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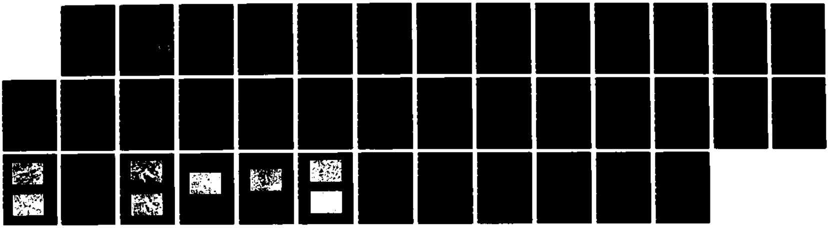

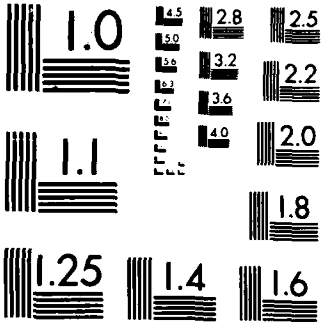

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# Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens
## 1. Side-Chain Liquid Crystalline Polymethacrylates and Polyacrylates Containing 2,5-Disubstituted-1,3-Dioxane Mesogens

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## ABSTRACT

Polymethacrylates and polyacrylates containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane as a mesogenic unit and an aliphatic spacer containing eleven methylene units were synthesized. Their phase behavior was studied by differential scanning calorimetry and optical polarization microscopy, and compared with the phase behavior of the corresponding polymethacrylates and polyacrylates based on 4-methoxy-4'-hydroxybiphenyl mesogen. All polymers present smectic mesomorphism. The 2,5-disubstituted-1,3-dioxane mesogen resembles a terphenyl mesogen in which the internal phenyl ring was hydrogenated. Even so, when compared with the biphenyl containing polymers, the glass transition temperatures of the 1,3-dioxane containing polymers are lower, although their isotropization occurs at higher temperatures. Keywords: [illegible]

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## Summary

Polymethacrylates and polyacrylates containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane as a mesogenic unit and an aliphatic spacer containing eleven methylene units were synthesized. Their phase behavior was studied by differential scanning calorimetry and optical polarization microscopy, and compared with the phase behavior of the corresponding polymethacrylates and polyacrylates based on 4-methoxy-4'-hydroxybiphenyl mesogen. All polymers present smectic mesomorphism. The 2,5-disubstituted-1,3-dioxane mesogen resembles a terphenyl mesogen in which the internal phenyl ring was hydrogenated. Even so, when compared with the biphenyl containing polymers, the glass transition temperatures of the 1,3-dioxane containing polymers are lower, although their isotropization occurs at higher temperatures.

## Introduction

Over the past few years several research groups reported systematic investigations concerning the replacement of aromatic structures from mesomorphic low molar mass compounds by heterocycloalkane units. Of particular interest to us is the replacement of one benzene ring from biphenyl or terphenyl structural units by 1,3-dioxane and 1,3-dithiane groups. This is because biphenyl- and terphenyl- analogues 1,3-dioxanes (1-5) and 1,3-dithianes (6-8) were already extensively studied, and their liquid crystalline properties were characterized. A recent review article discusses and compares the liquid crystalline properties of biphenyl and terphenyl mesogens with their corresponding biphenyl- and terphenyl- analogues, 1,3-dioxanes and 1,3-dithianes (3).

According to our knowledge there is only one preliminary report in the literature concerning the synthesis and characterization of one side-chain liquid crystalline polymer containing a 1,3-dioxane based mesogen (9).

The goal of this paper is to present the synthesis and characterization of liquid crystalline polyacrylates and polymethacrylates containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane mesogenic units connected to the acryloyl and methacryloyl groups by an undecane spacer. The liquid crystalline properties of these polymers will be compared with those of the analogous polymers containing 4-methoxy-4'-hydroxybiphenyl mesogenic groups.

# Experimental

## A. Materials

4,4'-Dihydroxybiphenyl (Polysciences), ethyl p-methoxyphenyl-acetate, 11-bromo-1-undecanol (Aldrich), methacryloyl chloride, acryloyl chloride (Fluka) were used as received. 1,4-Dioxane was first refluxed over sodium and then distilled under argon. α,α'-Azoisobutyronitrile (AIBN) (Fluka) was freshly recrystallized from methanol (below 40°C). All the other reagents were used as received.

## B. Techniques

200 MHz $^1$H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard unless noted. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. In all cases heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. After the first heating scan, the sample was "annealed" at about 10°C above the isotropization temperature for 5-10 min. Under these registration conditions, beginning with the second heating and cooling scans all the DSC scans produced perfectly reproducible data. The transitions reported were read during the second or third heating and cooling scans unless otherwise specified. A Carl Zeiss optical polarizing microscope (magnification: 100 x) equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was used to observe

the thermal transitions and to analyze the anisotropic textures (10,11). Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10LC instrument equipped with LC-100 column oven, LC-600 auto sampler, and Sigma 15 data station. High pressure liquid chromatography (HPLC) determinations were performed with the same instrument. The measurements were made by using the UV detector, THF as solvent (1ml/min, 40°C), a set of PL gel columns of $10^2$, $5.10^2$, $10^3$, $10^4$ and $10^5$ Å, and a calibration plot constructed with polystyrene standards.

## C. Synthesis of Monomers and Polymers

### 4-Methoxy-4'-Hydroxybiphenyl

4-Methoxy-4'-hydroxybiphenyl was synthesized after a modified literature procedure (12,13). 4,4'-Dihydroxybiphenyl (100g, 0.54 mol) was dissolved in a solution of 43 g (1.08 mol) of NaOH in 400 ml of water. Dimethyl sulfate (68g, 0.54 mol) was added and the solution was stirred until the whole reaction mixture solidified. The precipitate was filtered and washed with 10% aqueous NaOH. Then it was dissolved in boiling water and traces of insoluble 4,4'-dimethoxybiphenyl were separated by hot filtration. Upon addition of dilute HCl the product precipitated. It was filtered off, washed with water, and recrystallized from ethanol to yield 60g (56%); mp 179-181°C (lit. (12), mp 183.5°C).

The synthesis of the 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane is outlined in Scheme 1.

## p-Acetoxybenzaldehyde

To an ice-water cooled mixture of p-hydroxybenzaldehyde (24.4g, 0.20 mol), triethylamine freshly distilled from KOH (22.2g, 0.22 mol), and dried methylene chloride (400 ml), acetyl chloride (17.7g, 0.22 mol) was added dropwise. After the addition was completed, the solution was stirred at room temperature for 12 hrs., filtered to remove $NEt_3 \cdot HCl$, washed with 2% sodium bicarbonate water solution, water and dried over anhydrous sodium sulfate. The solvent was evaporated in a rotavapor and the residual oil was distilled at 92-93°C/7 mm Hg to yield 28g (85%). $^1H$-NMR ($CDCl_3$, TMS, $\delta$, ppm): 2.28 (s, 3H, $-\overset{O}{\overset{\|}{C}}C\underline{H}_3$), 7.17-7.85 (m, 4H, $-C_6\underline{H}_4-$), 9.87 (s, 1H, $-C\underline{H}{=}O$ ).

## Diethyl-2-(p-methoxyphenyl)malonate

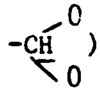
A literature procedure which was initially used for the synthesis of ethyl phenylmalonate (14) was adapted for the synthesis of diethyl-2-(p-methoxyphenyl)malonate. 11.5g (0.5 mol) of cleanly cut sodium was added in portions into 250 ml of absolute ethyl alcohol. When the sodium was completely dissolved, the solution of sodium ethoxide was cooled to 60°C and 73g (0.5 mol) of ethyl oxalate were added rapidly with vigorous stirring followed immediately by the addition of 97.5 g (0.53 mol) of ethyl-p-methoxyphenylacetate. Stirring was discontinued at once. About 10 minutes after the addition of ethyl-p-methoxyphenylacetate, the entire reaction mixture started to crystallize. The content of the flask was transferred into a beaker immediately after the first crystalls appeared. The solid paste of the sodium derivative was allowed to cool to room temperature, and then was strongly stirred with 400 ml of dry ethyl ether. The remained solid was separated by filtration, washed with dry ethyl ether and dissolved in dilute sulfuric acid (14.5 ml of concentrated sulfuric acid in 250 ml of water). An almost colorless oil separated from the aqueous phase. The two layers were separated. The aqueous layer was extracted with ethyl ether. The oil and ethyl ether layers were combined, dried over anhydrous sodium sulfate and the ether was removed in a rotavapor. The residual oil was heated at 175°C under a pressure of about 15 mm Hg until the evolution of carbon monoxide was complete. The oil which had distilled was returned to the flask, and the product was distilled at 137-138°C/7 mm Hg to yield 92 g (70%).

$^1$H-NMR ($CDCl_3$, TMS, $\delta$, ppm): 1.23 (t, 6H, $-C\underline{H}_3$), 3.77 (s, 3H, $-OC\underline{H}_3$), 4.20 (q, 4H, $-C\underline{H}_2-$), 4.60 (s, 1H, $-C\underline{H}=$), 6.77-7.42 (q, 4H, $-C_6\underline{H}_4-$).

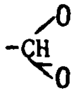
## 2-(p-Methoxyphenyl)propan-1,3-diol

To a suspension of 3.8g (0.1 mol) $LiAlH_4$ in 200 ml of dry ethyl ether, a solution of 26.6g (0.1 mol) of diethyl-2-(p-methoxyphenyl)malonate in 50 ml ethyl ether was added dropwise. After the addition was complete, the reaction mixture was stirred at 40°C for 20 hrs, cooled to room temperature and 5 ml of ethyl acetate was added to consume the excess of $LiAlH_4$. The resulted solution was treated with 300 ml of 10% sulfuric acid and extracted with chloroform. The organic phase was washed with 2% aqueous sodium bicarbonate, water and dried over anhydrous sodium sulfate. The solvent was removed on a rotavapor to give a crude product which was recrystallized from benzene to yield 13.3g (76%). mp. 83-84°C.
$^1$H-NMR ($CDCl_3$, TMS, $\delta$, ppm): 2.47 (s,2H, $-O\underline{H}$), 3.03 (s, 1H, $-C\underline{H}=$), 3.78 (s, 3H, $-OC\underline{H}_3$), 3.91 (s, 4H, $-C\underline{H}_2-$), 6.86-7.16 (q, 4H, $-C_6\underline{H}_4-$).

## 2-(p-Acetoxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane

2-(p-Methoxyphenyl)propan-1,3-diol (10.1g, 0.055 mol), p-acetoxybenzaldehyde (8.2g, 0.05 mol) and p-toluenesulfonic acid (500 mg) were dissolved in 500 ml of dry benzene. The resulting solution was refluxed until 0.9 ml of water were collected in a Dean-Stark trap. After cooling, the reaction mixture was washed with 2% aqueous solution of sodium bicarbonate, water, dried over anhydrous magnesium sulfate, after which the solvent was evaporated on a rotavapor. The remaining solid was recrystallized from ethanol to yield 12.6 g (77%). mp 155-157°C. $^1$H-NMR, $(CD_3)_2CO$, TMS, $\delta$, ppm): 2.27 (s, 3H, $-COC\underline{H}_3$), 3.28 (m, 1H, $-C\underline{H}=$), 3.78 (s, 3H, $-OC\underline{H}_3$), 3.91-4.35 (m, 4H, $-OC\underline{H}_2-$), 5.56 (s, 1H,  $-C\underline{H}\langle^{O}_{O}$ ), 6.86-7.56 (m, 8H, $-\underline{C_6H_4}-$).

2-(p-Hydroxyphenyl)-5-(p-Methoxyphenyl)-1,3-dioxane

2-(p-Acetoxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane (12.6g) was hydrolyzed by refluxing for 1 hr with a solution of 10 g NaOH in 400 ml 90% ethanol. Ethanol was removed from the resulted solution on a rotavapor. The obtained solid was dissolved in distilled water and the water solution was neutrallized with dilute hvdrochloric acid. The obtained solid was filtered, dried and recrystallized from toluene to yield 10g (91%). mp. 215°C. $^1$H-NMR (DMSO-$d_6$, $\delta$, ppm): 3.16 (m, 1H, $-C\underline{H}=$), 3.37 (s, 1H, $-O\underline{H}$), 3.73 (s, 3H, $-OC\underline{H}_3$), 3.90-4.18 (m, 4H, $-OC\underline{H}_2-$), 5.51 (s, 1H,  $-C\underline{H}\langle^{O}_{O}$ ), 6.73-7.26 (m, 8H, $-\underline{C_6H_4}-$). The next steps used in the synthesis of acrylates and methacrylates are outlined in Scheme 2.

4'-(11-Hydroxyundecanyloxy)-4-methoxybiphenyl (IA) and 11-hydroxyundecanyl-1-oxy-[2-(p-oxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane] (IIA)

Both compounds were synthesized by the etherification of the corresponding phenol with 11-bromo-1-undecanol. An example is presented below. 4-Methoxy-4'-hydroxybiphenyl (5g, 0.025 mol) and KOH (0.24g, 0.04 mol) were dissolved in 100 ml of ethanol. 11-Bromo-1-undecanol (10.0g, 0.04 mol) was added to the reaction mixture, and the obtained solution was refluxed for 15 hr. The reaction mixture was then poured into water and the precipitated product was filtered, washed with dilute NaOH to remove the unreacted phenol, water, dried and purified by recrystallization from ethanol to yield 8.8g (95%) of white crystals. IA (DSC, 20°C/min): mp. 140.19 (onset). IIA (DSC, 20°C/min): 93.18°C (melting), 102.02°C (smectic → isotropic). $^1$H-NMR chemical shifts for both compounds are presented in Table 2.

### Synthesis of I-AC, I-MA, II-AC and II-MA

All methacrylates and acrylates were synthesized by the esterification of the corresponding alcohols (I-A and II-A from Scheme 2) with methacryloyl chloride or acryloyl chloride. An example for their synthesis follows. I-A (2.0g, 0.0054 mol) was dissolved in 250 ml of dried THF and 2 ml of triethylamine (distilled from KOH). The obtained solution was cooled in an ice-water bath to 0°C, and 0.78 ml (0.008 mol) of methacryloyl chloride was added dropwise. The reaction mixture was let to warm up to room temperature slowly and kept stirring overnight. The obtained reaction mixture was poured into water and the precipitated product was filtered and dried under vacuum. The obtained product was purified by recrystallization from methanol to yield 2.1 g (90%) of white crystals. $^1$H-NMR chemical shifts are reported in Table 1 for all monomers. Table 2 summarizes the thermal characterization of all monomers.

## D. Polymerizations

Radical polymerization of the monomers were carried out in Schlenk tubes, equipped with septums, under argon. The polymerization tubes containing the monomer solution in dioxane (10%, wt./vol.) and the initiator (AIBN, 1 wt% vs monomer) were first degassed by several freeze-pump-thaw cycles under vacuum, and then filled with argon. All polymerizations were carried out at 60°C for 15 hrs. After the polymerization time the polymers were precipitated into methanol, filtered and purified by reprecipitation from THF solutions into methanol. Table 3 summarizes the polymerization results.

## Results and Discussion

Previous work from our laboratory on side-chain liquid crystalline polymers was mainly focussed on the role of interconnecting groups between the spacer and the polymer backbone as well as on the role of polymer main chain on the mesomorphic properties of the polymers. This research lead to the synthesis of side-chain liquid crystalline: poly(vinyl ether)s and poly(propenyl ether)s (13), poly(N-acylethyleneimine)s (15), copoly(epichlorohydrine)s and substituted poly(2,6-dimethyl-1,4-phenylene oxide)s (16).

Although the literature on low molar mass liquid crystalline compounds is quite rich (17-20) most of the research on side-chain liquid crystalline polymers containing rod-like mesogens is based on biphenyl- or phenylbenzoate-derivatives (21,22). Only recently terphenyl-based side-chain liquid crystalline polymers were synthesized (23). Recent work from several laboratories has demonstrated that the replacement of one of the benzene rings from biphenyl- or terphenyl-mesogenic units by 1,3-dioxane (1-5) or 1,3-dithiane (6-8) leads to a convenient synthetic procedure to tailor the mesomorphic properties of biphenyl- and terphenyl-analogues.

1,3-Dioxane-like cyclic acetals can be obtained by acid catalyzed condensation of 2-substituted propan-1,3-diols with aldehydes as shown in Scheme 3. A mixture of cis and trans isomers is usually obtained. Only the trans isomer presents liquid crystalline properties. Since the trans isomer is less soluble than the cis isomer they can be easily separated by recrystallization.

Scheme 1 presents the synthetic procedure used to prepare the 4-methoxy-4'-hydroxy-p-terphenyl analogue in which the internal benzene ring was replaced by a 2,5-disubstituted-1,3-dioxane unit. As it has been presented in the experimental part each reaction step was accomplished in high yields and the trans isomer was isolated with 100% purity as determined by 200 MHz $^{1}$H-NMR spectroscopy, thin layer chromatography and HPLC. Scheme 2 outlines the synthesis of the acrylate and methacrylate monomers. The acrylate and methacrylate monomers containing 4-methoxy-4'-oxybiphenyl were prepared in order to compare their behavior with those of the 1,3-dioxane based mesogen. Although liquid crystalline polyacrylates and polymethacrylates containing 4-methoxy-4'-hydroxybiphenyl were previously reported in the literature, the two polymers presented here have not been synthesized previously (13, 21, 22, 24, 25).

Table 2 summarizes the thermal behavior of the monomers. Their characterization is quite difficult because above the melting temperature they polymerize and become mesomorphic. Only the monomers II-AC and II-MA are liquid crystal. Their optical textures show smectic mesomorphism.

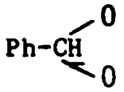
Table 4 summarizes both the thermal transitions and the thermodynamic parameters for the entire set of polymers synthesized according to the results presented in Table 3. Since some of the thermal transitions present several peculiarities, we will discuss all of them on some representative DSC traces.

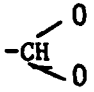
Figure 1 illustrates the heating and cooling DSC scans for poly(I-MA). The heating scan presents the glass transition temperature (Tg) at 54°C, followed two endothermic transitions at 87°C and 142°C. The cooling scan looks almost identical to the heating scan except that a very small supercooling (less than 10°C) is observed for both exothermic transitions. In addition, as Table 4 shows, the enthapy and entropy changes for both transitions are identical or almost identical regardless of the scan they are calculated from. Recent work from our laboratory concerning the influence of molecular weight on both thermal transitions and on their thermodynamic parameters (26) revealed that liquid crystalline transitions and isotropization are much less supercooled than crystalline transitions. At the same time the enthalpy and entropy changes related to liquid crystalline transitions are not dependent on the scans they were calculated from (heating or cooling).

However, the crystallization temperatures are always supercooled in comparison to melting, and the thermodynamic quantities are smaller on the cooling scan. Therefore, poly (I-MA) presents two liquid crtystalline mesophases. Optical polarization microscopy reveals very fluid textures typical to low molar mass smectic liquid crystals (Figure 2). Poly (I-MA) behaves completely different from the previous methacrylates containing the same mesogenic side group but a different methylenic spacer. The homologue polymer containing two methylenic units in the spacer is nematic (13,25), while the polymethacrylate containing six methylenic units in the spacer is crystalline and presents a very narrow range of smectic mesomorphism (13,25). The increase in the length of the spacer from six to eleven methylenic units is accompanied by an enlargement of the thermal stability of the polymer mesophase. This is in complete agreement with a better decoupling of the mobility of the mesogen as it has been predicted by the spacer concept (25).

Figure 3 outlines typical DSC traces for poly (I-AC). The glass transition temperature is as expected, lower than that of the corresponding polymethacrylate. The first endothermic transition appears suppercooled 28°C on the cooling scan. At the same time, the enthalpy change associated with this transition is smaller on the cooling scan than on the heating scan (Table 4). The isotropization temperature is 5°C higher than of the corresponding polymethacrylate. It is interesting to observe that the enthalpy change associated with the transition at 131°C is both higher than that of the isotropization temperature and of the first transition ($T_2$) in the heating scan of poly (I-MA) (Table 4, Fig. 1). Although at this time we do not have x-ray diffraction data available, the transition at 131°C could be associated with melting of a crystalline phase. Poly (I-AC) reveals similar liquid crystalline textures to poly (I-MA), i.e., typical smectic textures. Fig. 4 presents some characteristic textures.

Representative DSC traces for poly (II-MA) are shown in Fig. 5 and for poly (II-AC) in Fig. 6. The thermal transitions and the thermodynamic parameters from the first heating and cooling scans are collected in Table 4. The first unexpected result consists in the lower values of Tg compared to those of the I-MA and I-AC polymers. This result cannot be explained based on the difference in the size and weight of the two mesogens. The second unexpected result consists in the influence of the polymer thermal history of its phase transitions (Fig. 5 and Fig. 6). When the polymers are heated only up to above the first (Fig. 5) and respectively, the second transition (Fig. 6) and then cooled, the reheating scans (curves C, Figs. 5 and 6) are similar to the first heating scans (curves A, Figs. 5 and 6). The first three DSC scans can be used to assign phase transitions as previously discussed for poly (I-MA) and poly (I-AC). We can easily conclude that poly (II-MA) presents two liquid crystalline mesophases. At the same time, the first transition of poly (II-AC) is due to melting, and the next two transitions are due to two liquid crystalline mesophases. Figure 7 presents some typical textures for poly (II-AC). There is a similarity in the thermal behavior of both sets of polymers. Both polyacrylates present a crystalline phase followed by one or two liquid crystalline mesophases. Both polymethacrylates present only liquid crystalline mesophases.

On cooling from above the isotropization temperatures, both the cooling and the following heating scans show thermal transitions which appear at much lower temperatures irrespective of the polymer backbone nature, i.e., polyacrylate or polymethacrylate. Thermal annealing within the range of temperatures of any of the liquid crystalline phases brings the next DSC heating trace to an almost identic behavior with the first heating scan. 200 MHz $^1$H-NMR spectrum of the thermal treated samples that present lower phase transitions, demonstrated that the mesogenic unit underwent either trans-cis isomerization or a conformational change which was frozen because of the low polymer mobility. The extent of this isomerization can be followed by the presence of a second signal due to the  $\mathrm{Ph{-}CH}\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$ in cis sequences which appears downfield from the signal of the trans isomer, i.e., trans at $\delta = 5.03$ ppm, cis at $\delta = 5.06$ ppm. At the present time we cannot advance any pure thermal mechanism for a trans-cis isomerization. There are two obvious mechanisms which can explain such an isomerization. The first one would require acidic conditions (27). The second mechanism would require basic conditions to deprotonate the methinic proton. The obtained carbanion can undergo isomerization and therefore, lead to a mixture of cis and trans isomers. Extensive purification of the polymers in order to remove traces of acidic or basic impurities did not change the thermal behavior of these polymers. At the same time several different classes of liquid crystalline polymers containing the same mesogen but presenting thermal transitions at lower temperatures and more flexible polymer backbones did not present this behavior (28). Both GPC and DSC analysis did not reveal any thermal degradation of the polymer during this thermal treatment.

A second possible explanation for this behavior could be due to a frozen rotational isomer which does not display liquid crystallinity. The conformational isomers of 1,3-dioxane were extensively studied and reviewed (27,29-31). There are seven conformational isomers for 1,3-dioxane compounds: chair, half-chair, twist toat, boat, twist boat, half-chair and chair. The difference between the two, chairs, half-chairs and twist boats consists in the axial or equatorial arrangement of their substituents. The two chair conformers are in a dynamic equilibrium and can be distinguished by NMR spectroscopy only at low temperatures. At high temperatures their interchange is too fast. It could be, that due to the rigidity of the polymer backbone the axial trans-chair conformer is frozen on cooling. According to the enthalpy change for the first and second scans, about 50% of the mesogens would be frozen into the trans axial chair conformation. When the polymer is dissolved and its 200 MHz $^1$H-NMR spectrum is recorded, only less than 10% of the second isomer is observed. This would not be unexpected, because of its high mobility in solution. Unfortunately, the chemical shift of the  $-\mathrm{CH}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ proton in the $^1$H-NMR spectra of the cis-isomer and of the trans-axial isomer could be quite similar. Therefore, at this time we cannot discriminate in between conformational and geometrical isomerism as being the cause of this particular thermal behavior, although theoretically the geometrical isomerism can be excluded. Research on this subject is in progress in our laboratory and it will be reported soon.

## Acknowledgements

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## Figure Captions

Figure 1: Normalized DSC thermograms (20°C/min) for poly (I-MA): A) heating scan; B) cooling scan.

Figure 2: Optical polarization micrographs of poly (I-MA) (original magnification: 100x): A) smectic focal-conic texture obtained after 15 hrs of annealing at 137°C; B) same as in A, after cooling to room temperature.

Figure 3: Normalized DSC thermograms (20°C/min) for poly (I-AC): A) heating scan; B) cooling scan.

Figure 4: Optical polarization micrographs of poly (I-AC), (original magnification: 100x): A) smectic focal-conic texture obtained after 21 hrs of annealing at 141°C; B) same as in A after cooling to 122°C at 0.5°C/min; C) same as in B after cooling to room temperature.

Figure 5: Normalized DSC thermograms (20°C/min) for poly (II-MA): A) heating scan up to 150°C; B) cooling scan following scan A; C) heating scan following scan B; D) cooling scan following scan C; E) heating scan following scan D.

Figure 6: Normalized DSC thermograms (20°C/min) for poly (II-AC): A) heating scan up to 160°C; B) cooling scan following scan A; C) heating scan following scan B; D) cooling scan following scan C; E) heating scan following scan D.

Figure 7: Optical polarization micrographs of poly (II-AC) (original magnification: 100x): A) smectic focal-comic texture obtained after 20 hrs of annealing at 163°C; B) same as in A after cooling at 0.5°C/min to 132.5°C; C) same as in B after cooling to 50°C.

## List of Schemes

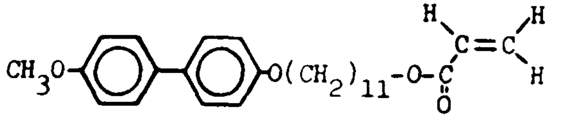
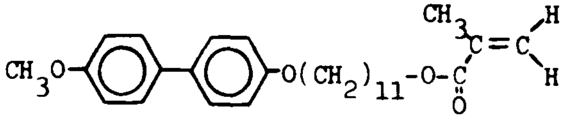
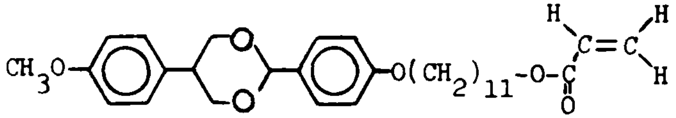
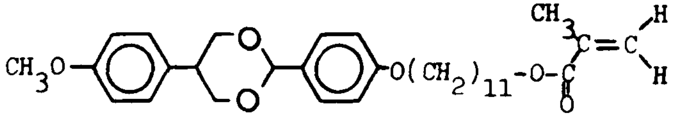
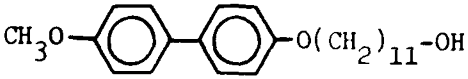
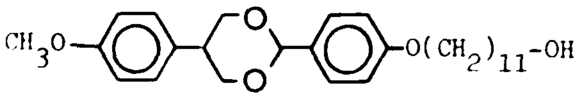
Scheme 1: Synthesis of 2-(p-Hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane.

Scheme 2: Synthesis of methacrylates and acrylates containing 4-methoxy-4'-hydroxybiphenyl and 2-(p-hydroxy-phenyl)-5-(p-methoxyphenyl)-1,3-dioxane mesogens.

Scheme 3: Synthesis of 2,5-disubstituted-1,3-dioxanes.

## TABLE 1

### Characterization of Monomers and Intermediary Compounds

| Compound | 200 MHz $^1$H-NMR ($\delta$,ppm) |
|---|---|
|  (I-AC) | 1.31 to 1.83(m, $-(C\underline{H}_2)_9-$); 3.83(s, $C\underline{H}_3O-$); 3.97(t, $-C\underline{H}_2O-Ph-$); 4.15(t, $-C\underline{H}_2O-\overset{O}{\overset{\|}{C}}-$); 5.80, 6.11 and 6.39(m, $-\underline{CH} = C\underline{H}_2$); 6.95 and 7.46(m, 8 aromatic protons). |
|  (I-MA) | 1.30 to 1.82(m, $-(C\underline{H}_2)_9-$); 1.94(s, $C\underline{H}_3-C = C-$); 3.82(s, $C\underline{H}_3O-$); 3.97(t, $-C\underline{H}_2O-Ph-$); 4.13(t, $-C\underline{H}_2O-\overset{O}{\overset{\|}{C}}-$); 5.53 and 6.09(s, $C\underline{H}_2 = C-$); 6.93 and 7.45(m, 8 aromatic protons). |
|  (II-AC) | 1.30 to 1.80(m, $-(C\underline{H}_2)_9-$); 3.22(m, $-Ph-\overset{C}{\underset{C}{C\underline{H}}}-$); 3.80(s, $-OC\underline{H}_3$); 3.99(t, $-C\underline{H}_2O-Ph$); 4.16(t, $-C\underline{H}_2O-\overset{O}{\overset{\|}{C}}$); 3.97 and 4.50(m, $_2-C\underline{H}_2O-$); 5.54(s, $-Ph-\overset{O}{\underset{O}{C\underline{H}}}$); 5.79 to 6.46(m, $-C\underline{H} = C\underline{H}_2$); 6.89 to 7.47 (m, 8 aromatic protons). |
|  (II-MA) | 1.28 to 1.78(m, $-(CH)_9-$); 1.94(s, $C\underline{H}_3-C = C$); 3.27(m, $-Ph-\overset{C}{\underset{C}{C-\underline{H}}}$); 3.78(s, $-OC\underline{H}_3$); 3.96(t, $-C\underline{H}_2O-Ph-$); 4.12(t, $-C\underline{H}_2O-\overset{O}{\overset{\|}{C}}$); 3.94 and 4.28(m, 2 $-C\underline{H}_2O-$), 5.50 and 6.07(m, $-Ph-\overset{O}{\underset{O}{C\underline{H}}}$ and $-C = C\underline{H}_2$) 6.86 to 7.44(m, 8 aromatic protons). |
|  | 1.15 to 1.83(m, $-(C\underline{H}_2)_9-$); 3.63(t, $-C\underline{H}_2OH$); 3.83(s, $C\underline{H}_3O-$); 3.98(t $-C\underline{H}_2OPh-$); 6.95 and 7.45(m, 8 aromatic protons). |
|  | 1.14 to 1.82(m, $-C\underline{H}_2)_9-$); 3.28(m,$-Ph-\overset{C}{\underset{C}{C\underline{H}}}$); 3.61(t, $-C\underline{H}_2OH$); 3.78(s, $C\underline{H}_3O-$); 3.88 to 4.33(m, $2-C\underline{H}_2O-$ and $-C\underline{H}_2OPh-$); 5.53(s, $-Ph-\overset{O}{\underset{O}{C-\underline{H}}}$) 6.84-7.44(m, 8 aromatic protons). |

## Table 2

Thermal Transitions and Thermodynamic Parameters of Monomers[a]

| Monomer Type | Thermal Transitions ($^{o}$C) and Thermodynamic Parameters: ΔH(kcal/mol); ΔS(cal/mol$^{o}$K) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heating | | | | | | Cooling | | | | | |
| | Tm | ΔHm | ΔSm | Ti | ΔHi | ΔSi | Tc | ΔHc | ΔSc | Ti | ΔHi | ΔSi |
| I-AC | 90 | 5.73 | 15.78 | --- | --- | --- | 78 | 4.92 | 14.02 | --- | --- | --- |
| I-M | 89 | 5.96 | 16.46 | --- | --- | --- | 73 | 5.88 | 16.99 | --- | --- | --- |
| II-AC | 66[c] | 4.55 | 13.42 | 77 | 7.18 | 20.51 | 30 | 0.15 | 0.50 | 47 | 6.42 | 20.06 |
| II-MA | 75[c] | 5.35[b] | --- | 78 | --- | --- | 45 | 5.2[b] | --- | 48 | --- | --- |

a) Determined by DSC at 20$^{o}$C/min; b) overlapped transitions $\Delta H_m = \Delta H_m + \Delta H_i$ and respectively, $\Delta H_c = \Delta H_c + \Delta H_i$; c) transitions obtained from first heating and cooling scans; nematic mesophases; all monomers polymerize during thermal characterization.

## Table 3

### Radical Polymerization of Monomers

| Monomer Type | Conversion % | $\overline{M}n \times 10^{-3}$ | $\overline{M}w \times 10^{-3}$ | $\overline{M}w/\overline{M}n$ |
|---|---|---|---|---|
| I-MA | 85 | 34.7 | 77.6 | 2.24 |
| I-AC | 83 | 8.8 | 12.1 | 1.36 |
| II-MA | 80 | 42.4 | 75.2 | 1.77 |
| II-AC | 65 | 7.4 | 10.0 | 1.34 |

## Table 4

### Thermal Transitions and Thermodynamic Parameters of Polymers

Thermal Transitions ($^{o}C$) and Thermodynamic Parameters:
$\Delta H$ (kcal/mru); $\Delta S$(cal/mru$^{o}$K)

| Polymer Type | Heating | | | | | | | Cooling | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tg | $T_1$ | $\Delta H_1/\Delta S_1$ | $T_2$ | $\Delta H_2/\Delta S_2$ | Ti | ΔHi/ΔSi | $T_1$ | $\Delta H_1/\Delta S_1$ | $T_2$ | $\Delta H_2/\Delta S_2$ | Ti | Hi/ΔSi |
| Poly(I-AC) | 48 | -- | -- | 131[c)] | 3.18/7.87 | 147 | 1.02/2.43 | -- | -- | 103[d)] | 2.89/7.69 | 140 | 1.10/2.66 |
| Poly(I-MA) | 54 | -- | -- | 87 | 0.26/0.72 | 142 | 1.62/3.90 | -- | -- | 81.5 | 0.26/0.73 | 132 | 1.62/4.00 |
| Poly(II-AC) | 32 | 59 | 0.56/1.69 | 116[c)] | 0.35/0.90 | 177 | 0.61/1.36[a)] | 38 | 0.35/1.13 | 99[d)] | 0.15/0.40 | 140 | 0.10/0.24 |
| Poly(II-MA)[a)] | 44 | -- | -- | 127 | 0.36/0.90 | 190 | 0.68/1.47[b)] | -- | -- | 80 | 0.21/0.59 | 124 | 0.36/0.91 |

a) Data from scan C in Figure 6; b) data from scan C in Figure 5;
c) $T_2$ = Tm; d) $T_2 = T_c$.

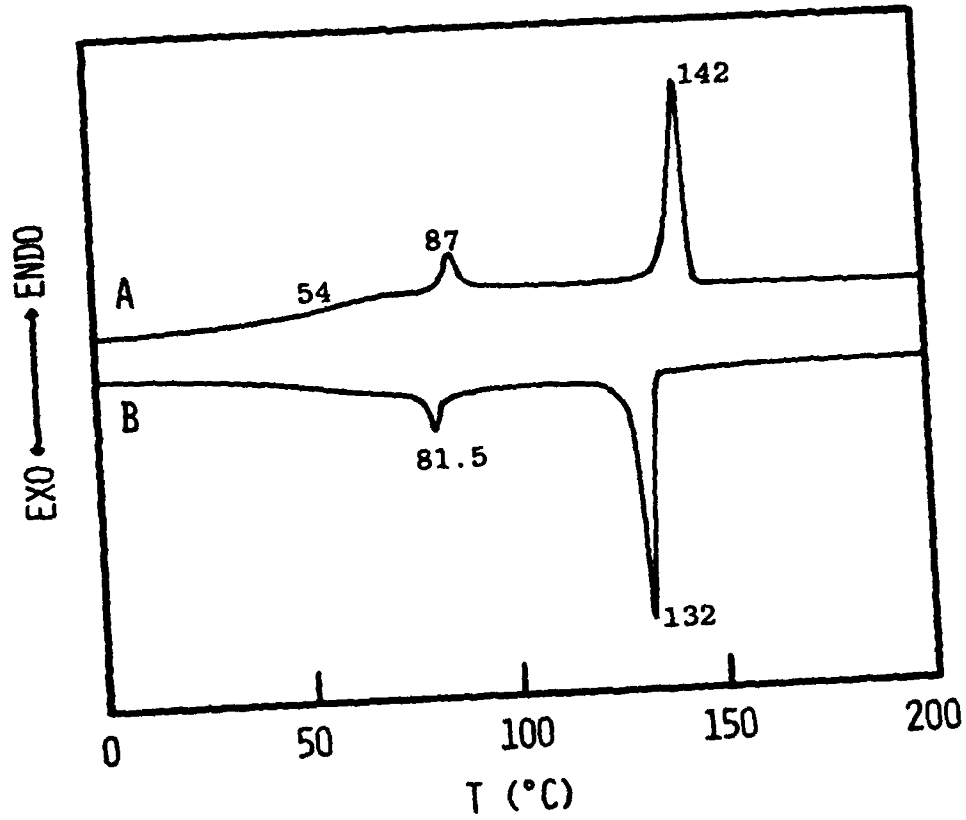


Fig. 1

Fig. 2A

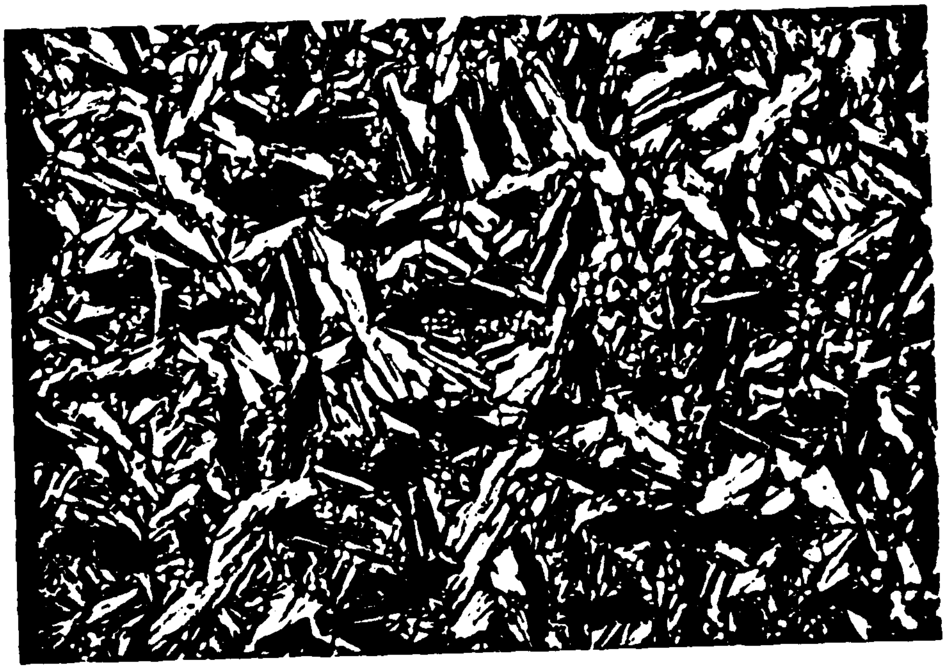


Fig. 2B

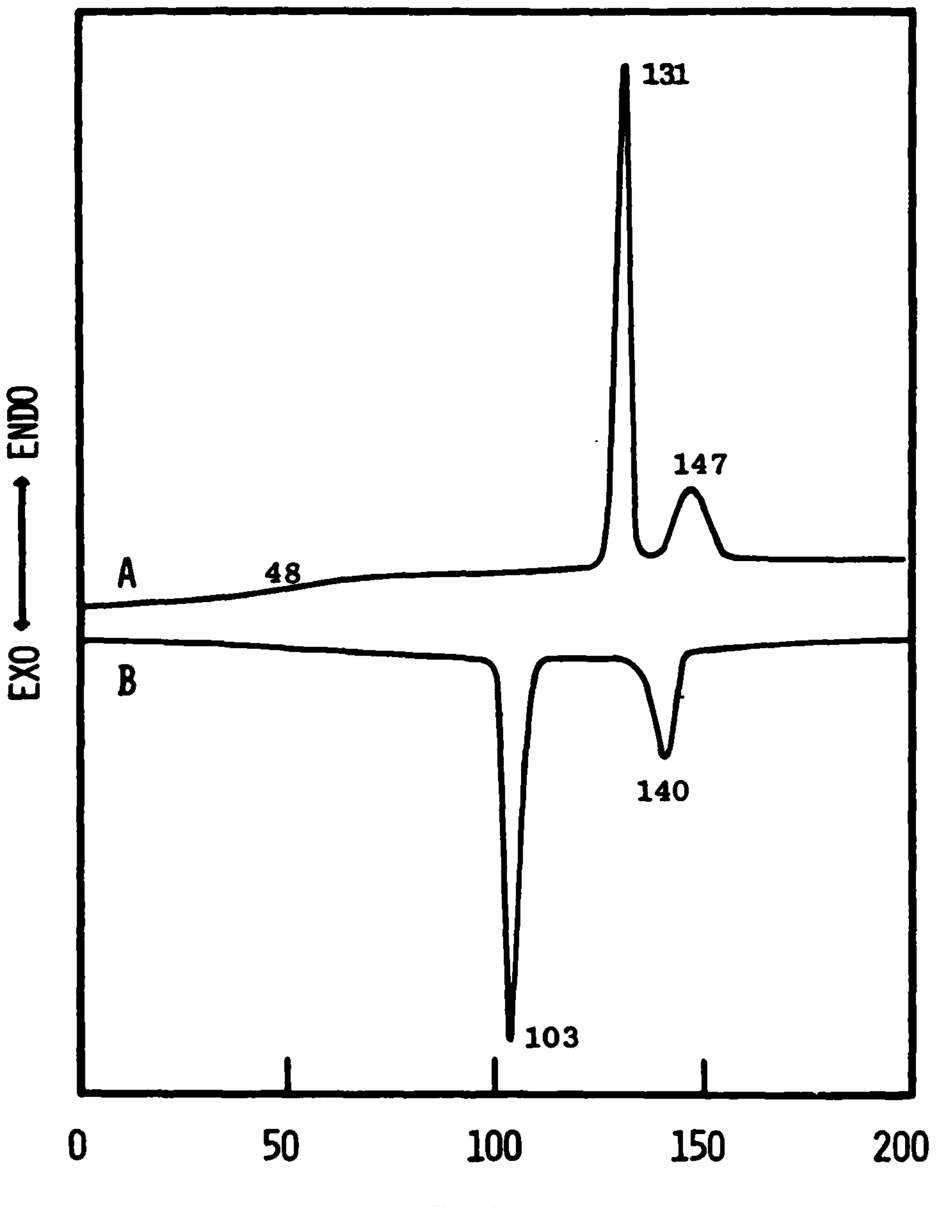


Fig. 3

Fig. 4A

Fig. 4B

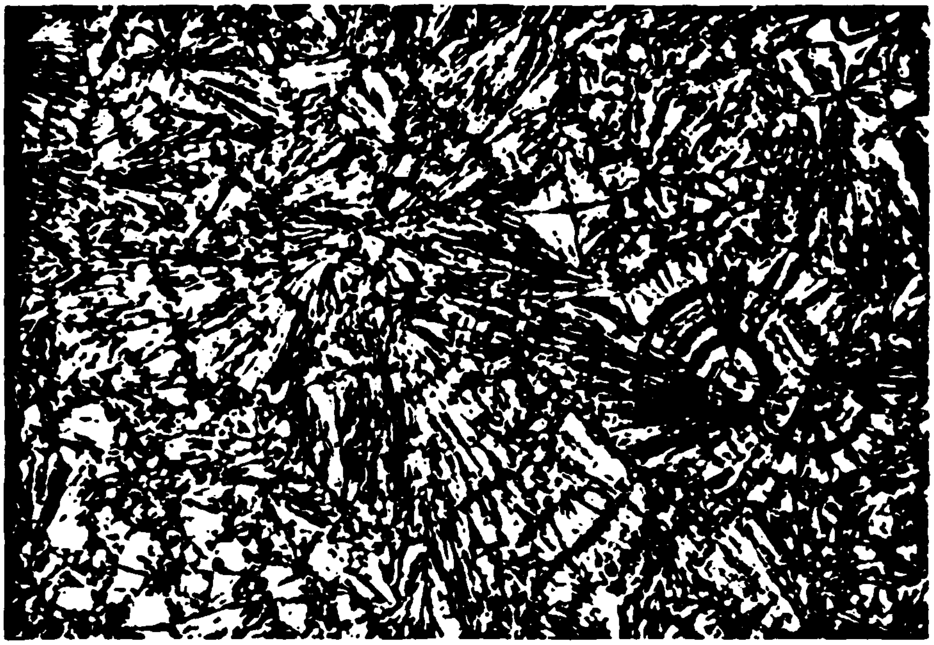


Fig. 4C

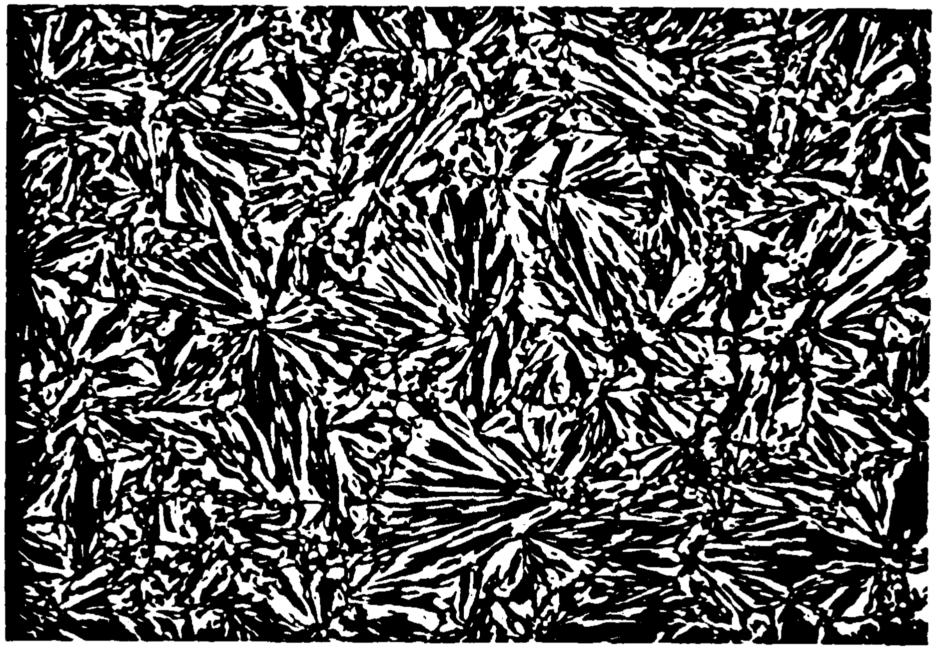


Fig. 7C

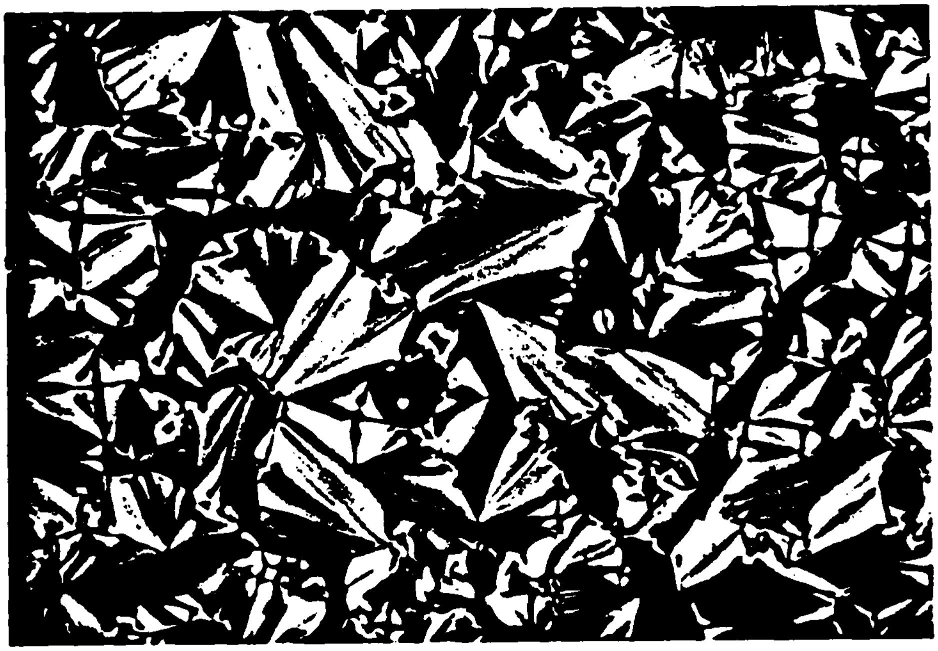


Fig. 7A

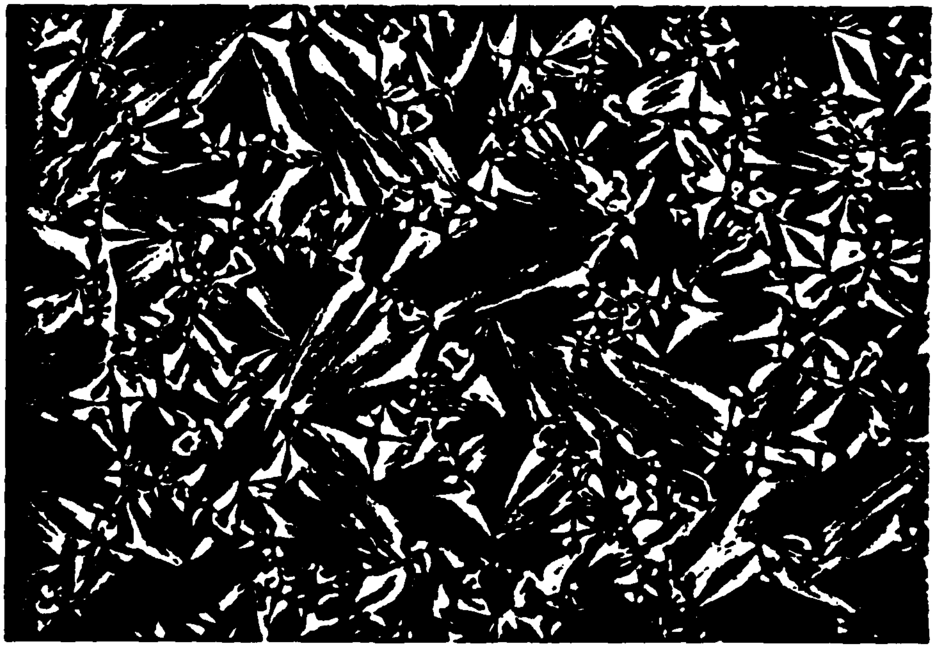
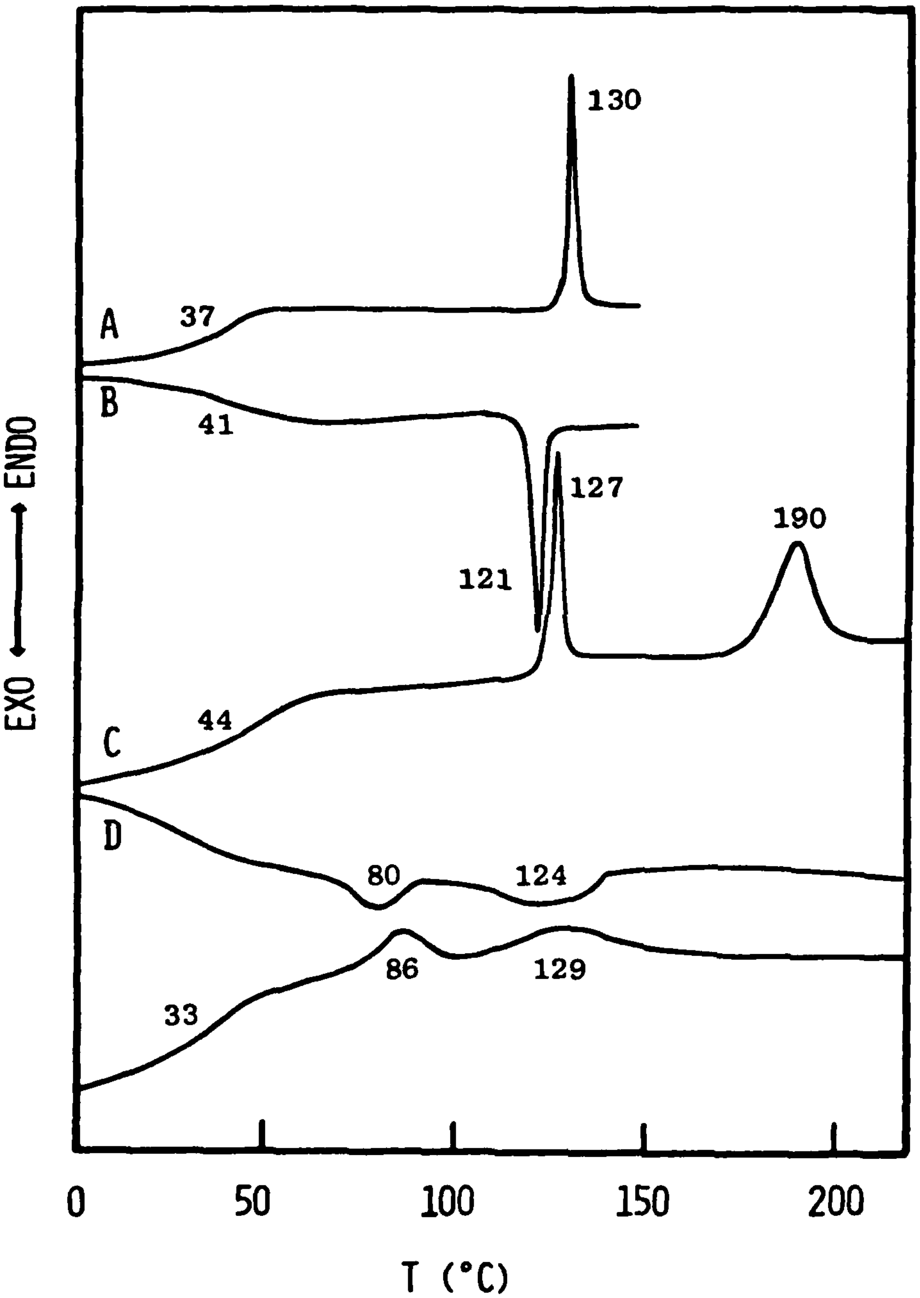


Fig. 7B



130
A
37
B
41
EXO ⟷ ENDO
127
190
121
C
44
D
80
124
86
129
33
0
50
100
150
200
T (°C)

Fig. 5

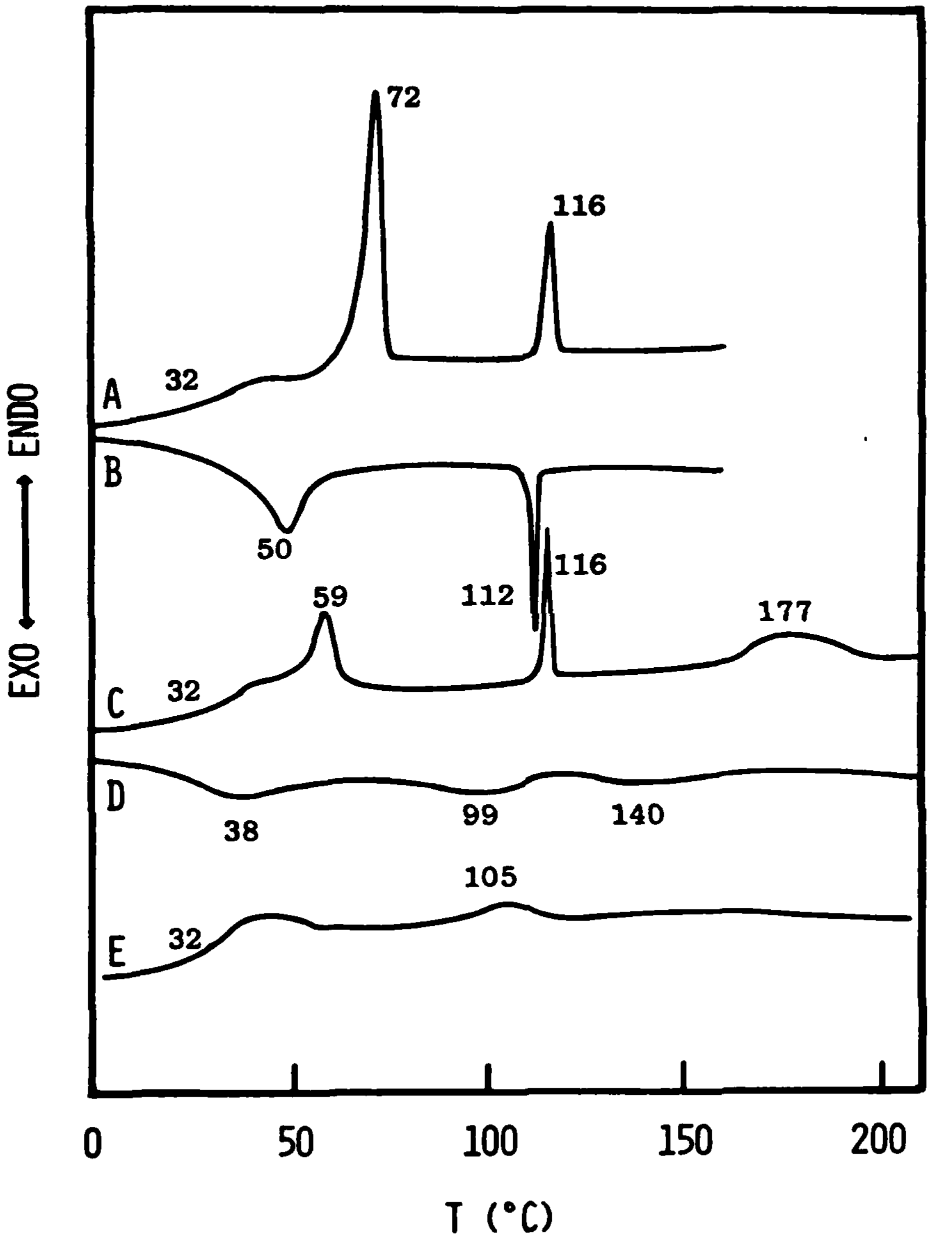
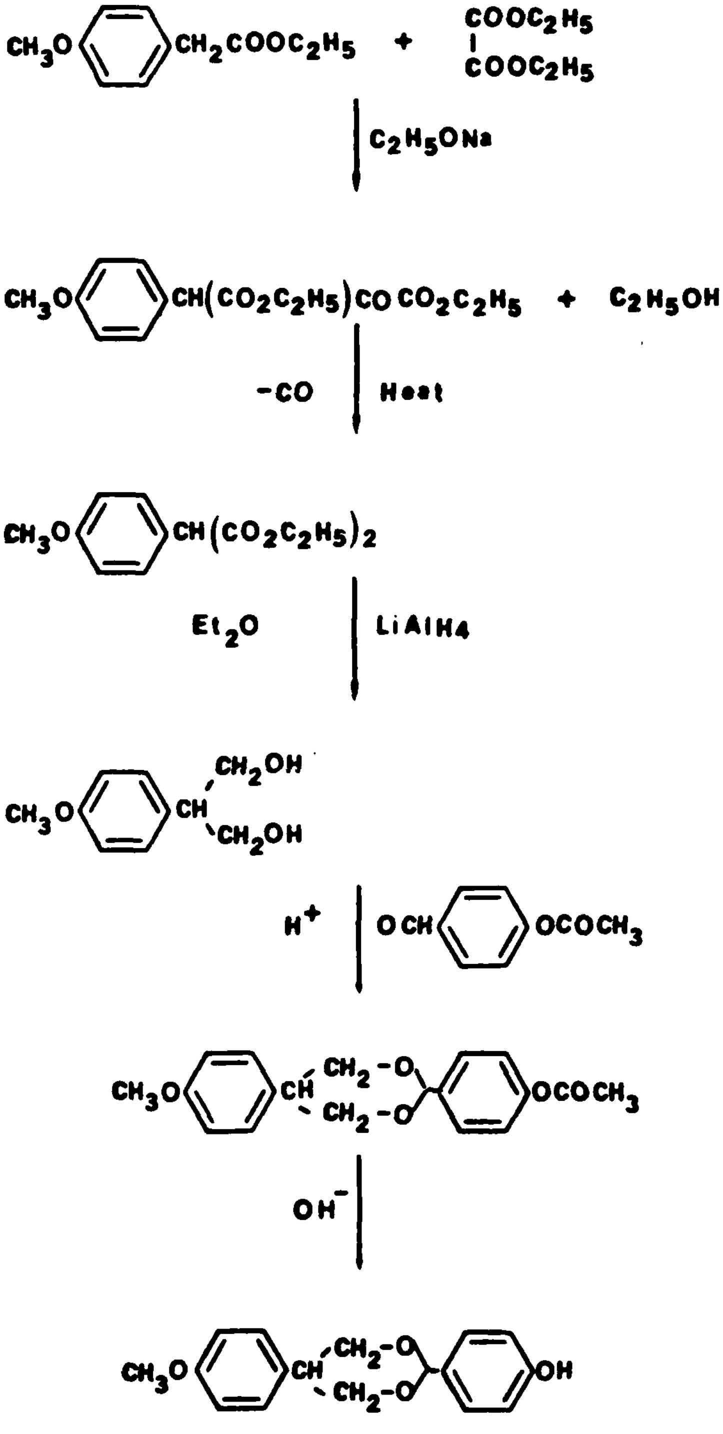
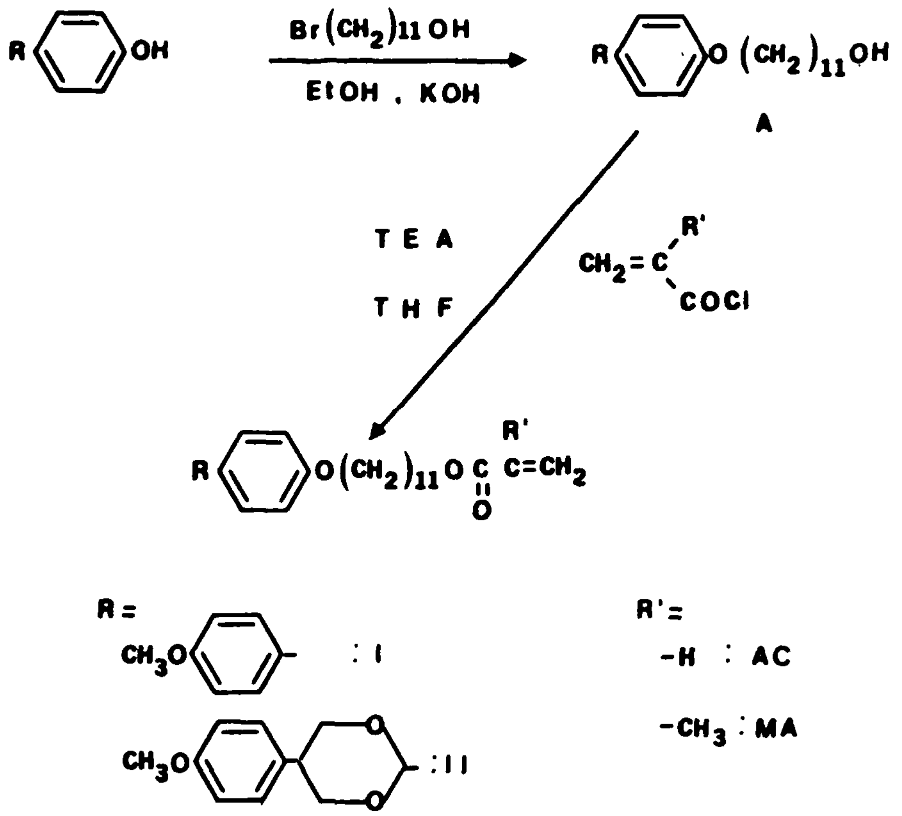

72
116
A
32
B
50
59
112
116
177
C
32
D
38
99
140
105
E
32
EXO ⟷ ENDO
0
50
100
150
200
T (°C)

Fig. 6

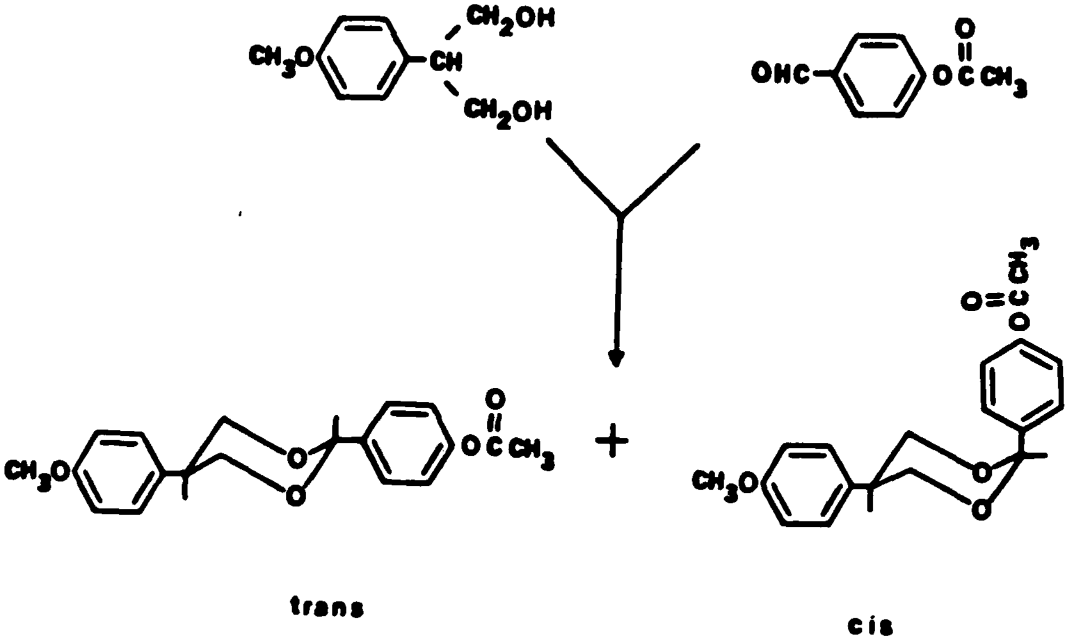


$CH_3O$ … $CH_2COOC_2H_5$ + $COOC_2H_5$ | $COOC_2H_5$
$C_2H_5ONa$
$CH_3O$ … $CH(CO_2C_2H_5)COCO_2C_2H_5$ + $C_2H_5OH$
$-CO$
Heat
$CH_3O$ … $CH(CO_2C_2H_5)_2$
$Et_2O$
$LiAlH_4$
$CH_3O$ … $CH$ $CH_2OH$ $CH_2OH$
$H^+$
$OCH$ … $OCOCH_3$
$CH_3O$ … $CH$ $CH_2-O$ $CH_2-O$ … $OCOCH_3$
$OH^-$
$CH_3O$ … $CH$ $CH_2-O$ $CH_2-O$ … $OH$

Scheme 1


R
OH
Br(CH2)11OH
EtOH . KOH
R
O (CH2)11OH
A
T E A
T H F
CH2=C R' COCl
R
O(CH2)11O C C=CH2
R'
O
R =
CH3O
: I
CH3O
: II
R' =
-H : AC
-CH3 : MA

Scheme 2



Scheme 3

END

1-87

DTIC