regime in polymers created by the various main chain and side group flexible spacers between the mesogenic groups. A helpful consequence for the systematic studies of introducing, for instance, methylene and oxymethylene groups as the flexible spacers, is that similar thermotropic and thermodynamic transitions are seen for low molecular weight oligomers as for the high polymers of the same unit structure.

This study is a further effort to predict the possible liquid crystalline morphology of p-hydroxybenzoic acid modified polymers by the synthesis and characterization of model, low molecular weight oligomers with mesogenic and flexible spacer structures.

THE CONCEPT OF LIQUID CRYSTALLINE STRUCTURES AND PROPERTIES

The concept of "liquid crystalline" (hereafter referred to as "LC") compounds has been reported in the literature since 1889.[1] It is only recently, however, that this unique classification of polymers has aroused the interest of the industrial and scientific community simultaneously. LC polymers in the form of high modulus fibres spun from both lyotropic aromatic polyamides[2-4] and thermotropic p-hydroxybenzoic acid modified polyesters[5-8] have exhibited superior mechanical properties[9] due to their anisotropic nature.

Liquid crystals are often characterized as substances exhibiting a high degree of anisotropy yet maintaining the properties of fluids.[10] Often in the literature, liquid crystal substances are referred to as mesomorphic or mesogenic, often because objections have been raised to the term "liquid crystal". Polymers exhibiting mesomorphic behavior can basically be separated into two categories:

1. Lyotropic systems of natural and synthetic polypeptides and synthetic polyamides (i.e., poly (p-benzamide) in DMAc and poly - (γ -benzyl-L-glutamate) in dichloromethane) where the liquid crystalline order is *solvent-induced,* and
2. Thermotropic systems including poly-Schiff base polymers and aromatic polyesters where the liquid crystalline order is *thermally induced.*

Thermotropic liquid crystalline (mesomorphic) polymers of one of two basic types have been prepared; one type being those with pendant small-molecule liquid crystalline moieties attached to a vinyl polymer backbone (sidegroup). The other type of thermotropic mesogenic polymer is one in which the liquid crystalline moeity is incorporated in the polymer backbone or main chain. The thermotropic, liquid crystalline behavior of polymers having rigid mesogenic units interconnected through flexible spacers along the main chain has been predicted theoretically and is well known experimentally.[11-15] This type of behavior, for small molecules, is the subject of this study.

To facilitate the study of these polymers, one can substantially lower the crystal-to-liquid crystal transition temperatures by separating the rigid mesogenic moieties with regularly spaced sequences of flexible methylene or oxymethylene groups. Work employing the use of disymmetrically substituted hydroquinones and terepthalic acids, and the preparation of copolymers containing either linear or non-linear comonomers with methylene spacers is detailed by (a) Roviello and Sirigu[11] based upon polymeric Schiff base derivatives of p, p'-dihyroxy-α, α'-dimethylbenzalane and by (b) Blumstein and coworkers[12] using polyester derivatives of p, p' dihydroxybiphenyl and dihydroxystilbene. More recently, similar work has been carried out in Dr. R. W. Lenz's laboratory.[16-19] In contrast to the theoretical predication[20] of polymers with rigid mesogenic moieties in the backbone, which will exhibit a nematic phase or a degree of order approaching the nematic state at a critical concentration, it has been found that as the length of the flexible spacer increases, there is increased chance that a smectic phase will appear. For this study, the thermal analysis of these compounds was made by Differential Scanning Calorimetry (DSC) and closely follows the work pioneered by Porter, et al.[21]

The type of non-amphiphilic mesophase (either nematic, smectic or cholesteric) present requires not only thermal analysis but also optical measurements which are usually carried out on a hot-stage of a polarising microscope.[22] One measurement without the other can easily lead to inaccurate or unreliable conclusions. Because mesophases generally contain parallel arrangements of elongated molecules, these mesophases are birefringent. Furthermore, the nematic mesophases derive their name from the mobile thread-like lines observed when they have been prepared by rapid cooling of the isotropic melt. An example of how this appeared as observed on a cross-polarising microscope and typical of a nematic "Schlieren" texture, is shown in Figure 1.[23] Photomicrographs obtained in this study of n-dodecyl [(p-benzyloxy terepthaloyloxy)] benzoate on the polarising microscope, in its nematic state is shown

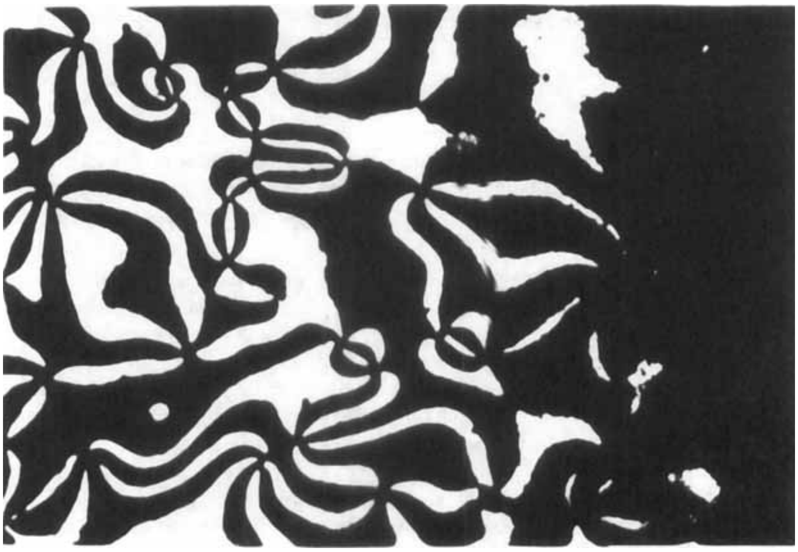


FIGURE 1 Nematic "Schlieren" Texture

in Figure 2. The photomicrographs of this section have been included so that a comparison can be made with the photomicrographs of the compounds of this study with other studies to verify the presence of nematogenic liquid crystal structures in these model compounds.

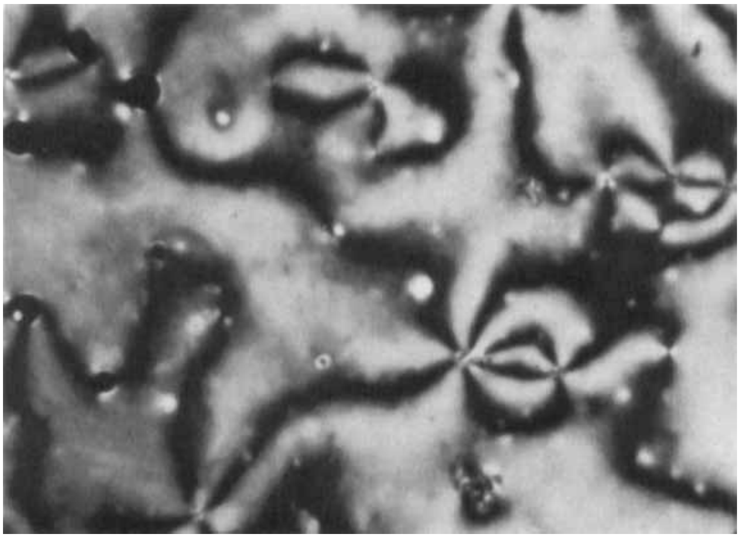


FIGURE 2 Photomicrograph Of Compound 2 Taken On Cooling At 172.6°C (300X Magnification). (See Color Plate I).

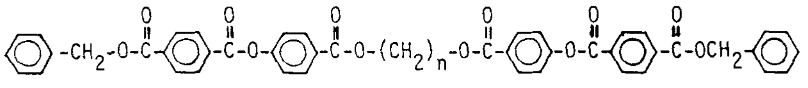
The classification of the mesophases were originally made on the basis of the characteristic phenomena of the liquid crystalline phases by means of microscopic observation with polarised light.[24] Further work on mesophase classification has also been attempted with x-ray diffraction techniques.[25]

Emphasis has also been placed on the purity of the compounds characterized in this study, because mesophase-forming materials are extremely sensitive to very small amounts of impurity.[26] Which method of purity determination is employed depends on the system of study, but only 0.01 mole % of impurity is important in the thermodynamic order of mesophase-forming material. These impurities affect the results obtained on DSC and polarising microscopy determinations and hamper any final interpretation of the mesogenic species in question, and for this reason, HPLC (high-pressure liquid chromatography) was employed to determine a qualitative purity of the compounds studied. The thermodynamic data obtained is thus questionable due to the fact that no quantitative data was determined as to the purity of the compounds synthesized. Attempts to purify each compound via recrystallization were made and the HPLC results illustrate that in most cases, these efforts improved purity. In addition, the sharp melting endotherms and high resolution photomicrographs indicate that pure species, for at least four of the seven compounds synthesized, were obtained.

SYNTHESIS AND CHARACTERIZATION OF THE p-Benzyl (Oxyterepthaloyloxy) benzoic acid (BTBA) MESOGEN

Purpose for Mesogen Synthesis

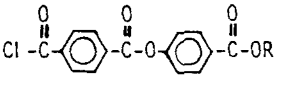
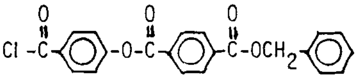
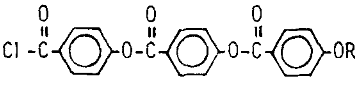
Different schemes were proposed for synthesis and characterization of three different desired mesogenic groups which are shown in Table 1. Of these three possible mesogenic units, structure B was selected for this study. The acid chloride was synthesized, and used as the mesogenic group precurser by reaction with diols of increasing molecular weight in order to prepare the model compounds for characterization. All of the diols selected have a flexible methylene spacer group between hydroxyl groups which react with the mesogenic acid chloride to form the ester as shown below:



n = 4, 5, 6 and 12

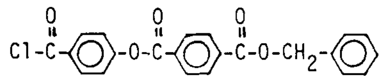
The varying length of these flexible spacers should affect melting and clearing transition temperatures T_m and T_i, similar to the effects seen on higher molecular weight polyesters derived from the reaction of 4, 4' - dihydroxy-α - ω -diphenyl-oxyalkanes, and terepthalic acid, and terepthalic acid and 4, 4' α -dihydroxy-, ω - dibenzoyl-oxyalkanes (Series 1 and 2) prepared previously, as reported in Lenz and coworkers.[18]

TABLE 1 Proposed Mesogens for Synthesis

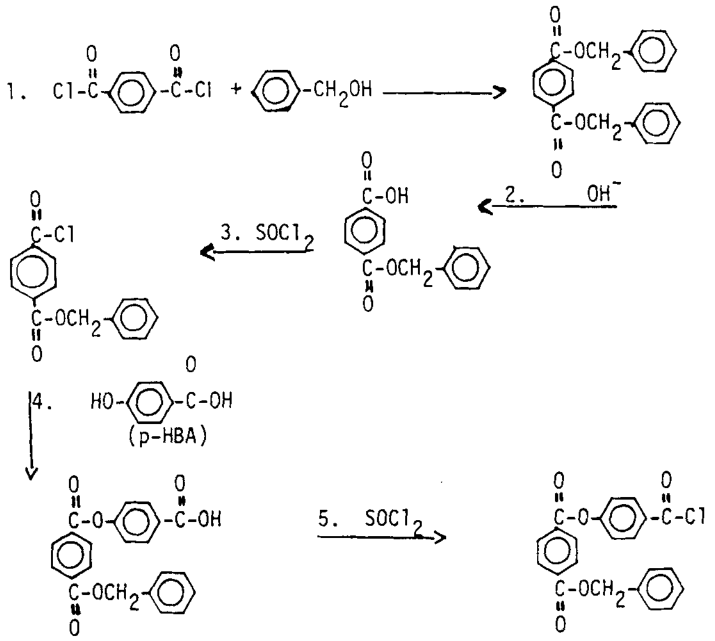
A.		
B.		R = H or CH_3
C.		

Synthesis of p-(Benzyloxyterepthaloyloxy) benzoyl chloride Mesogen (BTBC)

The desired mesogen for the prepolymer modeling synthesis is shown below and named as the acid chloride of Benzyloxyterepthaloyl-p-hydroxy benzoate and hence referred to as "BTBC".



A 5-step synthetic route was developed according to the literature[27-30] along the following reaction sequence:



SYNTHESIS OF MODEL COMPOUNDS

The following alcohols and diols were reacted with the acid chloride of the BTBA mesogen to synthesize the model compounds of this study:

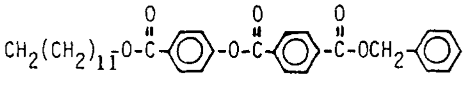
1. n-$C_6H_{13}OH$
2. n-$C_{12}H_{25}OH$
3. $HO(CH_2)_5OH$
4. $HOCH_2CH_2OCH_2CH_2OH$
5. $HO(CH_2)_6OH$
6. $HO(CH_2)_{12}OH$
7. $C(CH_2OH)_4$

Of the seven model compounds prepared, only compounds synthesized from the alcohols and diols of 2, 3, 4 and 5 will be discussed here.

SYNTHESIS AND CHARACTERIZATION OF n-Dodecyl (p-Benzyloxyterepthaloyloxy) benzoate

Synthesis of n-Dodecyl (p-Benzyloxyterepthaloyloxy) Benzoate

The only monoester prepared for this study to be discussed, was by the reaction of BTBC with 1-dodecanol (n-dodecyl alcohol) which gave the following structure:



2

The synthesis procedure included preparation of a solution of approximately 10% excess (1.25 gm., 0.0067 mol) dodecanol, with 6 ml. dried dioxane and 1.5 ml. of purified pyridine, in relation to the acid chloride. The acid chloride, BTBC, solution was dissolved in 24 ml. of dried dioxane. The dodecanol solution was added dropwise to a stirred solution of BTBC. After total addition, a cloudy white precipitate appeared then disappeared as refluxing began. The reaction mixture was allowed to reflux overnight followed by cooling of the flask and pouring the solution into a beaker of distilled H_2O with stirring. The precipitate was filtered on a small Buchner funnel and a dilute (10:1) HCl solution was used to remove any remaining pyridinium salts from compound 2. The compound was dried in a vacuum desiccator. Recrystallization was performed by dissolving 3 gm. of compound 2 in 20 ml. of carbon tetrachloride at reflux conditions and then filtered hot by gravity filtration through fluted filter paper. The product yield prior to recrystallization was 92.2%.

Characterization of n-Dodecyl (p-Benzyloxyterepthaloyloxy) benzoate

Structure verification was partially determined by elemental analysis as follows: Observed: C, 74.77%; H, 8.49%; Calculated: C, 75.00%; H, 8.18% for $C_{35}H_{40}O_6$.

The infrared spectra, although poor in resolution, does not show any BTBC peak remaining, indicating that the acid chloride reacted fully. Also prevalent is the dodecyl group in the 2800-3000 cm^{-1} region.

Thermal analysis of compound 2 included melting and isotropic transition determinations by use of the Fischer-Johns melting point apparatus, differential scanning calorimetry and a hot stage on a polarising microscope. Comparison of these transitions are listed in Table 2. Perhaps due to the small Δ T between the melting and clearing transitions, the DSC results did not show the two distinct peaks as normally associated with nematogenic compounds.

TABLE 2 Thermal Analysis of Compound 2

Method of Analysis	T_m(°C)	T_i(°C)	ΔT(°C)
Fischer-Johns	188°	193-195°	5-7°
DSC	181°?	191°?	10°?
Polarising Microscopy	188.5°	191.6°	2.1°

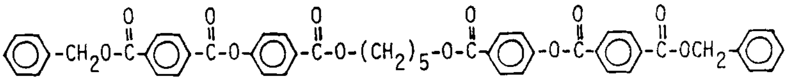
Slides for use on the polarising microscope were made by taking 10 mg. of the sample, placing a cover slip over this portion of the slide, then placing the prepared slide on the mettler hot stage. The n-dodecanol compound, 2, was then heated at 2 C/min to 192.4 C and then cooled at the same rate to room temperature. On heating, compound 2 flowed into a birefrigent marble-like texture characteristic of many of the compounds of this study and shown in Figure 3. Before and during the isotropic transition, a more mosaic-type pattern emerged (the remnants of which appear in Figure 4). This compound cooled into a typical nematic state as already evidenced in Figure 2.

HPLC analysis was performed for both the crude and recrystallized form of compound 2 and the sharper resolution indicates a higher degree of purity existed for the recrystallized form as expected.

SYNTHESIS AND CHARACTERIZATION OF 1,5-Bis [p-Benzyloxyterepthaloyloxy) benzoyl] pentane

Synthesis of 1,5 Bis [(p-Benzyloxyterepthaloyloxy) benzoyl] pentane

This compound was the first diester synthesized in the series of oligomeric compounds for this study. It was prepared by the reaction of BTBC with 1,5 pentanediol to yield the following product structure:



3

This compound, 3, was synthesized according to the same reaction scheme of compound 2 with the important exception that a stoichiometric ratio of acid chloride (BTBC) to pentanediol was maintained at 2:1. The 1,5 pentanediol solution was also added in a dropwise manner to a stirring solution of BTBC in the identical manner. Again, a cloudy white precipitate was formed which disappeared after reflux was reached. Recrystallization proceeded slowly and large yellow tinted crystals developed over a 24-hour period. The crude product yield was 96.3%.

Characterization of 1,5 Bis [(p-Benzyloxyterepthaloyloxy) benzoyl] pentane

Elemental analysis was performed for compound 3 and the results are listed in Table 3. The problem with using the elemental analysis data is evident when a comparison is made between the mono and diesters. The monoester would be formed due to incomplete reaction of the acid chloride with both hydroxyl groups of the pentanediol. The experimental analysis for 3 fell between the two theoretical values of C% and H% of the mono and diester. Therefore further work was needed to ascertain which structure was synthesized.

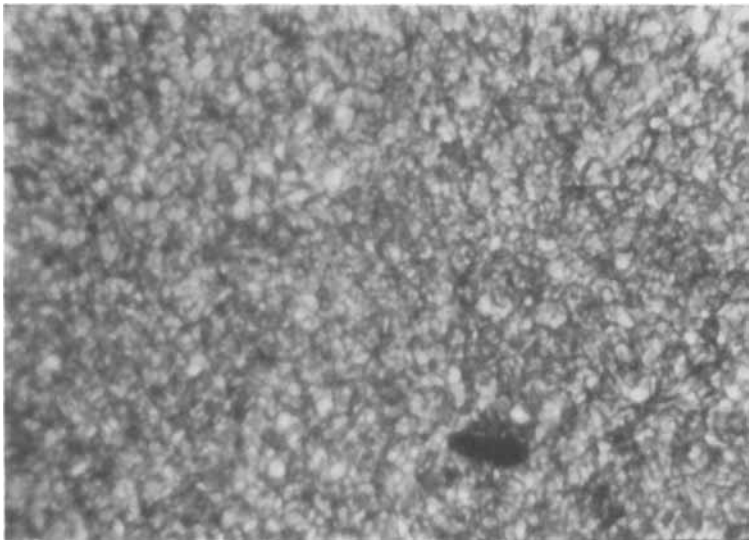


FIGURE 3 Photomicrograph Of Compound 2 Taken On Heating At 188.5°C (300X Magnification). (See Color Plate II).

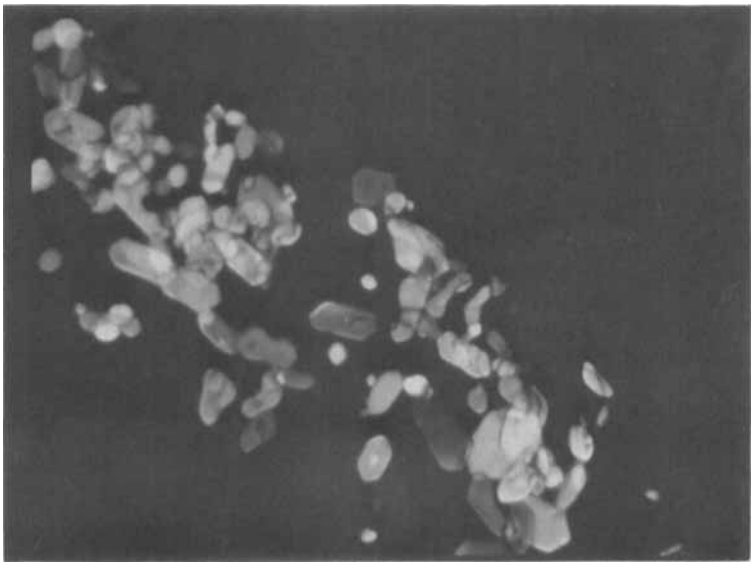


FIGURE 4 Photomicrograph Of Compound 2 Taken On Heating At 191.6°C (300X Magnification). (See Color Plate III).

TABLE 3 Elemental Analysis for Compound 3

Compound Formula	MW	Theoretical C%	Theoretical H%
Monoester $C_{27}H_{26}O_7$	462gm/mol	70.13	5.63
Diester $C_{49}H_{40}O_{12}$	820gm/mol	71.71	4.88
Observed Analysis		71.02	5.09

The verification that the diester structure was isolated was found by the use of both N.M.R. and infrared spectra. Integration of the peaks for the hydrogen protons in NMR analysis suggests the following ratio exists:

$$\begin{array}{ccccc} H_a & : H_b & : H_c & : H_d & : H_e \\ 4 & : 14 & : 12 & : 4 & : 16 \end{array}$$

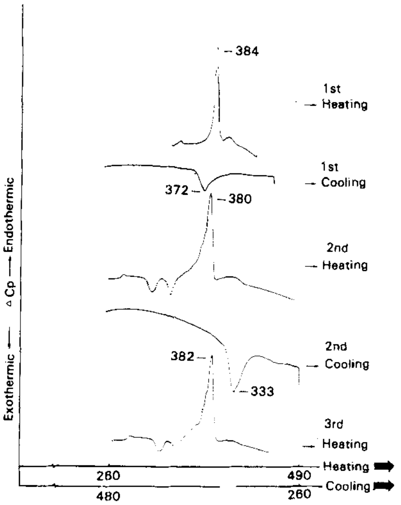
which is only possible for the diester structure. Also, the monoester would include a hydroxyl group in its structure which does not appear in either the N.M.R. or the infrared spectra, further confirming the presence of the diester.

A comparison of the transition temperatures obtained by the three methods employed is given in Table 4.

TABLE 4 Thermal Analysis of Compound 3

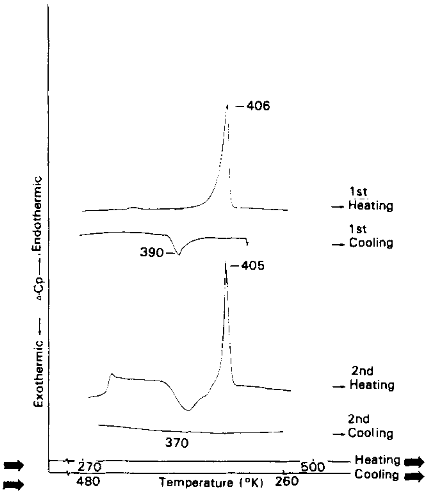
Method of Analysis	T_m(°C)	T_i(°C)	ΔT(°C)
Fischer-Johns	112°	150°	38°
DSC	107°	137°	30°
Polarising Microscopy	112°	157°	45°

The thermograms obtained by DSC analysis for compound 3 are found in Figure 5a. The first heating curve shows a typical melting and nematic isotropic transition, followed by a recrystallization exotherm during the first cooling cycle. The second and third heating scans depict a series of exotherms indicating crystalline transitions before the melting endotherm. Interestingly, a very similar DSC curve resulted for compound 4 (the diester of the reaction of BTBC with diethylene glycol) shown in Figure 5b and for a sample of poly (butylene terepthalate) as shown in Figure 5c. Perhaps the fact that five or the equivalent flexible spacers exist between ester groups causes the premelting endotherm phenomen. In a recent study by Meurisse[14], it states that the effect of oxygen in a (CH_2-CH_2-O) segment appears stereochemically equivalent to a methylene unit. Perhaps this similarity also extends to the realm of thermal analysis.



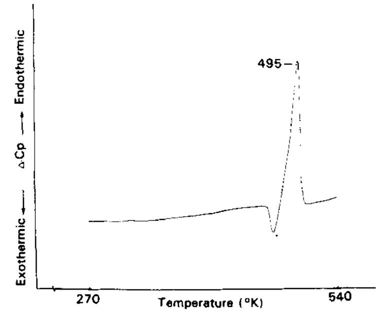
DSC Thermogram of
1,5 Bis, p-(Benzyloxy(terepthaloyl) oxy(benzoyl) pentane
Heating Rate: 10°K/min. Cooling Rate: 5°K/min.
Sensitivity: 5 mcal/sec

FIGURE 5a



DSC Thermogram of
1,5 Bis (p-(Benzyloxyterepthaloyl oxy(benzoyl) ethyl ether
Heating Rate: 10°K/min. Cooling Rate: 5°K/min.
Sensitivity: 5 mcal/sec

FIGURE 5b



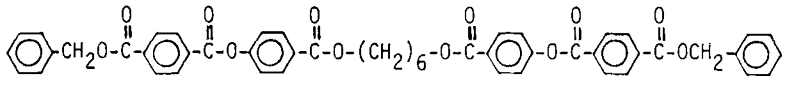
DSC Thermogram of
Polybutylene terepthalate
Heating rate: 20°K/min. Sensitivity: 5 mcal/sec

FIGURE 5c

SYNTHESIS AND CHARACTERIZATION OF 1,6-Bis (p-Benzyloxyterepthaloyloxy) benzoyl] -hexane

Synthesis of 1,6-Bis [(p-Benzyloxyterepthaloyloxy) Benzoyl] -hexane

This third oligomer in the series of diesters which was prepared, was synthesized by the reaction of BTBC was 1,6 hexanediol to yield the following structure:



5

This compound, 5, was synthesized in the same manner as used for the diesters of 1,5-pentanediol and DEG (compounds 3 and 4). This crude product was the cleanest looking of all of the synthesized oligomers, and the high yield of 95% on recrystallization suggests that this may be the most pure of the compounds synthesized. The yield prior to recrystallization was 87.7%.

Characterization of 1,6-Bis [(p-Benzyloxyterepthaloyloxy) benzoyl]-hexane

Again, due to the fact that the compound, 5, synthesized is supposed to be a diester, the elemental analysis was insufficient for structure determination due to the possible presence of the monoester. The elemental analysis for both of the possible structures synthesized are given in Table 5.

TABLE 5 Elemental Analysis for Compound 5

Compound Formula	MW	Theoretical	
		C%	H%
Monoester $C_{28}H_{28}O_7$	476gm/mole	70.59	5.88
Diester $C_{50}H_{42}O_{12}$	834gm/mole	71.94	5.04
Observed Analysis		71.21	5.24

As with the diesters of compounds 3 and 4, further verification of the structure was necessary to confirm the presence of the diester. Again this was attempted by the use of N.M.R. and infrared analysis.

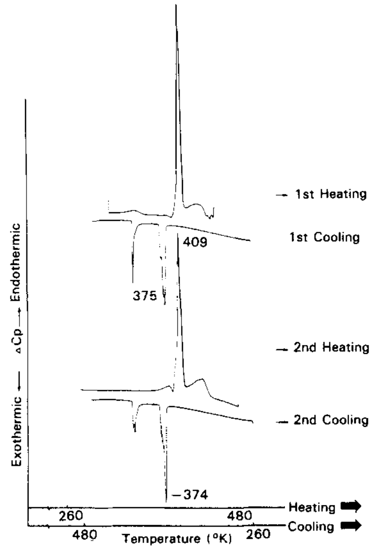
An indication that the compound was the diester after recrystallization and *not* the monoester was seen by inspection of High Pressure Liquid Chromatographs. The chromatogram for the crude product shows a distinct "tailing" which is most likely due to hydroxyl group interactions with the Si (OH) of the silica gel column. After recrystallization of the compound, no presence of "tailing", was seen, indicating that the monoester or diol impurity was removed.

Thermal analysis for compound 5 included the three methods of characterization as with all previous oligomers, and results are listed in Table 6.

TABLE 6 Thermal Analysis for Compound 5

Method of Analysis	T_m(°C)	T_i(°C)	ΔT(°C)
Fischer-Johns	136°	158°	22°
DSC	136°	161°	27°
Polarising Microscopy	135.3°	172.4°	37.1°

The correlation of the three methods is well within experimental error, especially considering that both T_m and T_i values obtained by DSC are for the endothermic peaks while the temperatures determined by microscopy are associated with the endpoint of the transition, so the correlation of T_m is surprisingly gratifying. As before, all data from DSC analysis is reported from the second heating thermogram in Figure 6.



DSC Thermogram of
1,6 - Bis, p-(Benzyloxy(terepthaloyl) oxy(benzoyl) -Hezane
Heating Rate: 10°K/min. Cooling Rate: 5°K/min. Sensitivity: 5 mcal/sec

FIGURE 6

A final experiment to determine if the structures found during heating and cooling are reproducible on the second heating and cooling cycle was run with compound 5, the diester formed from BTBA and 1,6-hexanediol. Figures 7 (a-c) show that almost identical structures were formed in the birefrigent regions at approximately the same temperature for both cycles. This result seems to confirm the presence of polymorphism and the ability to reform liquid crystal transitions on reheating as can also be deduced from the DSC thermogram of compound 5 in Figure 6.

FIGURE 7a Photomicrograph Of Compound 5 on First Heating At 136.5°C in Different Region (300X Magnification). (See Color Plate IV).

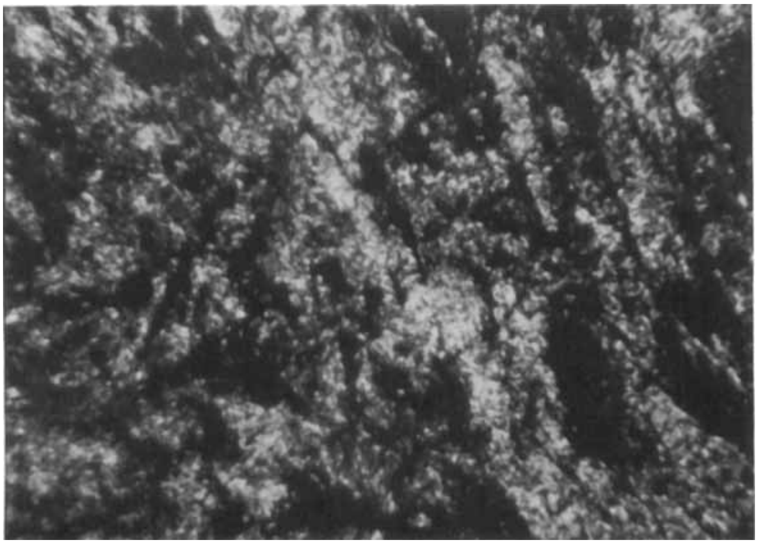


FIGURE 7b Photomicrograph Of New Structure Formed On First Cooling At 104.5°C (300X Magnification). (See Color Plate V).

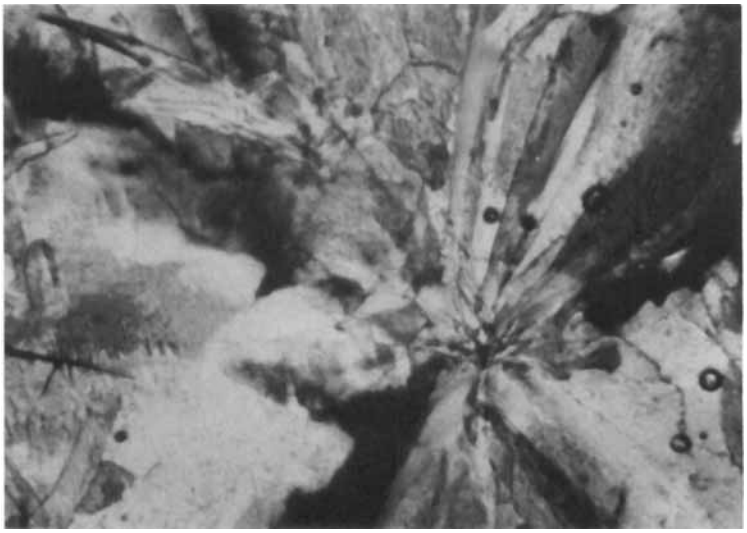


FIGURE 7c Photomicrograph Of Reformed Structure (a) On Reheating At 134.2°C (300X Magnification). (See Color Plate VI).

SUMMARY AND CONCLUSIONS

The compounds 2, 3, 4 and 5 discussed in this paper, all exhibited thermotropic liquid crystalline transitions. These thermotropic transitions were consistent and well defined by three techniques including DSC, polarising microscopy, and Fischer-Johns apparatus. Differential Scanning Calorimetry (DSC) of compounds 2-5, indicates that the formation of nematic mesogens occur within a specific temperature range. This conclusion is further supported by the photomicrographs of the birefrigent regions obtained during the heating and cooling cycles on the hot stage of a polarising microscope.

Finally, the morphological forms exhibited in compounds 3 and 4, indicate both crystalline and liquid crystalline thermotropic regions exist. These structures could be compared with the hard-soft segment morphology associated with polyurethanes.

ACKNOWLEDGEMENTS

I wish to thank Dr. Robert W. Lenz for his guidance and encouragement through the course of this work, as well as the aid of Dr. J. I. Jin and B. J. Jo who were largely responsible for the successful completion of the synthesis of the model compounds. The unselfish devotion of Dr. Martin Moeller and Dr. Hans-Rudi Dicke during the purification, characterization, and synthesis portions of this study will not be forgotten. Financial support from the Departments of Chemical Engineering and Polymer Science and Engineering at the University of Massachusetts and a grant in aid from the CUMIRP-NSF Fund, made this study possible.

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