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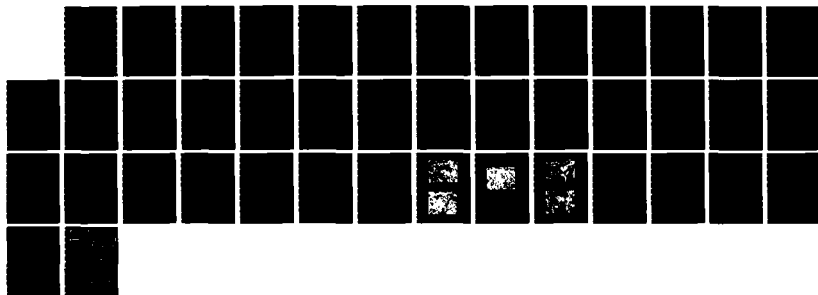
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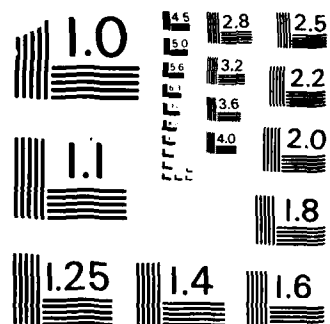
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Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens.

2. Side-Chain Liquid Crystalline Polysiloxanes
Containing 2,5-Disubstituted-1,3-Dioxane Mesogens

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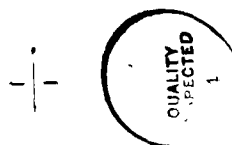
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ABSTRACT

Polysiloxanes and copolysiloxanes containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane and 5-(p-methoxyphenyl)-1,3-dioxan-2-yl as mesogenic units and an aliphatic spacer containing eleven and respectively, ten 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 polysiloxanes and copolysiloxanes containing 4-methoxy-4'-hydroxybiphenyl and 4-cyano-4'-hydroxybiphenyl mesogens attached to the polymer backbone through an aliphatic spacer containing eleven methylene units.

All synthesized polymers present smectic mesomorphism. The polymers containing 4-methoxy-4'-hydroxybiphenyl and 4-cyano-4'-hydroxybiphenyl are also crystalline, while the polymers containing 1,3-dioxane based mesogens do not crystallize.



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Summary

Polysiloxanes and copolysiloxanes containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane and 5-(p-methoxyphenyl)-1,3-dioxan-2-yl as mesogenic units and an aliphatic spacer containing eleven and respectively, ten 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 polysiloxanes and copolysiloxanes containing 4-methoxy-4'-hydroxybiphenyl and 4-cyano-4'-hydroxybiphenyl mesogens attached to the polymer backbone through an aliphatic spacer containing eleven methylene units.

All synthesized polymers present smectic mesomorphism. The polymers containing 4-methoxy-4'-hydroxybiphenyl and 4-cyano-4'-hydroxybiphenyl are also crystalline, while the polymers containing 1,3-dioxane based mesogens do not crystallize.

Introduction

Thermotropic side-chain liquid crystalline polysiloxanes were first synthesized by Finkelmann and Rehage (1) and Ringsdorf and Schneller (2). Since then, nematic, smectic (1-7), cholesteric (8), and elastomeric liquid crystalline networks (9,11) containing polysiloxane backbone have been synthesized. Ringsdorf et. al., (12,13) have recently reported the first examples of liquid crystalline polysiloxanes containing disc-like mesogens as side groups (12,13). The first examples of non-ionic lyotropic liquid crystalline polymers were also prepared with a polysiloxane main chain (14-17). Some of the synthetic work summarized above has been already reviewed (18-20).

Recently, high-temperature mesomorphic polysiloxane "solvents" have demonstrated excellent potential as gas chromatographic stationary phases (21-23).

Interest in the polysiloxane backbone for the preparation of side-chain liquid crystalline polymers, comes from the low glass transition temperature and the high thermal stability exhibited by this class of polymers.

Extensive studies concerning the morphology (24,25), the dielectric relaxation behavior (26-28) and the behavior in electric and magnetic fields (29-32) together with their optical properties (33) revealed a number of additional potential applications, most of them being based on the realization of anisotropic glasses having liquid crystalline properties. Applications based on light modulation can lead to optical filters, reflectors and linear polarizers (33). Of particular interest seems to be the possible use of smectic polysiloxanes for reversible storage of information (34-38).

Progress in this field is mostly based on the availability of suitable polymers presenting low glass transition temperatures and broad thermal stability of the mesophase. Most of the previous classes of liquid crystalline polysiloxanes were prepared with phenylbenzoate mesogens and only recently several polymers with cyano-containing mesogens became available (2,3,6).

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 in designing phase transitions seems to be the replacement of one benzene ring from biphenyl or terphenyl structural units by 1,3-dioxane (39-43) and 1,3-dithiane (44-46) groups.

In the previous paper from this series (47) we presented the synthesis and characterization of several polyacrylates and polymethacrylates based on mesogens containing 2,5-disubstituted-1,3-dioxane units. Prior to our work, there was only one report concerning the synthesis of a liquid crystalline polymer containing a 1,3-dioxane based mesogen (6). The goal of this paper is to present the synthesis and characterization of several liquid crystalline polysiloxanes and copolysiloxanes containing 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane, 2-(p-methoxyphenyl)-1,3-dioxane, 4-methoxy-4'-dihydroxybiphenyl and 4-cyano-4'-hydroxybiphenyl based mesogenic units, and discuss their phase behavior.

Experimental

A. Materials

Poly(methylhydrosiloxane) (\bar{M}_n = 4500-5000) and (30-35%)-methylhydro-(65-70%) dimethylsiloxane (\bar{M}_n = 2000-2100) were obtained from Petrarch Systems Inc., and used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon.

B. Techniques

200 MHz ^1H -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 $20^\circ\text{C}/\text{min}$ unless otherwise specified. Glass transition temperatures (T_g) 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 gave 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 FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. 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 (1 ml/min, 40°C), a set of PL gel columns of 10^2 , $5 \cdot 10^2$, 10^3 , 10^4 and 10^5 Å, and a calibration plot constructed with polystyrene standards.

C. Synthesis of Monomers and Polymers

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) and triethylamine (freshly distilled from KOH) (22.2g, 0.22 mol) in 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 $\text{NEt}_3 \cdot \text{HCl}$, washed with 2% aqueous sodium bicarbonate, water and dried over anhydrous sodium sulfate. The solvent was evaporated in a rotavapor and the residual oil was distilled at 92-93°C/7mm Hg to yield 28g (85%). $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 2.28 (s, 3H, $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}_3$), 7.17-7.85 (m, 4H, $-\text{C}_6\text{H}_4-$), 9.87 (s, 1H, $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=$).

Diethyl-2-p-Methoxyphenylmalonate

A literature procedure which was initially used for the synthesis of ethyl-2-phenylmalonate (48) 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 73 g (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 crystals 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 remaining 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/7mm Hg to yield 92g (70%). ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.23 (t, 6H, -CH₃), 3.77 (s, 3H, -OCH₃), 4.20 (q, 4H, -CH₂-), 4.60 (s, 1H, -CH=), 6.77-7.42 (q, 4H, -C₆H₄-).

2-(p-Methoxyphenyl)-propane-1,3-diol

To a suspension of 3.8g (0.1 mol) of 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 4 ml of ethyl acetate were added to consume the excess of LiAlH_4 . The resulting 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. $83-84^\circ\text{C}$. $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 2.47 (s, 2H, $-\text{OH}$), 3.03 (s, 1H, $-\text{CH}=\text{}$), 3.78 (s, 3H, $-\text{OCH}_3$), 3.91 (s, 4H, $-\text{CH}_2-$), 6.86-7.16 (q, 4H, $-\text{C}_6\text{H}_4-$).

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

2-(p-Methoxyphenyl) propane-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 solution was refluxed until 0.9 ml of water were collected on a Dean-Stark trap. After cooling, the reaction mixture was washed with 2% aqueous solution of sodium bicarbonate, water, dried over anhydrous magnesium sulfate, and then the solvent was evaporated on a rotavapor. The remaining solid was recrystallized from ethanol to yield 12.6g (77%). mp. $155-157^\circ\text{C}$, $^1\text{H-NMR}$, ($(\text{CD}_3)_2\text{CO}$, TMS, δ , ppm): 2.27 (s, 3H, $-\text{COCH}_3$), 3.28 (m, 1H, $-\text{CH}=\text{}$), 3.78 (s, 3H, $-\text{OCH}_3$), $-\text{CH} \begin{array}{l} \text{O-} \\ \text{O-} \end{array}$, 3.91-4.35 (m, 4H, $-\text{OCH}_2-$), 5.56 (s, 1H, $-\text{CH} \begin{array}{l} \text{O-} \\ \text{O-} \end{array}$), 6.86-7.56 (m, 8H, $-\text{C}_6\text{H}_4-$).

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 10g NaOH in 400 ml 90% ethanol. The ethanol was removed from the solution on a rotavapor, and the obtained solid was dissolved in distilled water. The water solution was neutralized with dilute hydrochloric acid and the obtained solid was filtered, dried and recrystallized from toluene to yield 10g (91%). mp. 215°C, ¹H-NMR (DMSO-d₆, δ, ppm): 3.16 (m, 1H, -CH=), 3.37 (s, 1H, -OH), 3.73 (s, 3H, -OCH₃), 3.90-4.18 (m, 4H, -OCH₂-), 5.51 (s, 1H, -CH₂-), 6.73-7.26 (m, 8H, -C₆H₄-).

4-Methoxy-4'-Hydroxybiphenyl

4-Methoxy-4'-hydroxybiphenyl was synthesized after a modified literature procedure (49,50). 4,4'-Dihydroxybiphenyl (100g, 0.54 mol) was dissolved in a solution of 43g (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. (49), mp. 183.5°C).

The synthesis of 4-cyano-4'-hydroxybiphenyl is outlined in Scheme 2.

4-Bromo-4'-nitrobiphenyl

4-Nitrobiphenyl was brominated following a literature procedure (51). A mixture of 4-nitrobiphenyl (45g, 0.23 mol), glacial acetic acid (90 ml) and bromine (22.3g, 0.14 mol) was heated at 100°C for 3.5 hrs., cooled and the obtained solid was filtered off. The product was recrystallized from glacial acetic acid to yield 32g (51%) mp. 173-174°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 7.59-8.44 (m, 8 aromatic protons).

4-Amino-4'-bromobiphenyl

It was synthesized according to a method developed by Gray et. al., (52). A mixture of 4-bromo-4'-nitrobiphenyl (31g, 0.11 mol), iron powder (22g, 0.39 mol), 90% ethyl alcohol (200 ml), and concentrated hydrochloric acid (11 ml) was refluxed at 100°C for 12 hrs. 8.4g of sodium carbonate were added and stirring was continued for 30 minutes, whereafter a slight excess of dilute aqueous ammonia was added. The resulting solution was cooled and extracted with ethyl ether. After the ethyl ether was distilled in a rotavapor at room temperature, the remained alcoholic solution was poured into an equal volume of cold water to precipitate the amine. The product was filtered and dried to yield 26g (93%). mp. 145-146°C. ¹H-NMR ((CD₃)₂CO, δ, ppm): 4.86 (s, 2H, -NH₂), 6.77-7.56 (m, 8 aromatic protons).

4-Bromo-4'-hydroxybiphenyl

The conventional Sandmeyer method used by Gray et. al., (52,53) for the synthesis of 4-bromo-4'-hydroxybiphenyl was modified according to a novel procedure developed for the synthesis of phenols by the decomposition of aromatic diazonium tetrafluoroborates in refluxing trifluoroacetic acid containing potassium trifluoroacetate (54).

4-Amino-4'-bromobiphenyl (20g, 0.08 mol) was dissolved in 700 ml of hot dilute (2%) hydrochloric acid solution. The mixture thus obtained was cooled to 0°C and treated in the usual manner with a solution of sodium nitrite (6g, 0.086 mol) in water (10 ml). After stirring at 0°C for 30 minutes, a solution of sodium tetrafluoroborate (8.9g, 0.081 mol) in water (30 ml) was added, and after another 30 minutes the product was collected by filtration, washed with a small amount of ice-water and then with a large amount of ethyl ether, and dried. Solid potassium carbonate (5.5g, 0.039 mol) was added cautiously at 0°C to trifluoroacetic acid (160 ml) and then the diazonium tetrafluoroborate (26.9g, 0.078 mol) was added all at once. The resulting solution was refluxed (with protection from moisture) until the solution no longer gave a positive test for the diazonium salt (alkaline β -naphthol). The obtained solution was poured into water (450 ml), stirred at room temperature for 1 hr and stored at 0°C for 20 hrs. The formed precipitate was filtered, washed with water, dried and recrystallized from ethanol to yield 17.6g (88%). m.p. 162-164°C [lit. (53)], m.p. 166-167°C.

4-Cyano-4'-hydroxybiphenyl

It was prepared by reacting 4-bromo-4'-hydroxybiphenyl with cuprous cyanide in dimethyl formamide (53,55). A mixture of 4-bromo-4'-hydroxybiphenyl (17g, 0.068 mol) and cuprous cyanide (7.3g, 0.082 mol) in dry dimethylformamide was refluxed at 160°C for 6 hrs. After cooling, the reaction mixture was poured into a mixture of hydrated ferric chloride (27g), concentrated hydrochloric acid (6.8 ml), and water (40 ml), and the resulting mixture was stirred at 60-70°C for 20 minutes. The reaction mixture was extracted with chloroform, and the chloroform solution was successively washed with 5 N hydrochloric acid, 10% aqueous sodium bicarbonate and water, and dried over anhydrous sodium sulfate. Chloroform was evaporated on a rotavapor to yield 8.6g (65%) of crude product. The product was purified by column chromatography on silicagel using a mixture of acetone-hexane (1:5) as solvent. m.p. 195-197°C; [lit. (53): m.p. 196-199]. ¹H-NMR ((CD₃)₂CO, δ, ppm): 3.80 (s, 1H, -OH), 6.98-7.82 (m, 8 aromatic protons).

2-(10-Decylenyl)-5-(p-methoxyphenyl)-1,3-dioxane

2-(p-Methoxyphenyl)-1,3-propanediol (6.0g, 0.033 mol), undecylenic aldehyde (5.0g, 0.03 mol) and p-toluenesulfonic acid (300 mg) were dissolved in 300 ml of dry benzene. The resulting solution was refluxed until 0.54 ml of water were collected on a Dean-Stark trap. After cooling to room temperature, the reaction mixture was washed with 2% sodium bicarbonate, water, dried over MgSO_4 , and the solvent was evaporated on a rotavapor. The obtained solid was recrystallized several times from n-hexane at 0°C to yield 5.5g (55%). m.p. $35-36^\circ\text{C}$. $^1\text{H-NMR}$ chemical shifts are presented in Table 1.

11-Chloro-1-undecene

A mixture containing 34g (0.2 mol) of 11-undecen-1-ol and 35.7g (0.3 mol) of SOCl_2 was stirred for 3 hrs at 40°C . Excess SOCl_2 was distilled off and the resulting product was subjected to a fractional distillation ($85^\circ\text{C}/7\text{ mm Hg}$) to yield 35g of product. The purity of the resulted product was higher than 99% as determined by gas chromatography.

10-Undecylenylethers of 4-methoxy-4'-hydroxybiphenyl, 4-cyano-4'-hydroxybiphenyl and 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane

A typical procedure for their synthesis is described. 4.6g (0.2 mol) of cleanly cut Na was added in portions to 100 ml of absolute ethanol. After the sodium was completely dissolved, 0.02 mol of p-substituted phenol were added, and the alcohol was removed on a rotavapor to separate the sodium salt of the substituted phenol. The dried sodium salt was dissolved in 150 ml of dry

N-methylpyrrolidone and 0.025 mol of 11-chloro-1-undecene were added. The resulting solution was stirred at 110°C under N₂ overnight. The reaction mixture was then poured into water and the precipitated product was filtered, washed with dilute NaOH water solution, dried and purified by column chromatography using CHCl₃ as eluent and silicagel as stationary phase. In all cases the yield was 60-70%. ¹H-NMR chemical shifts are presented in Table I. Table II summarizes the thermal behavior of all olefinic compounds.

Dicyclopentadienylplatinum (II) chloride catalyst

The platinum catalyst was synthesized according to a literature procedure (23,56).

Synthesis of Polymers and Copolymers

1.0g (10 mole% excess versus the Si-H groups present in polysiloxane) of the olefinic derivative was dissolved in 100 ml of dry, freshly distilled toluene together with the proper amount of polymethylhydrosiloxane or (30-35%)-methylhydro-(65-70%)-dimethylsiloxane. The reaction mixture was heated to 110°C under nitrogen, and 100 mg of dicyclopentadienylplatinum (II) chloride catalyst were then injected with a syringe as solution in methylene chloride (1 mg/ml). The reaction mixture was refluxed (110°C) under nitrogen for 24 hrs. After this reaction time both IR and 200 MHz ¹H-NMR analyses showed that the hydrosilation reaction was complete. The white polymers were separated by precipitation in methanol, and purified by several reprecipitations from chloroform solutions into methanol and then dried under

vacuum. The molecular weights of the obtained polymers were determined by GPC and correspond to the expected increase in molecular weight due to hydrosylation reaction.

Results and Discussion

1,3-Dioxane-like cyclic acetals were synthesized by the acid catalyzed condensation of 2-substituted propane-1,3-diols with aldehydes as shown in Scheme 3. Since their synthesis was performed under thermodynamically controlled conditions, a mixture of cis and trans isomers which is rich in the trans isomer usually is obtained. Only the trans isomer presents liquid crystalline properties. The trans isomer is less soluble than the cis isomer and therefore the two isomers can be easily separated by recrystallization.

Scheme 1 outlines the synthetic route followed 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. The analogue of 4-methoxy-4'-alkylbiphenyl (1A from Scheme 4) was synthesized as shown in Scheme 3. 2-(p-Hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane was synthesized from p-acetoxybenzaldehyde and 2-(p-methoxyphenyl)propane-1,3-diol followed by basic hydrolysis of the ester group. Attempts to prepare it directly from p-hydroxybenzaldehyde did not give the expected compound. 200 MHz ^1H -NMR characterization of 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane showed that only the trans isomer was obtained by the routes presented in Scheme 1.

This was not the case in the synthesis of 2-(10-decylenyl)-5-(p-methoxyphenyl)-1,3-dioxane where a mixture of cis and trans isomers was obtained, and several successive recrystallizations were required to separate the two isomers. Figure 1 presents typical 200 MHz ^1H -NMR spectra of the pure trans isomer and of the cis-trans mixture. A mixture of cis and trans isomers is also obtained after the etherification of trans 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane with 11-chloro-1-undecane. Since the cis content was always very small (below 1%) the product was used in the following step without any further purification.

4-Cyano-4'-hydroxybiphenyl was synthesized according to the procedure presented in Scheme 2. The simplest available method for the synthesis of 4-bromo-4'-hydroxybiphenyl is based on the bromination of 4-biphenylbenzene sulfonate followed by the hydrolysis of 4-bromo-4'-benzene sulfonate biphenyl (57). Repeated attempts to reproduce this procedure gave very low yields of impure 4-bromo-4'-hydroxybiphenyl. These results are in agreement with the data reported by Gray et. al., (52,53) on their attempts to reproduce this reaction.

The synthetic procedure outlined in Scheme 2 is based on a modification of a literature procedure (52,53). The least reproducible step according to this method (52,53) consisted in the transformation of 4-bromo-4'-aminobiphenyl into 4-bromo-4'-hydroxybiphenyl through a conventional Sandmeyer reaction. Repeated attempts to improve this step lead to orange colored products which are the result of an impurity appearing from the coupling of the 4-bromo-4'-hydroxyphenyl with the diazonium salt. Consequently, this step was modified according

to a more recent literature method (54) proposed for the synthesis of phenols, i.e., by the decomposition of 4-bromo-4'-diazoniumbiphenyl tetrafluoroborate in refluxing trifluoroacetic acid containing potassium trifluoroacetate. 4-Bromo-4'-hydroxybiphenyl obtained by this method was always white, free of coupling side products and was obtained with high yields.

Scheme 4 presents the last step in the synthesis of liquid crystalline polysiloxanes. All the olefinic derivatives (1A, 1B, 1C, 1D) containing mesogenic groups were characterized by DSC and their thermal behavior is summarized in Table 2. The compounds 1A, 1B, and 1D present enantiotropic liquid crystalline properties. 1C is only crystalline. Compound 1B presents two enantiotropic mesophases, S_B and N, and a monotropic S_G phase. Figure 2 presents some typical textures exhibited by 1B. 1D presents a S_A mesophase and a very narrow nematic mesophase. Two representative textures are shown in Figure 3.

Table III summarizes all thermal transitions and the corresponding thermodynamic parameters obtained for the synthesized polysiloxanes. Thermal transitions were assigned based on the data obtained on heating and cooling DSC scans. Melting and crystallizations could be discriminated from the liquid crystalline and isotropization transitions quite easily. Liquid crystalline and isotropization transitions are only slightly supercooled on the cooling scan and the enthalpy change associated with such a transition is not dependent on the scan it is calculated from. At the same time, crystallization temperature is supercooled versus the corresponding melting transition, and the crystallization enthalpy is lower than the melting enthalpy (Table III). Also after quenching a crystalline polymer, the following heating scan presents always a cold crystallization exotherm which precedes the melting transition.

It is well documented that the mesophase formed by a side chain liquid crystalline polymer is more organized than the one exhibited by the corresponding monomeric compound. At the same time, spacers containing more than six methylene units tend to give crystalline side-chain liquid crystalline polymers (18,19). Therefore, most of the work performed with side chain liquid crystalline polymers was performed with short spacers.

It is quite interesting to mention that both homopolymers based on trans 1,3-dioxane mesogens (2A, 2B) are amorphous liquid crystalline polymers (Table III). At the same time the copolymer 3B is crystalline, while 3A does not crystallize. The behavior of 2B is in contrast to that of the corresponding homopolymers containing the terphenyl mesogen which always gives crystalline liquid crystalline polymers (23). Figure 4 illustrates some representative DSC traces for both 2B and 3B.

Thermal characterization of the homopolymers 2C and 2D and of the copolymers 3C and 3D leads to an expected behavior. The two homopolymers are crystalline, and both on heating and cooling they present two liquid crystalline mesophases (Table III).

Table IV compares the thermal behavior of 2C with the thermal behavior of other polysiloxanes containing the same mesogen (1). As it is shown by these data the homologous polymers containing three and respectively four methylene units in the spacer are crystalline only.

Table V presents the thermal behavior and the isotropization enthalpy for the available polysiloxanes containing 4-cyano-4'-hydroxybiphenyl mesogen (3,6). These data follows the expected trend. T_g values are constantly decreasing with the increase in the spacer length. The polymers with up to six methylene units in the spacer are amorphous, while 3D is crystalline. The isotropization temperature follows an odd-even effect when the data from reference 6 are compared, while the isotropization enthalpy is constantly increasing. This last trend might assume that the highest degree of order in the liquid crystalline mesophase is obtained for the longest spacer.

The copolymers 3C and 3D present dissimilar behavior. While 3C does not crystallize, 3D is crystalline, but the melting transition dropped to room temperature, and the glass transition temperature to -27.2°C. For all other copolymers we could not detect a glass transition temperature up to as low as -70°C, and this is not unexpected for low molar mass polymers presenting smectic mesomorphism.

The most important conclusion obtained from these results seems to be that trans-2,5-disubstituted-1,3-dioxane based mesogens can be used to synthesize side-chain liquid crystalline homopolymers which do not crystallize even when the spacer is very long. Preliminary x-ray diffraction data support these results. This is quite important since the decoupling of the mesogen is strongly affected by the spacer length. This result could be due to the nonlinear but planar structure of the mesogenic unit as illustrated in Scheme 3.

Acknowledgements

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References

1. H. Finkelmann and G. Rehage, Makromol. Chem, Rapid Commun., 1, 31 (1980).
2. H. Ringsdorf and A. Schneller, Br. Polym. J., 13, 43 (1981).
3. H. Ringsdorf and A. Schneller, Makromol. Chem., Rapid Commun., 3, 557 (1982).
4. H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 1, 733 (1980).
5. H. Stevens, G. Rehage and H. Finkelmann, Macromolecules, 17, 851 (1984).
6. P.A. Gemmell, G.W. Gray and D. Lacey, Mol. Cryst. Liq. Cryst., 122, 205 (1985).
7. G.W. Gray, D. Lacey, G. Nestor and M.S. White, Makromol. Chem., Rapid Commun., 7, 71 (1986).
8. H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 3, 859 (1982).
9. H. Finkelmann, H.J. Kock and G. Rehage, Makromol. Chem., Rapid Commun., 2, 317 (1981).
10. H. Finkelmann, H.J. Kock, W. Gleim and G. Rehage, Makromol. Chem., Rapid Commun., 5, 287 (1984).
11. H.J. Kock, H. Finkelmann, W. Gleim and G. Rehage, in "Polymeric Liquid Crystals", Plenum Press, A. Blumstein Ed., New York, 1985, p. 275.
12. W. Kreuder and H. Ringsdorf, Makromol. Chem., Rapid Commun., 4, 807 (1983).
13. M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H.W. Schmidt and P. Tschirner, Pure Appl. Chem., 57, 1009 (1985).
14. H. Finkelmann, B. Luhmann and G. Rehage, Colloid Polym. Sci., 260, 56 (1982).
15. B. Luhmann, H. Finkelmann and G. Rehage, Angew. Makromol. Chem., 123/124, 217 (1984).
16. H. Finkelmann, B. Luhmann, G. Rehage and H. Stevens, in "Liquid Crystals and Ordered Fluids", vol. 4, A.C. Griffin and J.E. Johnson, Eds., Plenum Press, New York, 1984, p. 715.

17. B. Luhmann, H. Finkelmann and G. Rehage, *Makromol. Chem.*, 186, 1059 (1985).
18. H. Finkelmann and G. Rehage, *Adv. Polym. Sci.*, 60/61, 99 (1984).
19. V.P. Shibaev and N.A. Plate, *Adv. Polym. Sci.*, 60/61, 173 (1984).
20. H. Finkelmann, *Phil. Trans. R. Soc. Lond.*, A309, 105 (1983).
21. B.A. Jones, J.S. Bradshaw, M. Nishioka and M.L. Lee, *J. Org. Chem.*, 49, 4947 (1984).
22. G.M. Janini, R.J. Lamb and T.J. Shaw, *Makromol. Chem., Rapid Commun.*, 6, 57 (1985).
23. M.A. Apfel, H. Finkelmann, G.M. Janini, R.J. Lamb, B.H. Luhmann, A. Price, W.L. Roberts, T.J. Shaw and C.A. Smith, *Anal. Chem.*, 57 651 (1985).
24. P. Zugenmaier, *Makromol. Chem., Suppl.*, 6, 31 (1984).
25. P. Zugenmaier and J. Mugge, *Makromol. Chem., Rapid Commun.*, 5, 11 (1984).
26. G.S. Attard and G. Williams, *Polymer Commun.*, 27, 2 (1986).
27. G.S. Attard and G. Williams, *Polymer Commun.*, 27, 66 (1986).
28. G.S. Attard, G. Williams, G.W. Gray, D. Lacey and P.A. Gemmel, *Polymer*, 27, 185 (1986).
29. H. Finkelmann, H.J. Kock and G. Rehage, *Mol. Cryst. Liq. Cryst.*, 89, 23 (1982).
30. H. Finkelmann, H. Benthack and G. Rehage, *J. Chim. Phys.*, 80, 163 (1983).
31. H. Finkelmann, U. Krichle and G. Rehage, *Mol. Cryst. Liq. Cryst.*, 94, 343 (1983).
32. R.E. Goozner and H. Finkelmann, *Makromol. Chem.*, 186, 2407 (1985).
33. H. Finkelmann and H.J. Kock, *Displ. Technol.*, 1, 81 (1985).
34. R. Simon and H.J. Coles, *Mol. Cryst. Liq. Cryst., Letters*, 102, 43 (1984).
35. H.J. Coles and R. Simon, *Mol. Cryst. Liq. Cryst., Letters*, 102, 78 (1984).
36. H.J. Coles and R. Simon, *Polymer*, 26, 1801 (1985).
37. H.J. Coles and R. Simon, in "Recent Advances in Liquid Crystalline Polymers", L.L. Chapoy Ed., Elsevier Appl. Sci. Publ., London and New York, 1985, p. 323.

38. H.J. Coles and R. Simon, in "Polymeric Liquid Crystals", Plenum Press, A. Blumstein Ed., New York, 1985, p. 351.
39. H. Sorkin, Mol. Cryst. Liq. Cryst., Letters, 56, 279 (1980).
40. H.M. Vorbrodt, S. Deresch, H. Kresse, A. Wiegeleben, D. Demus and H. Zaschke, J. Prakt. Chemie., 323, 902 (1981).
41. H. Zaschke, A. Isenberg and H.M. Vorbrodt, in "Liquid Crystals and Ordered Fluids", vol. 4, A.C. Griffin and J.F. Johnson, Eds., Plenum Press, New York, 1984, p. 75.
42. M.M. Murza, M.G. Safarov and G.N. Miftakhova, Zh. Org. Khim., 21, 1550 (1980), Engl. Transl., J. Org. Chem., U.S.S.R., 1985, p. 1412.
43. K. Seto, S. Takahashi and T. Tahara, J. Chem. Soc., Chem. Commun., 1985, p. 122.
44. Y. Haramoto and H. Kamogawa, J. Chem. Soc., Chem. Commun., 1983, p. 75.
45. Y. Haramoto, A. Nobe and H. Kamogawa, Bull. Chem. Soc. Jpn., 57, 1966 (1984).
46. Y. Haramoto, K. Akazawa and H. Kamogawa, Bull. Chem. Soc. Jpn., 57, 3173 (1984).
47. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec, Makromol. Chem., submitted.
48. R. Adams and H.O. Calvery, Org. Synth., Coll. vol. II, A.H. Blatt, Ed., J. Wiley, New York, 1966, p. 288.
49. J.V. Alpern, Rec. Trav. Chim., 50, 657 (1931).
50. J.M. Rodriguez-Parada and V. Percec, J. Polym. Sci., Polym. Chem. Ed., 24, 1363 (1986).
51. R.J.W. LeFevre and E.E. Turner, J. Chem. Soc., 1926, 2045.
52. G.W. Gray, J.B. Hartley and B. Jones, J. Chem. Soc., 1952, 1959.
53. G.W. Gray, K.J. Harrison, J.A. Nash, J. Constant, D.S. Hulme, J. Kirton and E.P. Raynes, in "Ordered Fluids and Liquid Crystals", vol. II, R.S. Porter and J.F. Johnson, Eds., Plenum Press, New York, 1974, p. 617.
54. D.E. Horning, D.A. Ross and J.M. Muchowski, Can. J. Chem., 51, 2347 (1973).

55. L. Friedman and H. Shechter, J. Org. Chem., 26, 2522 (1961).
56. M.S. Kharasch and T.A. Ashford, J. Am. Chem. Soc., 58, 1733 (1936).
57. S.E. Hazlet, J. Am. Chem. Soc., 59, 1087 (1937).

Figure Captions

- Figure 1: 200 MHz ^1H -NMR spectrum of: A) trans 2-(10-decylenyl)-5-(p-methoxyphenyl)-1,3-dioxane; B) a mixture of cis and trans 2-(10-decylenyl)-5-(p-methoxyphenyl)-1,3-dioxane.
- Figure 2: Typical optical polarized micrographs (x100) of trans-1B: A) nematic texture at 120°C on cooling scan; B) S_B texture at 80°C on cooling scan; C) S_G texture at 70°C on cooling scans.
- Figure 3: Typical optical polarized micrographs (x100) of 1D: A) nematic texture at 70.8°C on cooling scan; B) S_A texture at 60°C on cooling scan.
- Figure 4: Normalized DSC thermograms (heating rate = $20^\circ\text{C}/\text{min}$ both on heating and cooling) of polysiloxanes containing 2,5-disubstituted-1,3-dioxane: A) homopolymer 2B, heating scan; B) homopolymer 2B, cooling scan; C) copolymer 3B heating scan; D) copolymer 3B cooling scan.

List of Schemes

- Scheme 1: Synthesis of 2-(p-hydroxyphenyl)-5-(p-methoxyphenyl)-1,3-dioxane.
- Scheme 2: Synthesis of 4-cyano-4'-hydroxybiphenyl.
- Scheme 3: Synthesis of 2,5-disubstituted-1,3-dioxane derivatives.
- Scheme 4: Synthesis of polysiloxanes and copolysiloxanes.

Table I

¹H-NMR Chemical Shifts for Vinyl Derivatives

Compound	Solvent	Chemical Shift (δ, ppm)
1A	CDCl ₃	1.31-2.06 (m, 16H, $-(CH_2)_8-$), 3.14 (m, 1H, $-CH=$), 3.70-4.20 (m, 7H, $-OCH_2-$, $-OCH_3$), 4.57 (t, 1H, $-CH=$), 4.97 (m, 2H, $=CH_2$), 6.63 (m, 1H, $=CH-$), 6.83-7.11 (q, 4H, $-C_6H_4-$).
1B	CDCl ₃	1.31-2.06 (m, 16H, $-(CH_2)_8-$), 3.29 (m, 1H, $-CH=$), 3.80 (s, 3H, $-OCH_3$), 3.91-4.34 (m, 4H, $-OCH_2-$), 4.96 (m, 2H, $=CH_2$), 5.52 (s, 1H, $-CH=$), 5.82 (m, 1H, $=CH-$), 6.86-7.44 (m, 8H, $-C_6H_4-$).
1C	CDCl ₃	1.28-2.08 (m, 16H, $-(CH_2)_8-$), 3.81 (s, 3H, $-OCH_3$), 3.96 (s, 2H, $-OCH_2-$), 4.95 (m, 2H, $=CH_2$), 5.80 (m, 1H, $=CH-$), 6.90-7.47 (m, 8H, $-C_6H_4-$).
1D	CDCl ₃	1.31-2.06 (m, 16H, $-(CH_2)_8-$), 4.0 (t, 2H, $-OCH_2-$), 4.96 (m, 2H, $=CH_2$), 5.80 (m, 1H, $=CH-$), 6.97-7.68 (m, 8H, $-C_6H_4-$).

Table II

Thermal Transitions and Thermodynamic Parameters of Olefinic Derivatives

Thermal Transitions, ($^{\circ}\text{C}$) and Thermodynamic Parameters, $\Delta\text{H}(\text{kcal/mru})$, $\Delta\text{S}(\text{cal/mru.}^{\circ}\text{K})$											
Compound (from Scheme 4)	Heating				Cooling						
	T_1 $\frac{\Delta H_1}{\Delta S_1}$	T_2 $\frac{\Delta H_2}{\Delta S_2}$	T_1 $\frac{\Delta H_1}{\Delta S_1}$	T_1 $\frac{\Delta H_1}{\Delta S_1}$	T_1 $\frac{\Delta H_1}{\Delta S_1}$	T_2 $\frac{\Delta H_2}{\Delta S_2}$	T_3 $\frac{\Delta H_3}{\Delta S_3}$	T_1 $\frac{\Delta H_1}{\Delta S_1}$			
1A	--	35.0	N	36.1	--	-2.0	--	N	1.0		
	--	7.26/- ^a	--	--	--	5.38/- ^a	--	-	--		
1B ^b	94.3	S _B	96.5	N	133.6	68.7	S _G	72.30	S _B	93.5	N
	8.1- ^c	--	--	0.16/0.39	--	6.74- ^c	--	1.0/2.72	0.23/0.56		
1C	--	--	--	106.8	--	--	--	--	95.6		
	--	--	--	14.8/38.7	--	--	--	--	14.3/38.8		
1D	58.06	S _A	74.3	N	75.3	28.2	S _A	70.4	N	--	71.4
	7.94/23.99	0.57/- ^a	--	--	6.42/21.3	0.59/- ^a	--	--	--		--

a) overlapped transitions, $\Delta\text{H}_2 = \Delta\text{H}_1 + \Delta\text{H}_i$ b) heating and cooling rate: 5°C/min c) overlapped transitions, $\Delta\text{H}_1 = \Delta\text{H}_i + \Delta\text{H}_2$

Table III

Thermal Transitions and Thermodynamic Parameters of Polymers and Copolymers

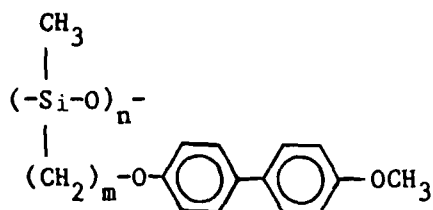
Thermal Transitions; ($^{\circ}\text{C}$) and Thermodynamic Parameters; $\Delta\text{H}(\text{kcal/mru})$, $\Delta\text{S}(\text{cal/mru}\cdot\text{K})$

Polymers and Copolymers	T_g	Heating				Cooling			
		T_1	$\Delta\text{H}_1/\Delta\text{S}_1$	T_2	$\Delta\text{H}_2/\Delta\text{S}_2$	T_1	$\Delta\text{H}_1/\Delta\text{S}_1$	T_2	$\Delta\text{H}_2/\Delta\text{S}_2$
2A	-7.0	--	--	84.0	1.22/- ^a	92.6	--	84.0	--
2B	44.0	--	--	76.1	0.17/0.49	158.4	0.30/0.71	153.0	0.27/0.63
2C	60.0	98.6 ^m	0.21/0.58	111.3	0.77/2.00	154.2	1.41/3.30	146.8	1.41/3.36
2D	-1.0	--	--	47.5 ^m	1.65/5.15	157.4	0.85/1.97	150.3	0.84/1.99
3A	--	--	--	27.0	1.13/- ^a	32.8	--	24.8	--
3B	--	73.3 ^m	1.79/5.18	111.0	0.17/0.45	143.3	0.63/1.52	126.3	0.27/0.68
3C	--	50.0	0.44/1.37	100.0	3.34/- ^a	109.0	--	95.0	--
3D	-27.2	--	--	21.9 ^m	0.85/2.88	85.1	0.67/1.86	81.9	0.67/1.88

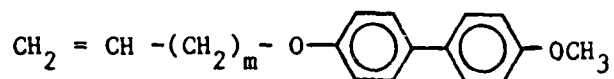
a) overlapped transitions, $\Delta\text{H}_2 = \Delta\text{H}_2 + \Delta\text{H}_1$; m) melting; c) crystallization.

Table IV

Characterization of Polysiloxanes Containing
4-Methoxy-4'-hydroxybiphenyl and of Corresponding Monomers



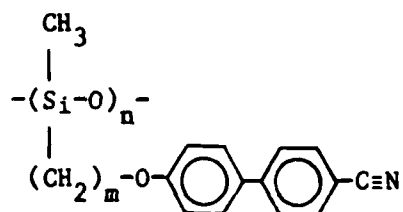
Polymer (m)	Thermal Transitions ($^{\circ}\text{C}$)				Reference
	T_g	T_m	T_1	T_1	
3	--	125	--	--	(1)
4	--	123	--	--	(1)
11	60	98.6	111.3	154.2	(present results)



(m)	T_m ($^{\circ}\text{C}$)	Reference
1	119	(1)
2	116	(1)
9	106.8	(present results)

Table V

Characterization of Polysiloxanes Containing 4-Cyano-4'-Hydroxybiphenyl



Polymer (m)	Thermal Transitions ($^{\circ}\text{C}$)					Reference
	T_g	T_m		T_i	ΔH_i (kcal/mru)	
3	40	--	S_A	152	0.30	(6)
3	32	--	S_A	117	--	(3)
4	28	--	S_A	132.5	0.25	(6)
5	14.5	--	S_A	169.2	0.42	(6)
5	16.0	--	S_A	152.0	--	(3)
6	13.5	--	S_A	165.5	0.44	(6)
11	-1.0	47.5	S_A	157.4	0.85	(present results)

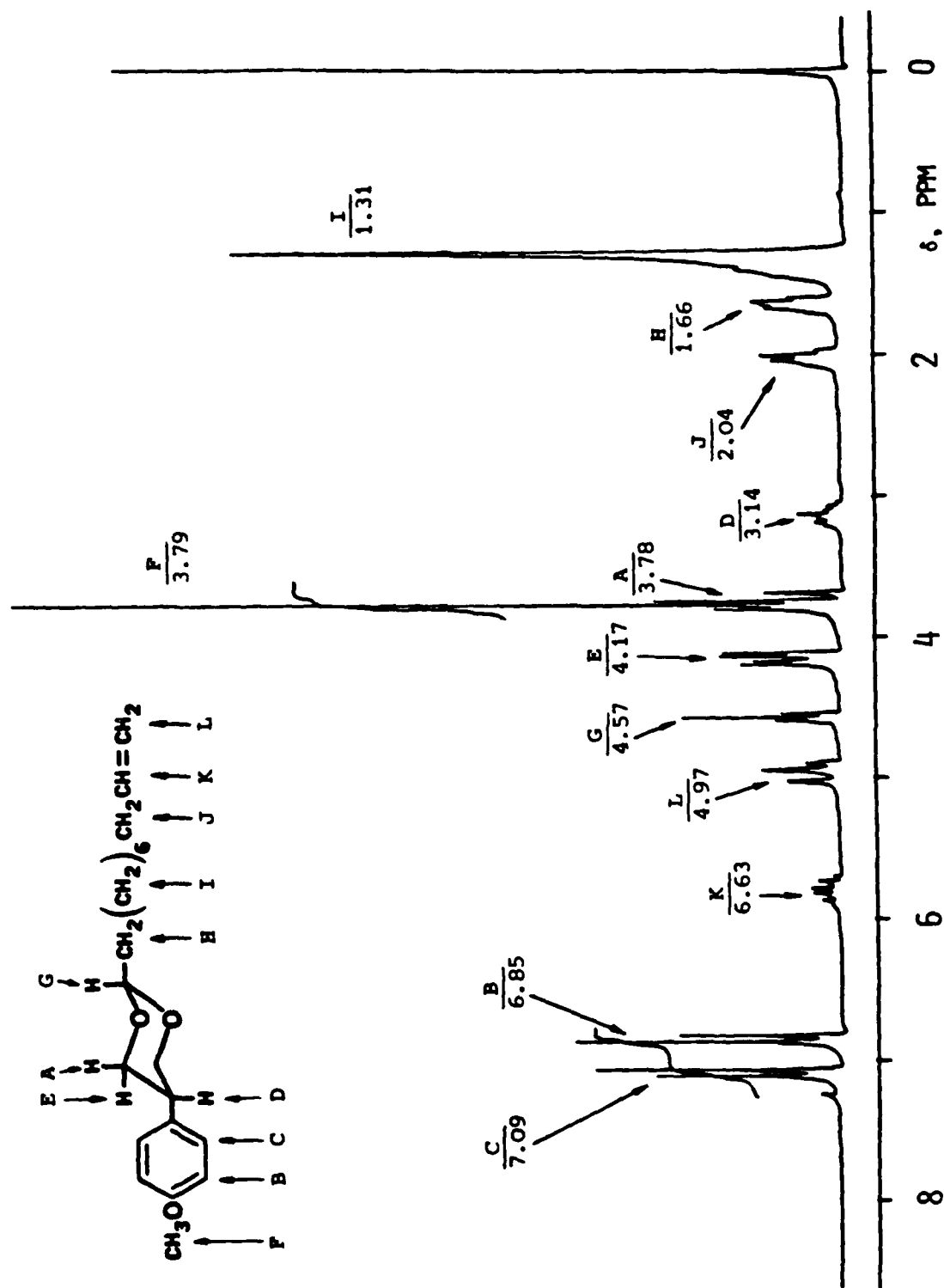


Figure 1A

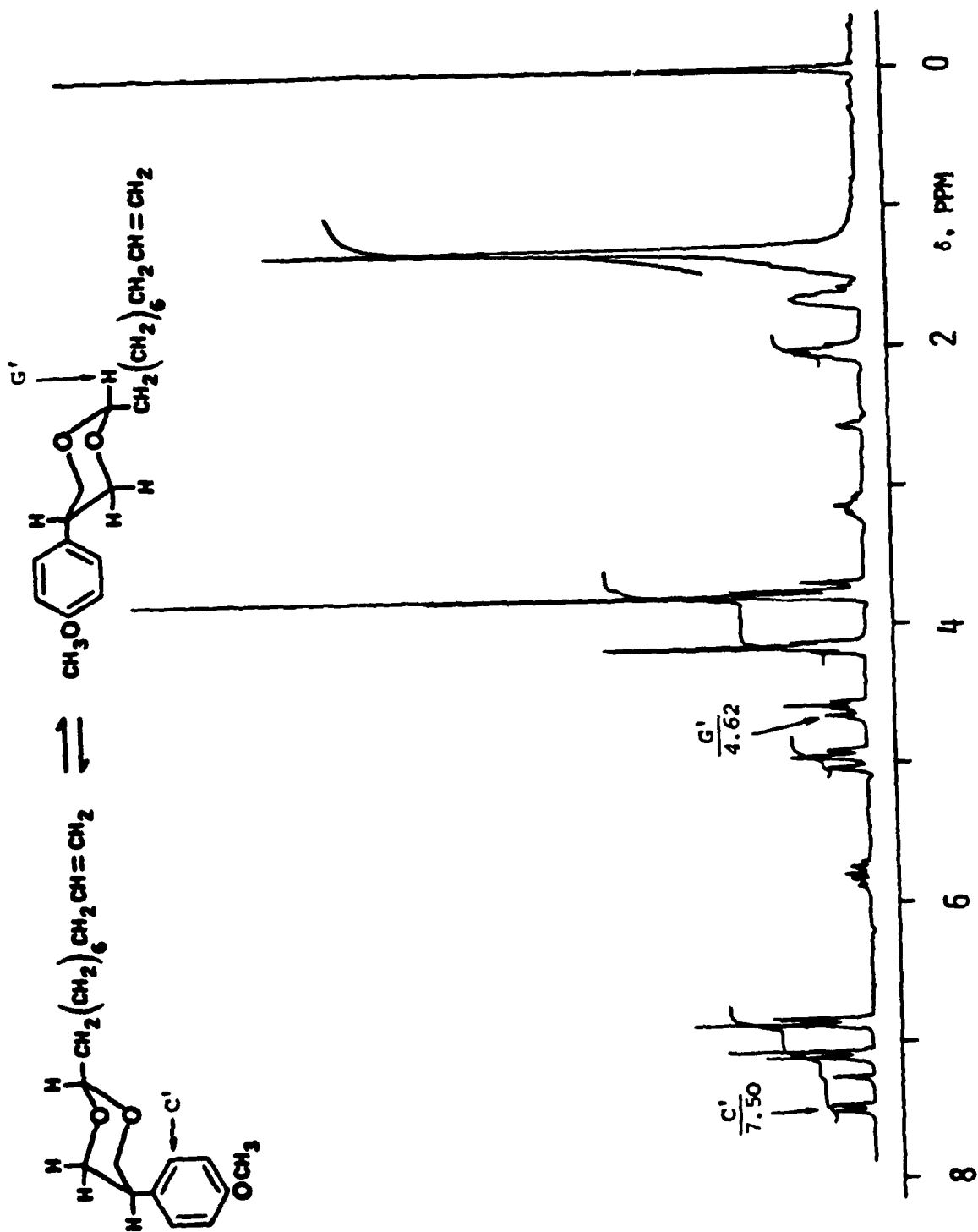


Figure 1B

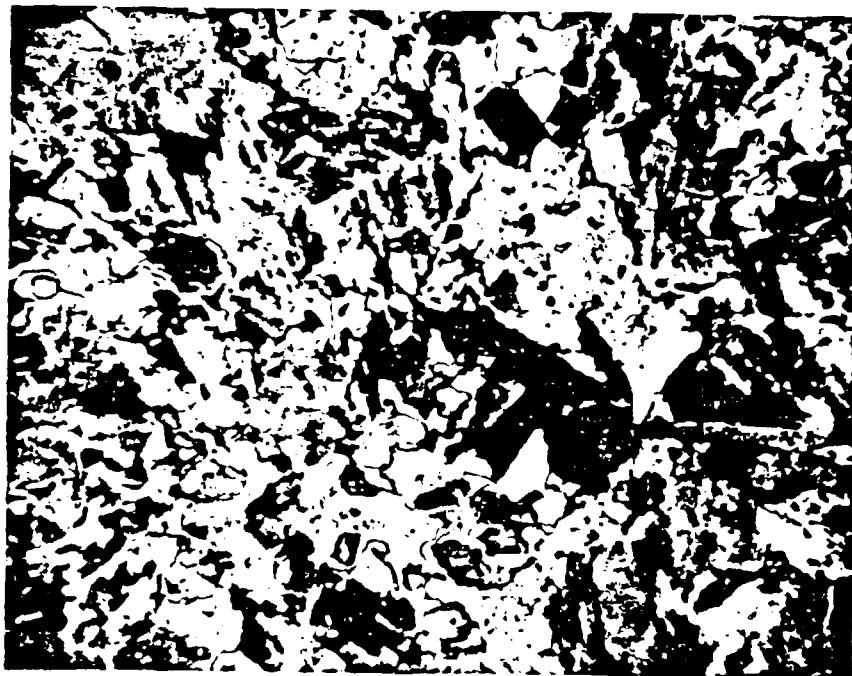


Figure 2A



Figure 2B



Figure 2C



Figure 3A

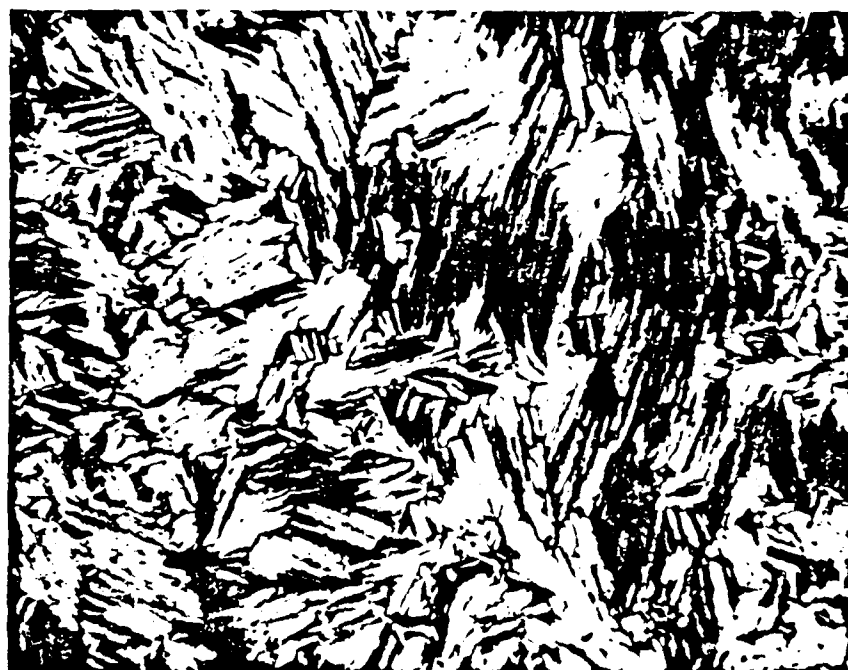


Figure 3B

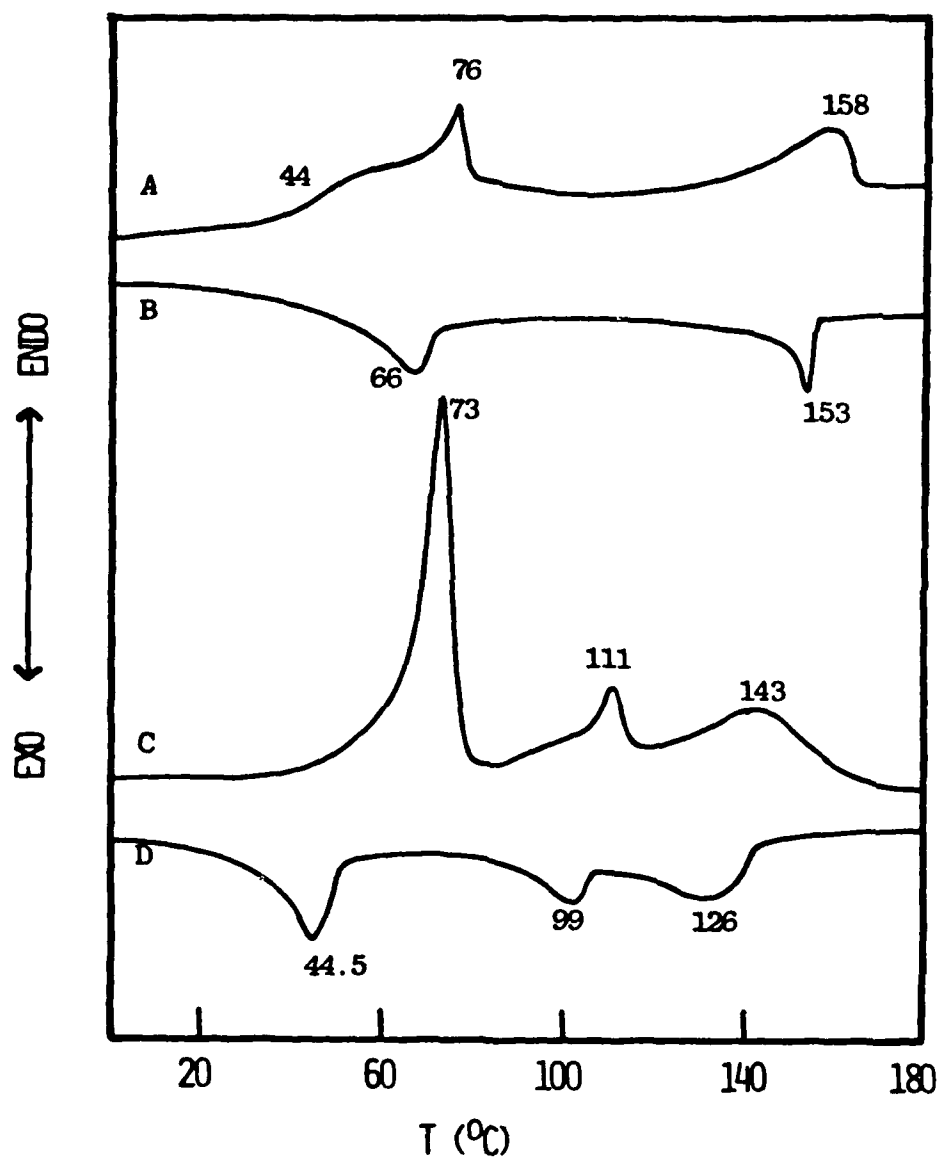
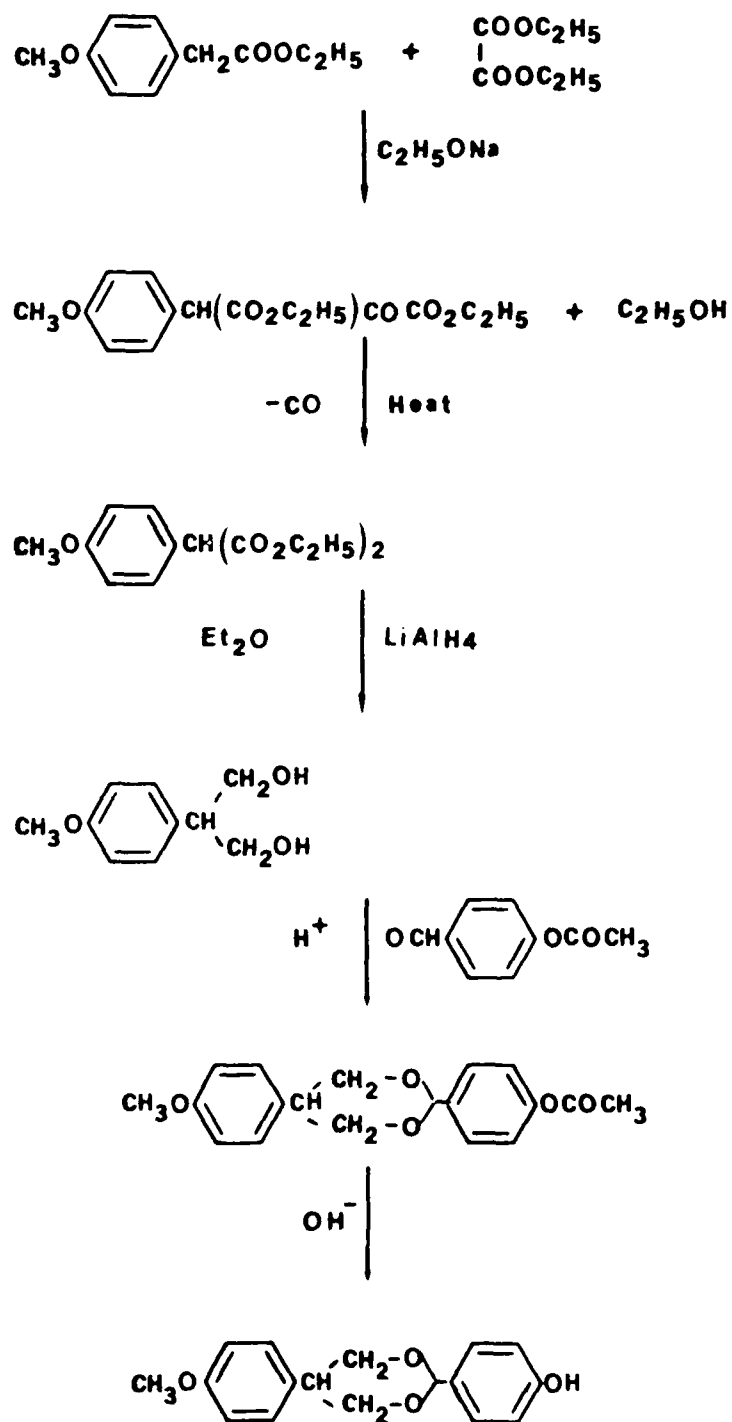
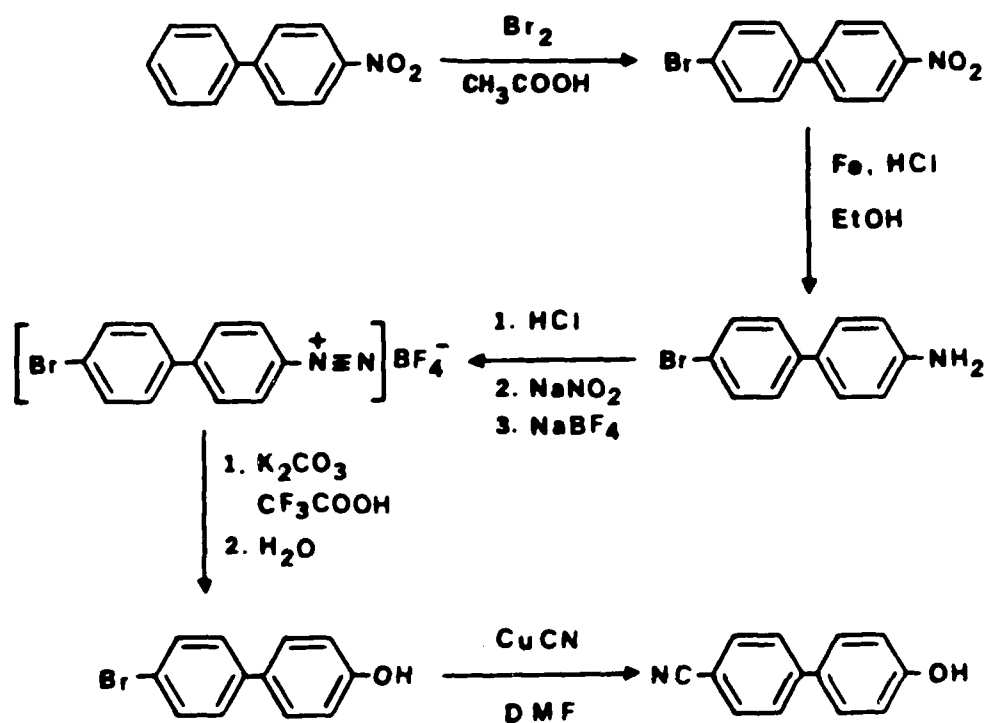


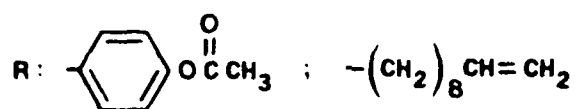
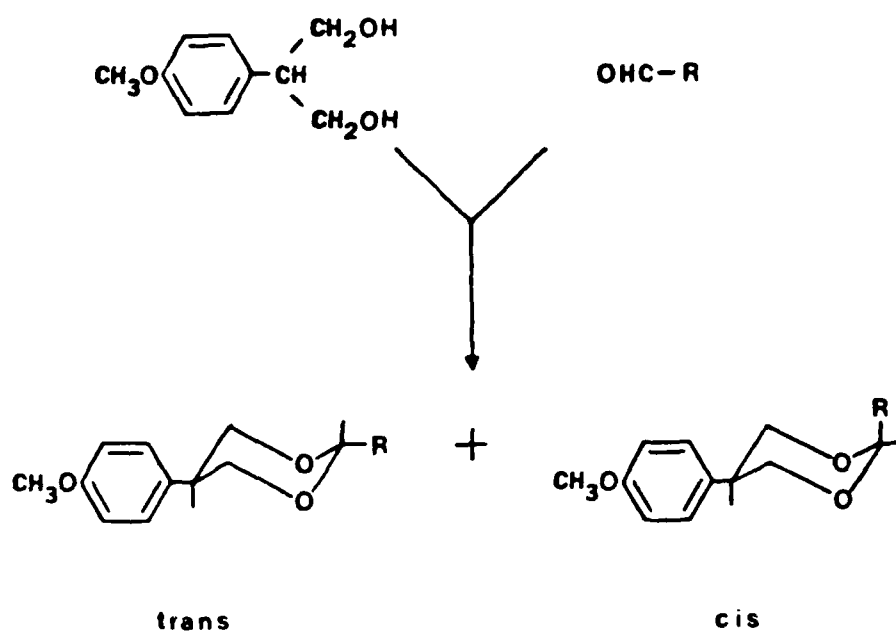
Figure 4



Scheme 1

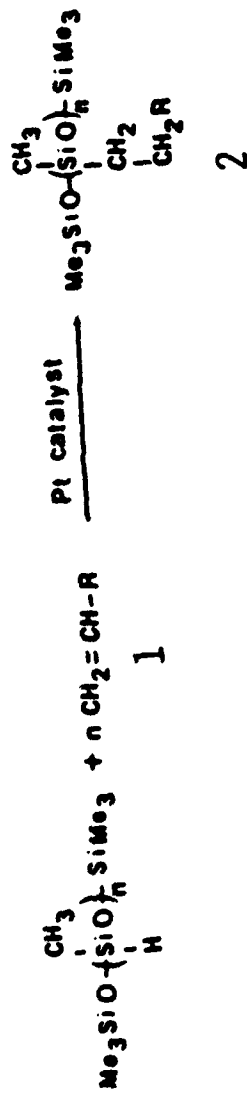


Scheme 2

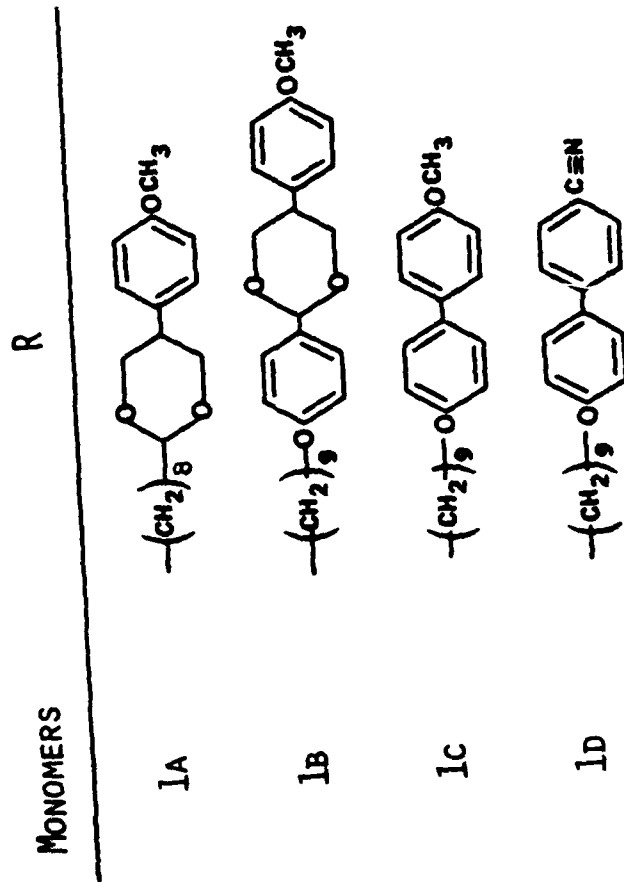
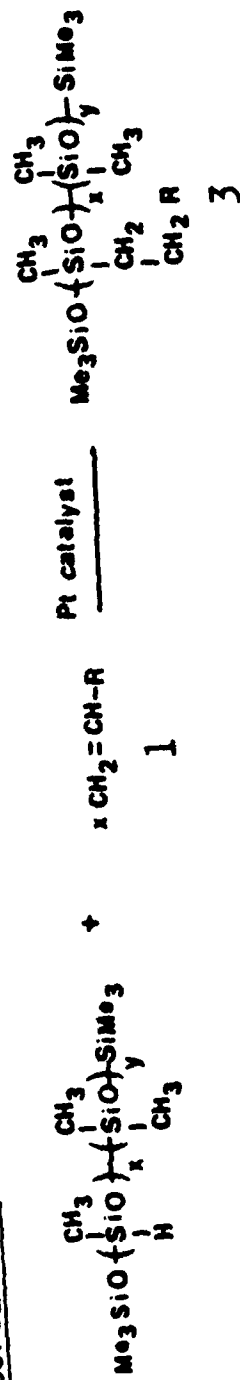


Scheme 3

HOMOPOLYMERS



COPOLYMERS



END

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DTIC