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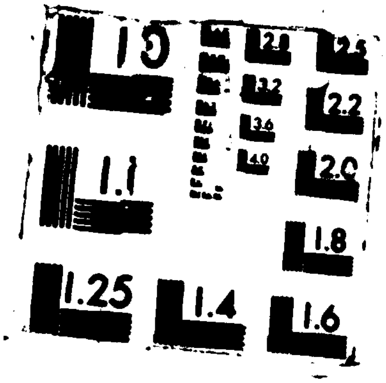
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Liquid Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 6. Liquid Crystalline Polymethacrylates and Polyacrylates of trans 2-[4-(11-Hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane

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ABSTRACT

The synthesis and characterization of polymethacrylate and polyacrylate of trans 2-[4-(11-hydroxyundecanyloxy-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane is presented. Both polymers exhibit nematic mesophases and do not present side-chain crystallization. At temperatures higher than 160°C the 1,3-dioxane-2,5-diyl groups undergo a thermally induced trans-cis isomerization. A radical mechanism was proposed for this isomerization. (Keywords) polyacrylates

Liquid Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 6. Liquid Crystalline Polymethacrylates and Polyacrylates of trans 2-[4-(11-Hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane [#]

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SUMMARY

The synthesis and characterization of polymethacrylate and polyacrylate of trans 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl) -1,3-dioxane is presented. Both polymers exhibit nematic mesophases and do not present side-chain crystallization. At temperatures higher than 160°C the 1,3-dioxane-2,5-diyl groups undergo a thermally induced trans-cis isomerization. A radical mechanism was proposed for this isomerization.

INTRODUCTION

[#] Previous paper in this series, reference 5

In the previous papers from this series we have demonstrated that mesogenic units based on 1,3-dioxane-2,5-diyl groups can be used to synthesize noncrystallizable side-chain liquid crystalline polymers (LCP) even when the polymers contain up to eleven methylenic units in the flexible spacer (1-5). The low tendency toward side-chain crystallization seems to be the consequence of the fact that the conformational isomers of trans 1,3-dioxane-2,5-diyl groups are in a dynamic equilibrium, and therefore a mixture of conformational isomers has a lower tendency toward crystallization than each of the individual isomers in part.

The mesogenic units based on 1,3-dioxane-2,5-diyl groups were particularly useful in the design of the first examples of highly decoupled micro-phase separated side-chain LCP, i.e., polymers which exhibit two glass transition temperatures, one due to the independent motion of the polymer backbone, and the other due to the cooperative but independent motion of the side-chains (3-5). The same structural particularities were used to prepare noncrystallizable chiral smectic-C^* side chain LCP (5).

The goal of this paper is to present the synthesis and characterization of polyacrylates and polymethacrylates of 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxy phenyl)-1,3-dioxane. Both polymers exhibit nematic mesophases and do not undergo side-chain crystallization. To our knowledge, these polymers represent the first examples of nematic side-chain LCP containing as many as eleven methylenic units in the flexible spacer. Previous examples of side-chain LC homopolymers exhibiting nematic mesophases always had less than six methylenic units in the flexible spacer (6, 7).

EXPERIMENTAL

Materials

2-(4-Methoxyphenyl)-1,3-propanediol was synthesized as was previously reported (1, 2). m.p.=83-84°C, ^{1}H-NMR ($CDCl_3$, δ, ppm): 2.47 (s, 2H, $-O\underline{H}$), 3.03 (m, 1H, $-CH_2-\overset{|}{C}\underline{H}-CH_2-$), 3.78 (s, 3H, $-OC\underline{H}_3$), 3.91 (s, 4H, $-C\underline{H}_2-$), 6.86-7.16 (q, 4H, $-C_6\underline{H}_4-$). 3,5-Dimethyl-4-hydroxybenzaldehyde was synthesized and purified according to a literature procedure (8). m.p.=109-111°C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 2.28 (s, 2 $-C\underline{H}_3$), 5.79 (s, $-O\underline{H}$), 7.38 (s, 2 aromatic protons), 9.59 (s, $-C\underline{H}O$).

Ethyl p-methoxyphenylacetate, 11-bromo-1-undecanol (from Aldrich), methacryloyl chloride, acryloyl chloride (both from

Fluka) were used as received. 1,4-Dioxane was first refluxed over sodium and then distilled under argon. 2,2'-Azoisobutyronitrile (AIBN) (from Fluka) was freshly recrystallized from methanol (below 40°C). All the other reagents were used as received.

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 polarized microscope (magnification: 100X) 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 (9). Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10LC instrument equipped with LC-100 column oven, LC-600 autosampler, 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, $5x10^2$, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards. X-ray diffraction data were taken at room temperature by using a Phillips PN 3550/10 diffractometer.

Synthesis of Monomers and Polymers

Scheme 1 outlines the synthesis of monomers and polymers.

11-Bromoundecanyl acetate

11-Bromoundecanol (25,1g, 0.1 mole) and triethylamine (16 ml, 0.12 mole) were dissolved in dry methylene chloride (200 ml). Acetyl chloride (8 ml, 0.11 mole) was then added dropwise. The reaction mixture was stirred at room temperature for 1hr, washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated on a rotavapor and the residue was vacuum distilled at 145°C/12 mm Hg to yield 23.7g (81%) of a colorless oily product. ^{1}H-NMR ($CDCl_3$, δ, ppm) 1.31-1.79 (m, $-(C\underline{H}_2)_9-$), 2.05 (s, $C\underline{H}_3-C$), 3.40 (t, $-C\underline{H}_2Br$), 4.05 (t, $-C\underline{H}_2-O-$).

4-(11-Acetoxyundecanyloxy)-3,5-dimethylbenzaldehyde

Cleanly cut Na (0.76g, 0.033 mole) was added in small portions into absolute ethyl alcohol (50 ml). When the sodium was completely dissolved, 3,5-dimethyl-4-hydroxybenzaldehyde (5g, 0.033 mole) was added to the reaction mixture. The alcohol was removed on a rotavapor to isolate the sodium salt of 3,5-dimethyl-4-hydroxybenzaldehyde. The dried sodium salt was then dissolved in N-methyl-2-pyrrolidinone (60ml) and 11-bromoundecanyl acetate (10g, 0.034 mole) was added. The reaction mixture was stirred at 110°C under N_2 overnight. The solvent and excess 11-bromoundecanyl acetate were distilled off under vacuum. The residual oil was purified by column chromatography (silicagel, chloroform as eluent) to yield 9.2g (77%) of a colorless liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.33-1.89 (m, $-(C\underline{H}_2)_9-$), 2.06 (s, $C\underline{H}_3-C$), 2.34 (s, 2 $C\underline{H}_3-Ph$), 3.83 (t, $-C\underline{H}_2-O-Ph$), 4.06 (t, $-C\underline{H}_2-O-C$), 7.56 (s, 2 aromatic protons), 9.86 (s, $-C\underline{H}O$).

trans 2-[4-(11-Acetoxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane

2(4-Methoxyphenyl)propane-1,3-diol (3.2g, 0.0176 mole), 4-(11-acetoxyundecanyloxy)-3,5-dimethylbenzaldehyde (6.4g, 0.0176 mole) and p-toluenesulfonic acid (176 mg) were dissolved in 250 ml of dry benzene. The resulting solution was refluxed until 0.3 ml of water were collected in a Dean-Stark trap. After cooling, the reaction mixture was washed with 2% aqueous solution of $NaHCO_3$, water, and dried over anhydrous $MgSO_4$. The solvent was evaporated on a rotavapor and the remaining solid was recrystallized from n-hexane to yield 6.5g (70%) of pure trans product. m.p.=65°C (DSC, 20°C/min). ^1H-NMR ($CDCl_3$, δ, ppm): 1.31-1.86 (m, $-(C\underline{H}_2)_9-$), 2.03 (s, $C\underline{H}_3-C$), 2.28 (s, 2 $C\underline{H}_3-Ph$), 3.30 (m, $-\overset{|}{C}\underline{H}-$), 3.71 (t, $-C\underline{H}_2-O-Ph$), 3.94 and 4.28 (m, $2-C\underline{H}_2O$), 4.05 (t, $-C\underline{H}_2-O-C$), 5.46 (s, $-\overset{|}{C}\underline{H}-$), 6.82-7.32 (m, 6 aromatic protons).

trans 2-[4-(11-Hydroxyundecanyloxy)-3,5-dimethylphenyl)-5-(4-methoxyphenyl)-1,3-dioxane (I)

2-[4-(11-Acetoxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane (6.5g, 0.012 mole) was dissolved in 50 ml tetrahydrofuran. To this solution were added a solution of 50% aqueous NaOH (30 ml) and 0.33g (0.001 mole) of tetrabutylammonium hydrogen sulfate, and the two phase reaction mixture was stirred at 60°C for 1 hr. The organic phase was separated and tetrahydrofuran was evaporated on a rotavapor. The concentrated solution was precipitated into distilled water , the mixture was neutralized with dilute hydrochloric acid, filtered and dried. The crude product was recrystallized several times from n-hexane to yield 4.5g (75%) of pure trans product. m.p.=78°C (DSC, 20°C/min). The chemical shifts of the ^{1}H-NMR spectrum of this compound are reported in Table I.

Synthesis of methacrylate (I-MA) and acrylate (I-AC) of 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxy phenyl)-1,3-dioxane

The methacrylate and the acrylate were synthesized by the esterification of 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxyphenyl)-1,3-dioxane (I) with methacryloyl and acryloyl chloride respectively. An example of their synthesis follows. I (1.5g, 0.0031 mole) was dissolved in 50 ml of dried tetrahydrofuran and 0.7 ml of triethylamine (distilled from KOH). The obtained solution was cooled in an ice-water bath at 0°C and 0.4 ml (0.0041 mole) of methacryloyl chloride were added dropwise. The reaction mixture was allowed to warm up to room temperature, and was kept stirring overnight. The resulting reaction mixture was filtered to remove the $NEt_3.HCl$, and most of the solvent was removed at room temperature in a rotavapor, after which the concentrated solution was poured into water. The precipitated product was filtered and dried under vacuum. The resulting monomer was purified by recrystallization from methanol to yield 1.4g (82%) of white crystals. The chemical shifts of the ^{1}H-NMR spectra of both monomers are supporting a trans structure of the 1,3-dioxane-2,5-diyl group, and are reported in Table I. Table II summarizes the thermal characterization of both monomers.

Polymerizations

The radical polymerization of monomers was 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 tetrahydrofuran solutions into methanol. Table III summarizes the polymerization results and the thermal characterization of the resulting polymers.

RESULTS AND DISCUSSION

Scheme 1 presents the synthetic procedures used to prepare the methacrylate and the acrylate of 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-5-(4-methoxy phenyl)-1,3-dioxane. As described 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. Both monomers exhibit only melting transitions (Table II).

Representative differential scanning calorimetric (DSC) thermograms for poly(I-MA) are presented in Figure 1, and for poly(I-AC) in Figure 2. Both polymers present glass transition temperatures followed by a liquid crystalline mesophase and isotropization transitions. The isotropization enthalpies for both ppolymers are consistent with nematic mesophases (Table III) (10). The nematic mesophase is supported by the texture observed on the optical polarized microscope, and by x-ray diffraction measurements which show a single broad diffraction hallow at $2\theta=19.45°$. Both polymers (Fig. 1A, Fig. 2A), present the isotropization transitions at much lower temperatures than the polymethacrylate and the polyacrylate of 2-[4-(11-hydroxyundecanyloxyphenyl)]-5-(4-methoxyphenyl)-1,3-dioxane which were previously reported from our laboratory

(1). At the same time, the previously synthesised polymers exhibited, as expected for this long spacer, only smectic mesophases (1). These results are suggesting that the side methyl groups attached to the mesogenic unit based on 2,5-disubstituted-1,3-dioxane are responsible for both the lower degree of order exhibited by the mesophase, as well as for the decrease in the thermal stability of the mesophase. These results are consistent with similar data reported by Gray et al (11), on different polymer structures containing mesogenic groups substituted with one methyl as side-group.

Since both, the polymers synthesized in this paper and in the previous one (1) exhibit liquid crystalline transitions which are thermal history dependent, a more detailed characterization of their thermotropic behavior will be discussed here.

Figures 1A and 2A present typical heating scans of poly(I-MA) and respectively poly(I-AC). Both polymers were heated up to 120°C. Figures 1B and 2B present the subsequent cooling scans for the same samples. Several additional heating scans up to 120°C and cooling scans from 120°C to room temperature have demonstrated that their thermal behavior is reproducible. As previously mentioned, both polymers present only a nematic liquid crystalline mesophase. When poly(I-MA) was heated to 140°C (curve C from Figure 1), the following cooling and heating scans (curves D and E from Figure 1) have shown that the isotropization temperature decreased with about 5-6°C, and at the same time the transition peak became broader. Nevertheless, the enthalpy change associated with this transition (ΔHi) did not change. Therefore, this behavior could be explained through a different dynamic equilibrium between the axial and equatorial conformational isomers of the trans 1,3-dioxane-2,5-diyl groups, as depicted in Figure 3. As Figure 3 shows, the width of the mesogenic groups (X) is different from a trans conformer having the substituents from the two and five positions of the heterocycle in an equatorial placement, versus the same trans conformer having the same two substituents in an axial placement. This dynamic equilibrium could be thermal history and phase history dependent (i.e., the same thermal history in solution, isotropic or anisotropic phase should lead to a different dynamic equilibrium), and therefore can affect the mesomorphic behavior of the polymer. Once the sample is annealed below 100°C, its thermal behavior comes back to the behavior from the scan A from Figure 1. The same behavior is observed for poly(I-AC). However, when the sample was heated to 160°C (curve E from Figure 1), the following cooling and heating scans (curves F and G from

Figure 1) demonstrate a completely different thermotropic behavior. The isotropic transition appears at lower temperatures and the enthalpy change associated to this transition is very small. If the sample was further heated to 180°C (curve G from Figure 1), the following cooling (curve H from Figure 1) and heating (not shown) scans present only a glass transition temperature and no thermotropic behavior. Figure 3 presents the 200 MHz ^{1}H-NMR spectrum of poly(I-MA) (spectrum A), and of the poly(I-MA) heated in the DSC instrument up to 180°C (spectra B and C). According to the assignment of the protonic resonances from Figure 4, poly(I-MA) from spectrum A represents a sample in which the 1,3-dioxane-2,5-diyl group is exclusively in a trans configuration. The thermal heated sample (spectra B and C from Figure 3) demonstrates that the 1,3-dioxane-2,5-diyl groups contains 70% trans and 30% cis units.

At the first site, we would expect either an electrophilic or a nucleophilic mechanism to be responsible for the isomerization of the trans 1,3-dioxane-2,5-diyl to cis-1,3-dioxane-2,5-diyl units (1, 12). Both ionic mechanisms seem to be improbable under the above reaction conditions. A thermal induced radical mechanism of isomerization could be the most probable pathway for this trans-cis isomerization.

One possible mechanism is outlined in Scheme 3. Trans I can lead under heating to the stabilized radical II and a hydrogen radical. Alternatively, radical II can be obtained through the thermal decomposition of the corresponding peroxide which could form by oxidation with air-oxygen. Radical II can theoretically undergo isomerization to the radical III. Since II is strongly stabilized through resonance by the two adjacent oxygen atoms and by the phenyl ring, it might prefer to combine with the hydrogen radical instead of forming III, and therefore can lead to a mixture of trans I and cis I. Evidence that III does not form, comes from the 200 MHz ^{1}H-NMR spectrum of the thermally treated poly(I-MA) (spectra B and C from Figure 3). The characterization of the resulting thermally treated poly(I-MA) by GPC does not reveal any change in the polymer molecular weight or its polydispersity. Therefore, any additional degradation of poly(I-MA) seems to be excluded.

Further, poly(I-MA) heated in the DSC instrument to 180°C (curve H from Figure 1) was dissolved in tetrahydrofuran and reprecipitated into methanol, filtered, dried and then reanalyzed by DSC. Although the previous heating scan (not shown) after the cooling scan H does not exhibit any other transition besides glass transition, the reprecipitated sample exhibits again liquid crystalline behavior (curve I from Figure 1). This recovery, supports that the dynamic equilibrium between the conformational isomers of the trans 1,3-dioxane-2,5-diyl is different in solution versus isotropic or anisotropic phase. Alternatively, it could be that even if this equilibrium does not differ from solution to isotropic or anisotropic melt, it is reached with a different rate which is depending on the corresponding phase.

The same behavior is exhibited by poly(I-AC). After the sample was heated to 180°C, the subsequent heating and cooling scans (curves C and D from Figure 2) show only a very small, almost undetectable isotropization transition. This transition can be again partially recovered after reprecipitation from solution.

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FIGURE CAPTIONS

Figure 1: Normalized DSC thermograms (20°C/min) of poly(I-MA): A) heating scan up to 120°C; B) cooling scan; c) heating scan up to 140°C; D) cooling scan; E) heating scan up to 160°C; F) cooling scan; G) heating scan up to

180°C; H) cooling scan; I) heating scan of the sample H after its precipitation with methanol from tetrahydrofuran solution

Figure 2: Normalized DSC thermograms (20°C/min) of poly(I-AC): A) heating scan up to 100°C; B) cooling scan; C) heating scan after sample B was heated to 180°C and then cooled to room temperature; D) cooling scan following scan C

Figure 3: 200 MHz ^{1}H-NMR spectrum of poly(I-MA): A) original sample; B) sample A heated in the DSC instrument up to 180°C; C) an expansion of the δ =5 to 8ppm region of the NMR spectrum of sample B

SCHEMES

Scheme 1: Synthesis of I-MA and I-AC

Scheme 2: The dynamic equilibrium between the axial and equatorial trans conformational isomers of the polymers containing pendant 1,3-dioxane-2,5-diyl mesogenic groups

Scheme 3: A possible mechanism of thermally induced radical trans-cis isomerization of the 1,3-dioxane-2,5-diyl units from poly(I-MA) or poly(I-AC)

TABLE I

Characterization of Monomers and Intermediary Compounds

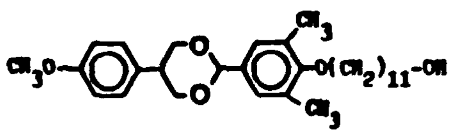
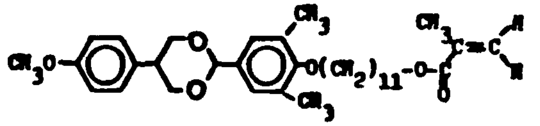
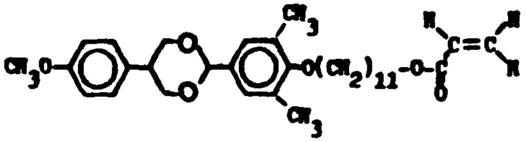
Compound	200 MHz ^{1}H-NMR (δ,ppm)
	1.31 to 1.86(m, 18H, $-(C\underline{H}_2)_9-$); 2.29(s, 6H, $\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}\!>\!ph-$); 3.31(m, 1H, $\begin{matrix}C\\C\end{matrix}\!>\!C\underline{H}-ph$); 3.65(t, 2H, $-C\underline{H}_2OH$); 3.74(t, 2H, $-C\underline{H}_2O-ph$); 3.80(s, 3H, $-OC\underline{H}_3$); 3.98 and 4.31(m, 4H, $-O-C\underline{H}_2-$); 5.48(s, 1H, $-\overset{O}{\underset{O}{C}}\underline{H}$); 6.86 to 7.26(m, 6 aromatic protons).
 (I-MA)	1.31 to 1.86(m, 18H, $-(C\underline{H}_2)_9-$); 1.97(s, 3H, $-\overset{C\underline{H}_3}{C}=C$); 2.30(s, 6H, $\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}\!>\!ph-$); 3.34(m, 1H, $C\underline{H}-ph$); 3.74(t, 2H, $-C\underline{H}_2O-ph$); 4.0 and 4.34(m, 4H, $-O-C\underline{H}_2-$); 4.16(t, 2H, $-C\underline{H}_2-O-\overset{O}{\overset{\|}{C}}-$); 5.51(s, 1H, $-\overset{O}{\underset{O}{C}}\underline{H}$); 5.57 and 6.11($C\underline{H}_2=$); 6.87 to 7.27(m, 6 aromatic protons).
 (I-AC)	1.31 to 1.86(m, 18H, $-(C\underline{H}_2)_9-$); 2.30(s, 6H, $\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}\!>\!ph-$); 3.30(m, 1H, $C\underline{H}-ph$); 3.72(t, 2H, $-C\underline{H}_2O-ph$); 3.96 and 4.30(m, 4H, $-O-C\underline{H}_2-$); 4.16(t, 2H, $-C\underline{H}_2O-\overset{O}{\overset{\|}{C}}$); 5.48(s, 1H, $-\overset{O}{\underset{O}{C}}\underline{H}$); 5.77 to 6.43($\underline{H}_2C=C\underline{H}-\overset{O}{\overset{\|}{C}}$); 6.85 to 7.25(m, 6 aromatic protons).

Table II: Thermal Transitions and Thermodynamic Parameters of Monomers.

Monomer type	Thermal Transitions (°C) and Thermodynamic Parameters : ΔH (Kcal/mol); ΔS (cal/mol.°K)					
	Heating			Cooling		
	Tm	ΔHm	ΔSm	Tc	ΔHc	ΔSc
I-MA	57	9.36	28.36	4	0.10	0.39
I-AC	55	10.67	32.54	11	0.19	0.66

Table III: Radical Polymerization of Monomers and Thermal Characterization of Polymers.

Monomer type	Polymers			Thermal Transitions, (°C) and Thermodynamic Parameters : ΔH(Kcal/mru*), ΔS(cal/mru*.°K)				
				Heating			Cooling	
	Conversion %	$\overline{Mn} \times 10^{-3}$	$\overline{Mw}/\overline{Mn}$	Tg	Ti	ΔHi/ΔSi	Ti	ΔHi/ΔSi
I-MA	70	33.6	1.51	21	107	0.32/0.86	93	0.32/0.87
I-AC	63	9.4	1.36	10	67	0.13/0.40	61	0.11/0.34

* mru = mole of repeat units.

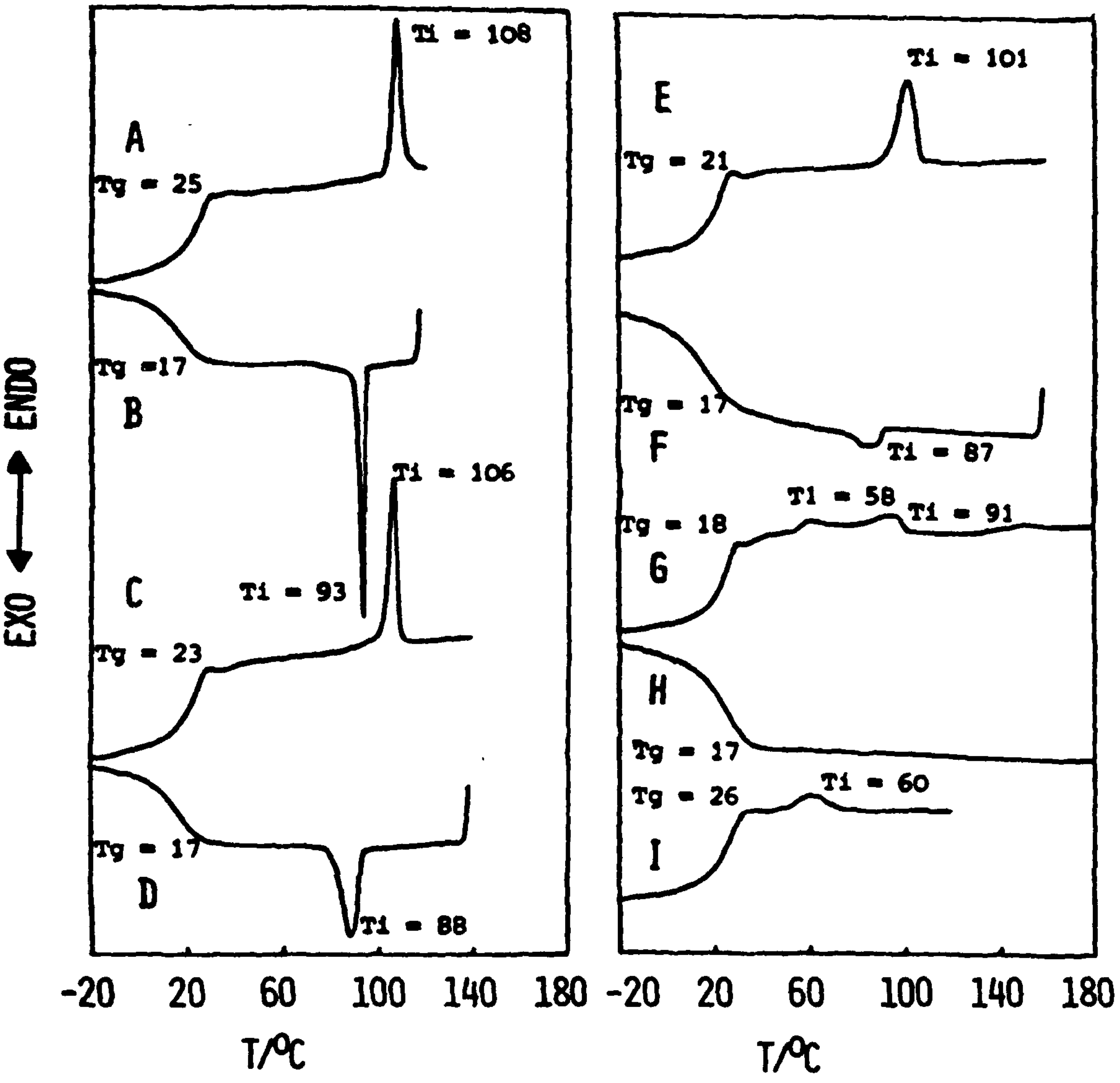

Ti = 108
A
Tg = 25
Tg =17
B
Ti = 106
C
Ti = 93
Tg = 23
Tg = 17
D
Ti = 88
EXO ⟷ ENDO
E
Ti = 101
Tg = 21
Tg = 17
F
Ti = 87
Ti = 58
Ti = 91
Tg = 18
G
H
Tg = 17
Tg = 26
Ti = 60
I
-20
20
60
100
140
180
T/°C

Figure 1

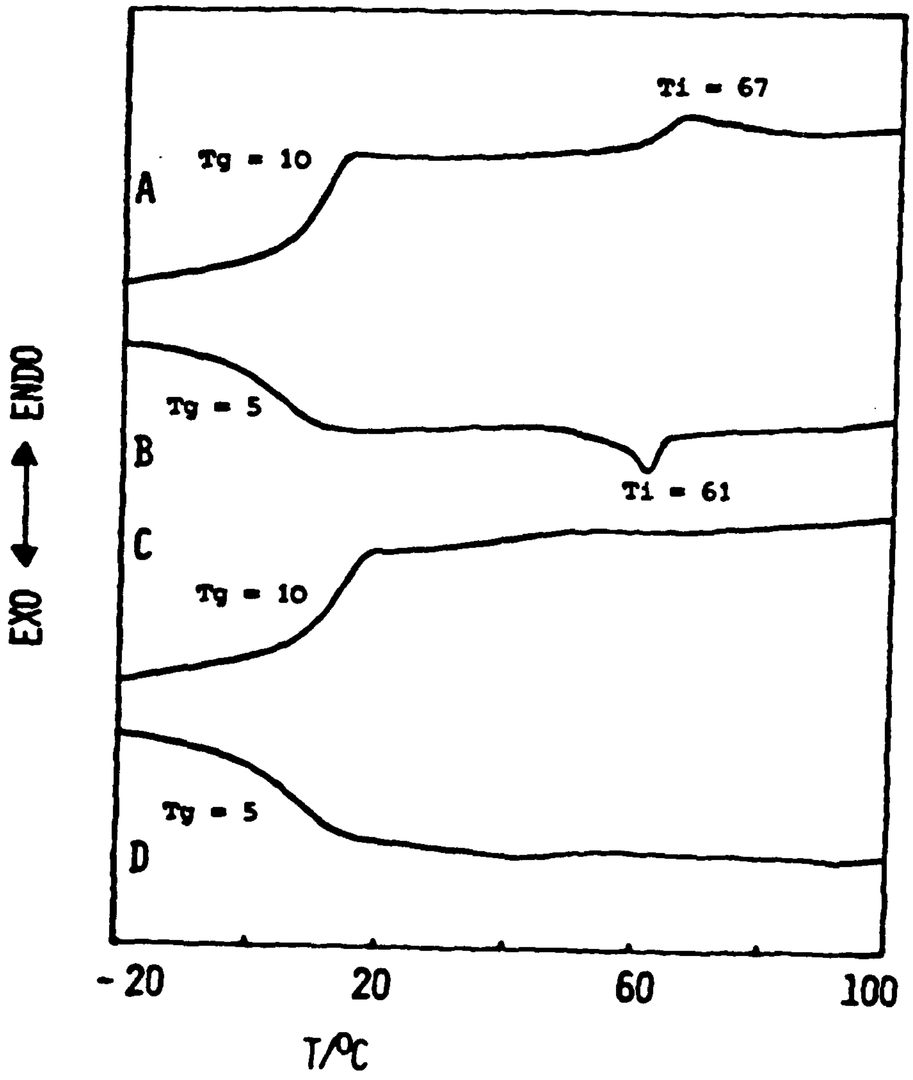


Figure 2

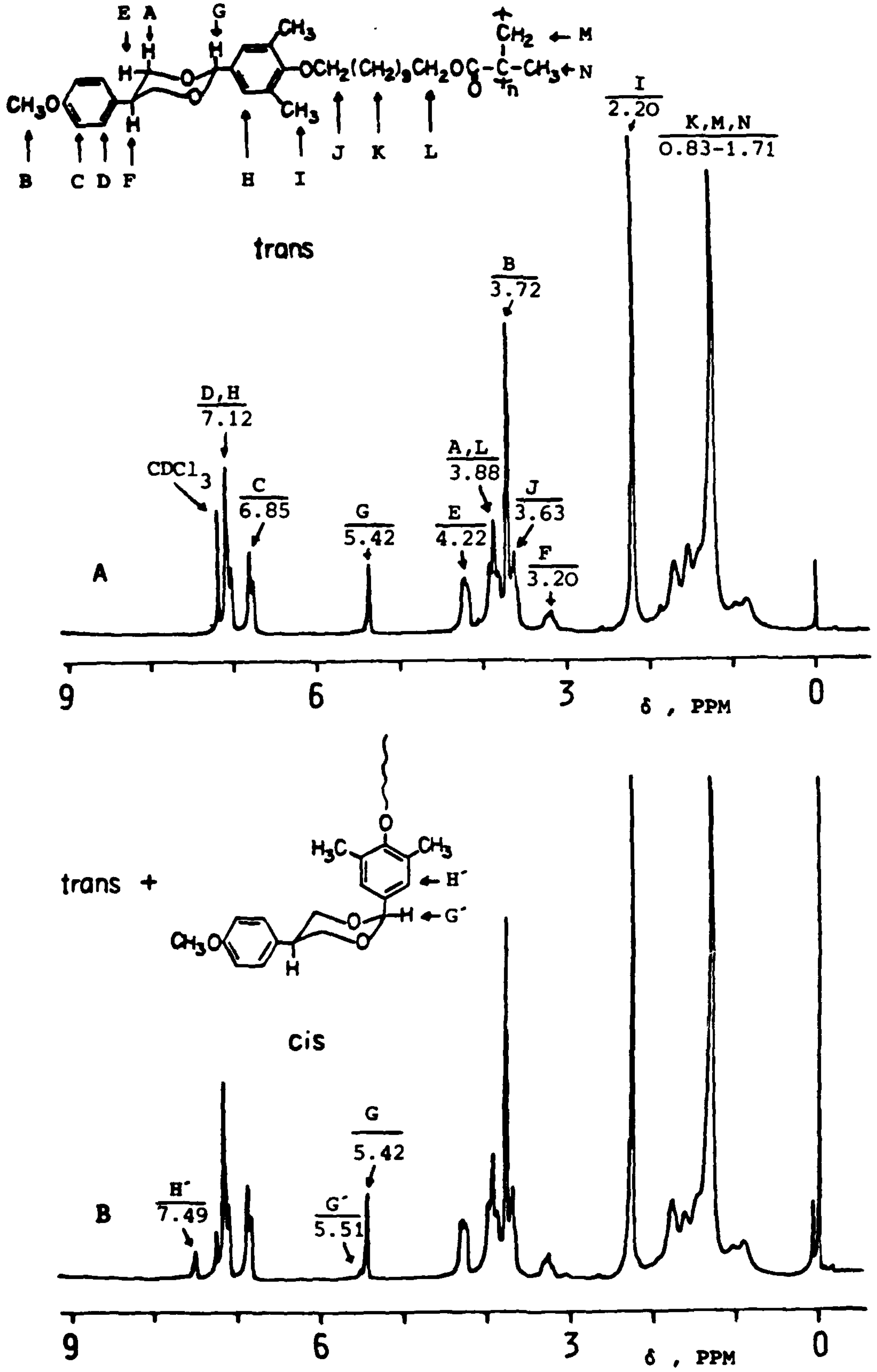


Figure 3, A and B

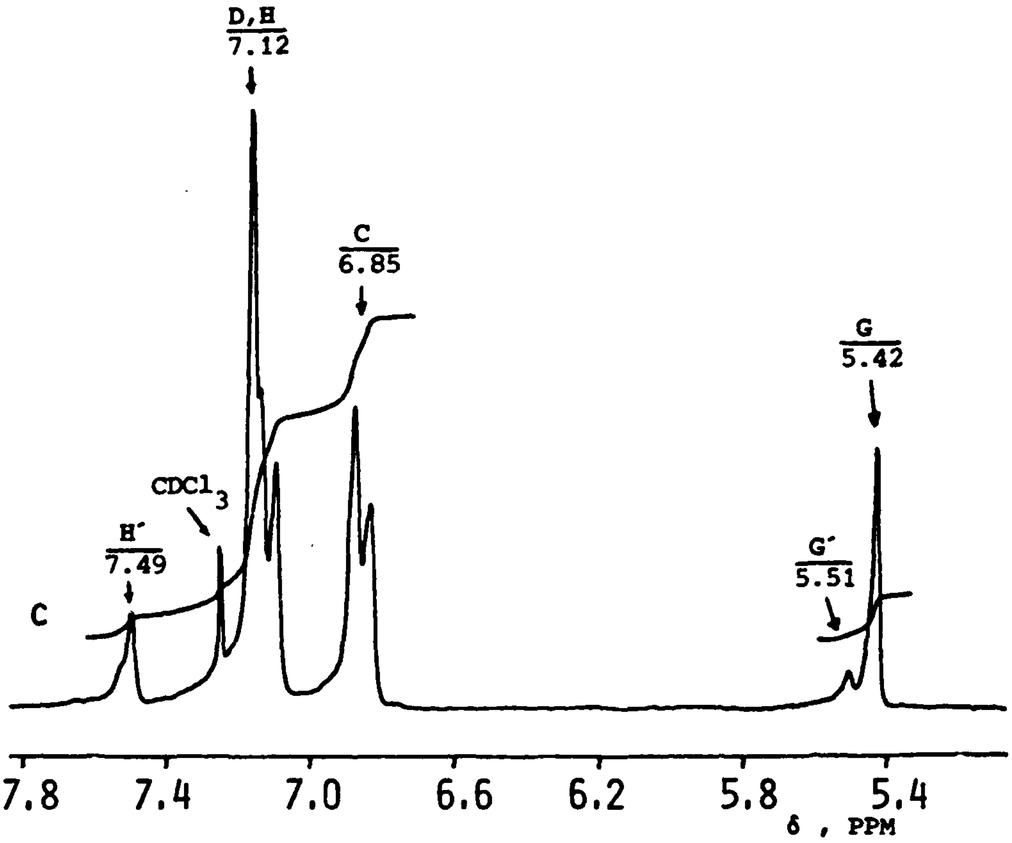
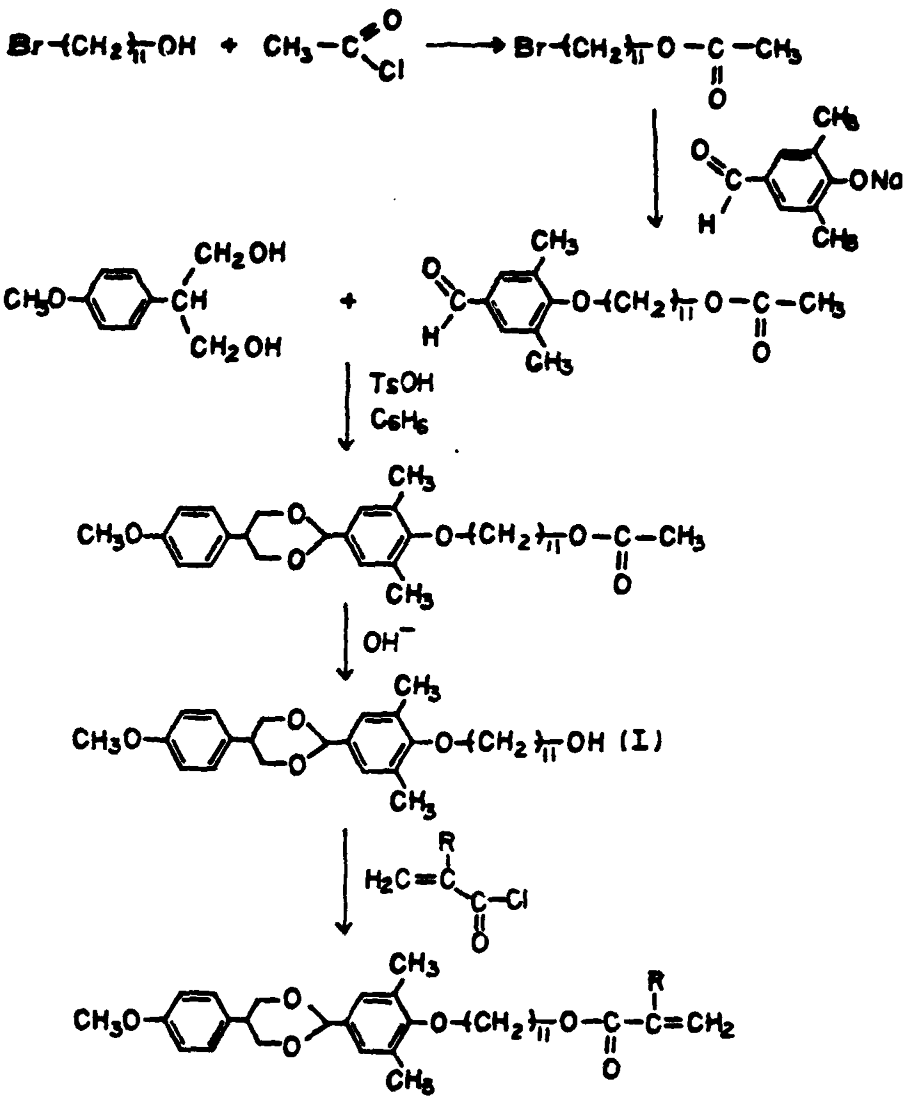
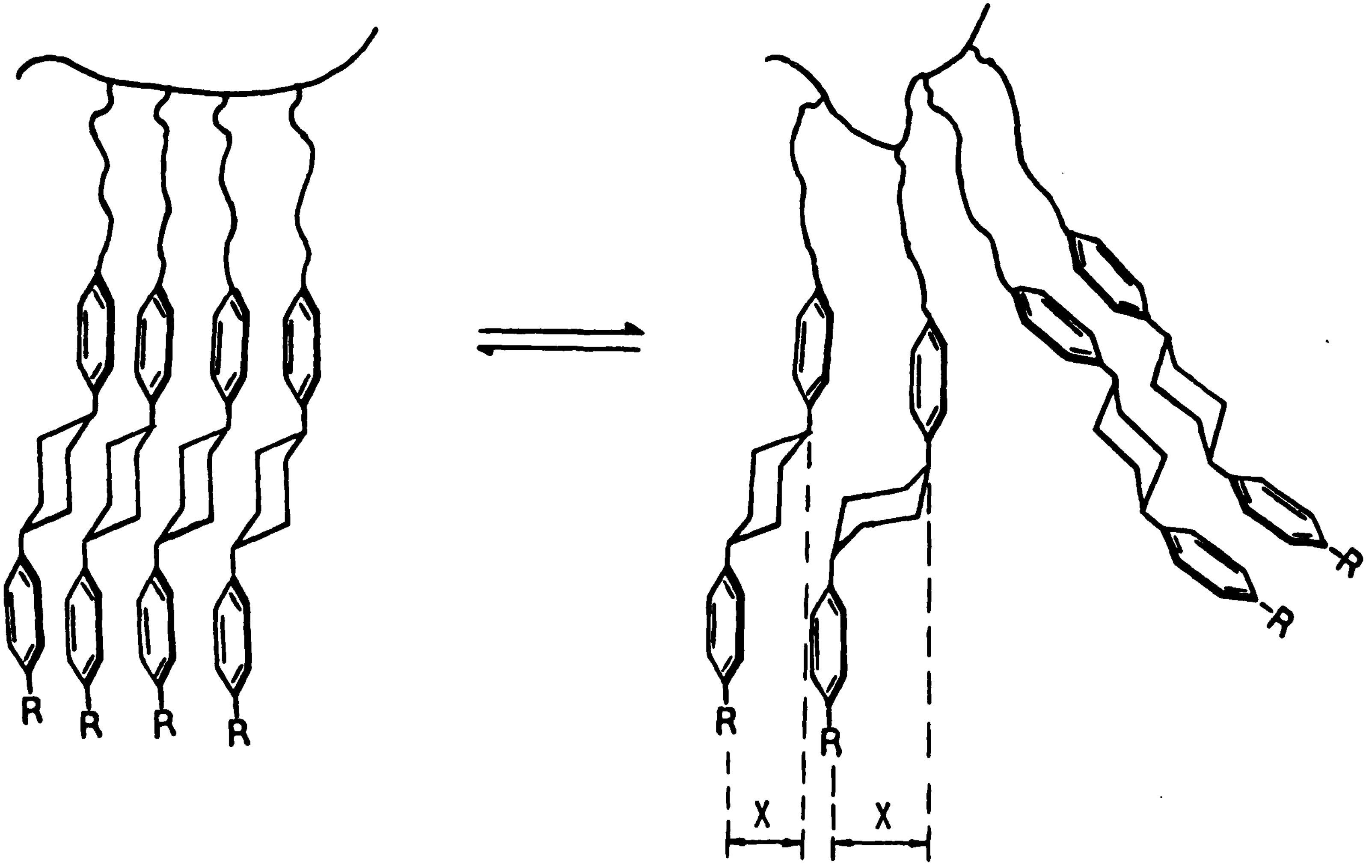


Figure 3, C

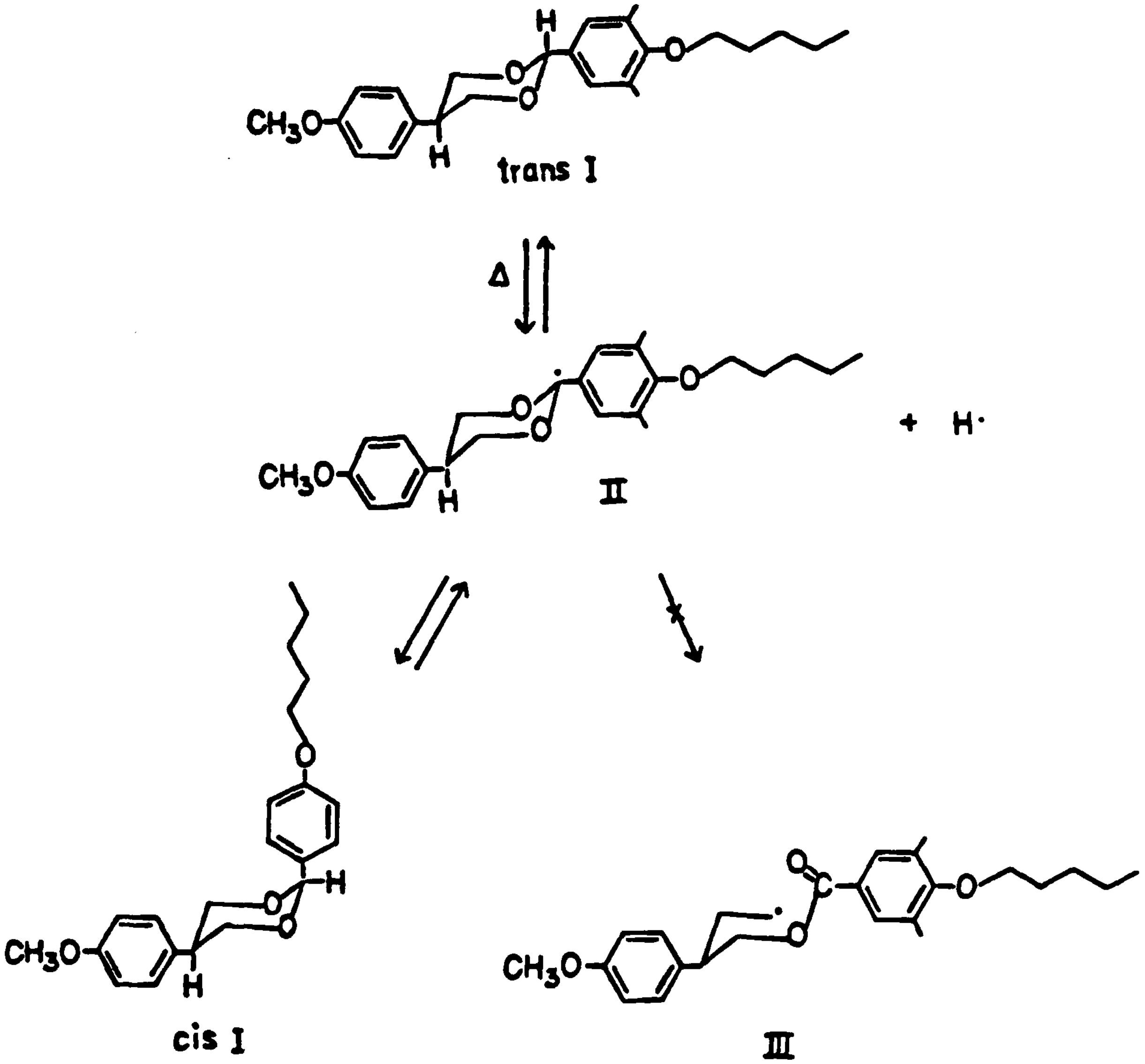


R: CH_3 (I-MA)
H (I-AC)

Scheme 1



Scheme 2



Scheme 3

END
9-87
DTIC