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Synthesis and Characterization of Liquid Crystalline Copolymethacrylates,
Copolyacrylates and Copolysiloxanes Containing
4-Methoxy-4'-Hydroxy- α -Methylstilbene and 4-Hydroxy-4'-Methoxy- α -Methylstilbene
Constitutional Isomers as Side Groups

By

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ABSTRACT

The synthesis of methacrylates and acrylates containing 4-methoxy-4'-hydroxy-4-methylstilbene and 4-hydroxy-4'-methoxy-4-methylstilbene constitutional isomers attached to the polymerizable group through flexible spacers containing eleven, eight, six, three and respectively two methylenic units is described. The radical copolymerization of a 1/2 or 2/1 mole ratio of the two constitutional isomeric monomers led to thermotropic side-chain liquid crystalline polymers in all cases. The synthesis of copolysiloxanes based on the same constitutional isomeric mesogens as side groups, and flexible spacers containing eleven, eight, six, five and respectively three methylenic units is also described. All polymers were characterized by differential scanning calorimetry and optical polarization microscopy. The polymers containing eleven methylenic units in the spacer exhibit S_C^A mesomorphism, while the other polymers are nematic. Copolymethacrylates do not undergo side-chain crystallization. Only the copolyacrylate containing eleven methylenic units in the spacer exhibits side chain crystallization. All the copolysiloxanes present side-chain crystallization. The number of melting transitions presented by these polymers decreases with the decrease of their spacer length. Copolysiloxanes containing dissimilar spacer length were also prepared. Only the copolymer synthesized with highly dissimilar spacer lengths i.e., containing three and eleven methylenic units, does not undergo side-chain crystallization. These results have demonstrated that while the type of mesophase is dictated only by the spacer length, the degree of decoupling of the motion of the side groups from the motion of the main chain is strongly dependent on the nature of the polymer backbone. For the same mesogenic unit and spacer length, the thermal stability of the mesophase is also dictated by the nature of the polymer backbone. The use of constitutional isomers of mesogenic units as side groups in liquid crystalline polymers, provides at least qualitative information on the degree of decoupling of the side groups from the polymer main chain.

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Synthesis and Characterization of Liquid Crystalline Copolymethacrylates, Copolyacrylates and Copolysiloxanes Containing 4-Methoxy-4'-Hydroxy- α -Methylstilbene and 4-Hydroxy-4'-Methoxy- α -Methylstilbene Constitutional Isomers as Side-Groups.

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SYNOPSIS

The synthesis of methacrylates and acrylates containing 4-methoxy-4'-hydroxy- α -methylstilbene and 4-hydroxy-4'-methoxy- α -methylstilbene constitutional isomers attached to the polymerizable group through flexible spacers containing eleven, eight, six, three and respectively two methylenic units is described. The radical copolymerization of a 1/2 or 2/1 mole ratio of the two constitutional isomeric monomers

led to thermotropic side-chain liquid crystalline polymers in all cases. The synthesis of copolysiloxanes based on the same constitutional isomeric mesogens as side groups, and flexible spacers containing eleven, eight, six, five and respectively three methylenic units is also described. All polymers were characterized by differential scanning calorimetry and optical polarization microscopy. The polymers containing eleven methylenic units in the spacer exhibit S_C mesomorphism, while the other polymers are nematic. Copolyacrylates do not undergo side-chain crystallization. Only the copolyacrylate containing eleven methylenic units in the spacer exhibits side-chain crystallization. All the copolysiloxanes present side-chain crystallization. The number of melting transitions presented by these polymers decreases with the decrease of their spacer length. Copolysiloxanes containing dissimilar spacer length were also prepared. Only the copolymer synthesized with highly dissimilar spacer lengths i.e., containing three and eleven methylenic units, does not undergo side-chain crystallization. These results have demonstrated that while the type of mesophase is dictated only by the spacer length, the degree of decoupling of the motion of the side-groups from the motion of the main chain is strongly dependent on the nature of the polymer backbone. For the same mesogenic unit and spacer length, the thermal stability of the mesophase is also dictated by the nature

of the polymer backbone. The use of constitutional isomers of mesogenic units as side groups in liquid crystalline polymers, provides at least qualitative information on the degree of decoupling of the side groups from the polymer main chain.

INTRODUCTION

Since Ringsdorf et al (1, 2) have advanced the spacer concept to decouple the motion of the side-groups from that of the main chain in liquid crystalline state, thermotropic side-chain liquid crystalline polymers (LCP) have received considerable research interest both from practical and fundamental point of view (3, 4). Subsequent work by Ringsdorf et al (5-7) has shown that complete decoupling does not occur although the degree of decoupling increases with the spacer length (6).

Several very brief publications have pointed out that not only the nature and length of the flexible spacer, but also the nature of the polymer backbone influences the range of thermal stability of the mesophase (8-14). In fact, it has been mentioned by several research groups that for the same spacer length and mesogenic unit, the broadest thermal stability of the mesophase is always obtained with the most flexible backbone (8-14).

We assume that the nature of the polymer backbone plays a more important role than previously considered in achieving a highly decoupled side-chain LCP. The enhanced thermal stability of the mesophase and the increased isotropization temperature exhibited by polymers presenting flexible backbones can be associated with a high degree of freedom of the side groups. This might be related not only to the mobility of the polymer backbone, but also to its miscibility with the side-groups. This statement can be more clearly understood if we make a comparison between side-chain LCP and graft copolymers. When the graft and the backbone are miscible, the overall properties of the graft copolymer are weight averaged. When the graft and the backbone are immiscible, the graft copolymer exhibits a micro-phase separated biphasic morphology and the graft copolymer presents synergistic properties exhibited by the individual graft and backbone segments. The micro-phase separated morphology of a graft copolymer when transplanted to a side-chain LCP, in our opinion, should give rise to a highly decoupled side-chain LCP. Therefore, it is not only the spacer length which controls the degree of decoupling, but also the miscibility between the side-chains and the polymer backbone.

Several previous papers from our laboratory have reported the first examples of biphasic i.e., micro-phase separated side-chain LCP (15-18). These polymers exhibit two glass transition

temperatures i.e., one due to the independent motion of the main-chain, and the other due to the cooperative but independent motion of the side-groups. These side-chain LCP might represent the first examples of highly decoupled side-chain LCP. One of the most important parameters in achieving such a micro-phase separated LCP consisted in the use of very long spacers and mesogenic units which did not undergo side-chain crystallization. Some of the most successful mesogenic units were those based on structures which undergo conformational isomerism i.e., 1,3-dioxane-2,5-diyls (13, 15-17), 1,3,2-dioxaborinane-2,5-diyls (17), benzyl ethers (19), and diphenyl ethanes (20). Since the conformational isomers of these mesogenic groups are in a dynamic equilibrium, a mixture of conformers has a lower tendency towards crystallization than each of the isomers in part, and therefore, side-chain crystallization could be avoided in many cases.

A slightly different approach to the same problem can be designed by using monomers containing mesogenic units which give rise to constitutional or structural isomerism. This concept has been previously of interest both to us (21), Pino's (22) and Suter's (23) research groups in connection with main chain LCP. Side-chain liquid crystalline "copolymers" of monomer-pairs containing mesogenic units which exhibit constitutional isomerism would be good candidates to depress the side-chain crystallization in certain classes of LCP as has been already

shown in a previous preliminary communication from our laboratory (24). At the same time, we speculate that in a highly decoupled side-chain LCP, each constitutional isomer might give rise to side-chain crystallization, and eventually the polymer might exhibit multiple meltings associated with each isomer in part. If this assumption is correct, the use of constitutional isomers as mesogenic groups could lead to a LCP system which functions as a "chemical detector", providing information concerning the degree of decoupling of the side-chains. Such a system would provide, at this time, at least qualitative information concerning the degree of decoupling achieved by using both different spacer lengths and different polymer backbones.

The goal of this paper is to present the synthesis and characterization of copolymethacrylates, copolyacrylates and copolysiloxanes containing the constitutional isomers 4-hydroxy-4'-methoxy- α -methylstilbene and 4-methoxy-4'-hydroxy- α -methylstilbene attached to the polymer backbone through flexible spacers of different lengths, and discuss their thermal behavior as a function of both spacer length and nature of polymer backbone.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) ($\bar{M}_n = 4500 - 5000$) was obtained from Petrarch Systems Inc., and was used as received. Methacryloyl chloride and acryloyl chloride (both from Fluka), allylbromide, 1,5-dibromopentane, 1,6-dibromohexane, 8-bromo-1-octene, 11-undecene-1-ol (all from Aldrich), 2-chloroethanol, 3-chloro-1-propanol, 6-chloro-1-hexanol, 8-chloro-1-octanol (all from Lancaster Synthesis), and 11-bromo-1-undecanol (from Fluka), were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon. 2,2'-Azobutyronitrile (AIBN) (from Fluka) was freshly recrystallized from methanol (below 40°C). Chloroacetone (Lancaster Synthesis) was freshly distilled just before use. Phenol (more than 99%, Fluka) was used as received. 1,4-Dioxane was first refluxed over sodium and then distilled under argon. All the other reagents were used as received, unless otherwise specified.

Techniques

200 MHz $^1\text{H-NMR}$ 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 (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 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 (25, 26). 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 10², 5x10², 10³, 10⁴, and 10⁵ Å, and a calibration plot constructed with polystyrene standards.

Synthesis of Monomers and Polymers

The synthesis of monomers and polymers is outlined in Schemes 1, 2 and 3.

4,4'-Dihydroxy-*o*-methylstilbene (HMS)

HMS was synthesized by the condensation of chloroacetone with phenol in the presence of concentrated sulfuric acid, according to a literature procedure (28) which was modified as follows. To a mechanically stirred mixture of phenol (112.8 g, 1.2 mole) and freshly distilled chloroacetone (55.5 g, 0.6 mole) cooled in an alcohol-dry ice bath maintained at -10°C , concentrated sulfuric acid (31.0 g, 0.32 mole) was added dropwise during 1.5 hr. The reaction mixture was stirred at this temperature for 2 additional hr. The orange-red pasty reaction mixture was quenched with cold water, poured into a beaker containing about 3 l of water and left stirring overnight. The white precipitate was filtered and recrystallized four times from a 1/1 (V/V) mixture of ethanol/water to yield 16.6 g (12.2%) of white crystals of 99.0% purity as determined by HPLC. m.p.= $184-186^{\circ}\text{C}$ (lit. 25, m.p.= $182-183^{\circ}\text{C}$). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, TMS, δ , ppm): 2.2 (s, $-\text{CH}_3$), 6.7 (s, $=\text{CH-}$), 6.85 (d, 4 aromatic protons, o to $q-\text{CH}_3$), 7.4 (d, 2 aromatic protons, o to $=\text{CH-}$).

4(4')-Methoxy-4'(4)-hydroxy-*o*-methylstilbene (MHMS)

Scheme 1 describes the synthesis of MHMS and of the corresponding methacrylates and acrylates. MHMS was synthesized as follows. 4,4'-Dihydroxy- α -methylstilbene (44.1 g, 0.195 mole) was dissolved in a solution of NaOH (18.7 g, 0.468 mole) in 180 ml of water. Dimethyl sulfate (24.6 g, 0.195 mole) was added dropwise to the ice-water cooled and strongly stirred solution, and the reaction mixture was stirred at room temperature overnight. The resulting precipitate was filtered and washed with 10% aqueous NaOH, and then with water. The separated solid was dissolved in boiling water and traces of insoluble 4,4'-dimethoxy- α -methylstilbene were separated by hot filtration. The resulting solution was cooled to room temperature and acidified with dilute HCl to precipitate the monomethoxylated product. It was filtered, washed with water, and recrystallized from methanol to yield 15.5 g of white crystals labeled over the rest of this paper as sample A. m.p.=150-160°C. The remaining methanolic solution was left overnight in a refrigerator to yield 3.3 g of a second fraction of crystals labeled as sample B. m.p.=133-136°C. The overall yield of this reaction was 40.1%. The purity of each fraction is about 99% (HPLC). HPLC equipped with UV detector, can not discriminate between the two isomers of MHMS. 200 MHz $^1\text{H-NMR}$ spectra of sample A and sample B are presented in Figures 1 and 2, together with the assignment of their protonic resonances. Sample A contains always an about 1/2

(mole/mole) ratio of 4-methoxy-4'-hydroxy- α -methylstilbene to 4-hydroxy-4'-methoxy- α -methylstilbene while sample B contains an 2/1 ratio of 4-methoxy-4'-hydroxy- α -methylstilbene to 4-hydroxy-4'-methoxy- α -methylstilbene.

4(4')-(ω -Hydroxyalkanyloxy)-4'(4)-methoxy- α -methylstilbenes (n-A)

All compounds were prepared by the etherification of MHMS with the corresponding bromo or chloroalcohol, in ethanol at reflux temperature, in the presence of KOH as base and a small amount of KI. An example of this procedure is outlined below. MHMS, sample A, (3 g, 0.0125 mole) and KOH (1.05 g, 0.0188 mole) were dissolved in 50 ml of 95% ethanol. 11-Bromo-1-undecanol (4.72 g, 0.0188 mole) and 0.2 g of KI were added and the solution was refluxed for 24 hrs. The alcohol was removed in a rotavapor, the resulting solid was poured into water, stirred, and the precipitated product was filtered, washed with dilute solution of aqueous NaOH, water, and recrystallized from methanol to yield 4.65 g (90.7%) of white crystals. m.p.=117-119°C. The ¹H-NMR chemical shifts for all compounds together with their melting points and conversions are presented in Table I.

Methacrylates and Acrylates (n-MA, n-AC)

All monomers were synthesized by the esterification of the corresponding alcohols, n-A, with methacryloyl or acryloyl chlorides. An example follows.

4(4')-(1-Hydroxyundecanyloxy)-4'(4)-methoxy- α -methylstilbene

obtained from MHMS sample A i.e., 11-A(A) (1.5 g, 0.0037 mole) was dissolved in 50 ml of dried tetrahydrofuran and 1 ml (0.007 mole) of dried triethylamine was added. The obtained solution was cooled to 0°C in an ice-water bath and 0.5 ml (0.005 mole) of methacryloyl chloride were added dropwise. The reaction was allowed to warm up to room temperature and was kept stirring at this temperature overnight. Finally, it was filtered to remove Et₃N.HCl, and the solvent was removed in a rotavapor at room temperature. The resulting solid was washed with water, NaHCO₃ aqueous solution, water, filtered, dried, and recrystallized from methanol to yield 1.26 g (72%) of white crystals. m.p.=60-85°C (DSC at 20°C/min). The ¹H-NMR chemical shifts for all monomers together with their melting temperatures and conversions are presented in Table II. The purity of all monomers is higher than 99.0% (HPLC).

Radical Polymerization of Monomers

All monomers were polymerized in dried dioxane by using AIBN as a radical initiator at 60°C for 15 hrs. Polymerizations were carried out in Schlenk tubes under an argon atmosphere after the monomer solutions were degassed by several freeze-pump-thaw cycles under vacuum. The monomer concentration was 10% (wt/V) and the initiator concentration was 1 wt% versus the monomer. After the polymerization time, the reaction mixture was diluted with tetrahydrofuran and precipitated into methanol. The filtered

polymers were dried under vacuum and then were purified by reprecipitation from tetrahydrofuran solutions into methanol. The characterization of the resulting polymers is presented in Tables III and IV.

5-Bromo-1-pentene and 6-Bromo-1-hexene.

Both compounds were synthesized according to a literature procedure (28). To stirred 1,5-dibromopentane (10 ml, 16.9 g), or 1,6-dibromohexane (10 ml, 15.9 g) at 195°C (oil bath temperature) was dropwise added hexamethylphosphoric triamide (15 ml) at a rate of about one drop per second. The temperature of the reaction was then raised to 220°C for 5 min. The product which distilled into a dry ice-cooled receiver was then redistilled at atmospheric pressure. 5-Bromo-1-pentene, b.p.=123-125°C, was isolated in a yield of 5.6 g (51%). ¹H-NMR (CDCl₃, δ, ppm): 1.97 and 2.20 (m, C=C-(CH₂)₂-), 3.43 (t, -CH₂Br), 5.07 and 5.76 (m, H₂C=CH-). 6-Bromo-1-hexene, b.p.=147-150°C, was isolated in a yield of 5.1 g (48%). ¹H-NMR (CDCl₃, δ, ppm): 1.54, 1.84 and 2.07 (m, C=C-(CH₂)₃-), 3.41 (t, -CH₂Br), 4.99 and 5.76 (m, H₂C=CH-). The purity of the resulted products was higher than 99% as determined by gas chromatography.

11-Chloro-1-undecene

A mixture containing 34 g (0.2 mole) of 11-undecen-1-ol and 35.7 g (0.3 mole) of SOCl₂ was stirred for 3 hrs at 40°C. Excess SOCl₂ was distilled off, and the resulting product was subjected

to a fractional distillation (85°C/7 mmHg) to yield 35 g of product. The purity of the resulted compound was higher than 99.0% as determined by gas chromatography.

4(4')-Allyloxy-4'(4)-methoxy- α -methylstilbene,

4(4')-(4-pentenylloxy)-4'(4)-methoxy- α -methylstilbene,

4(4')-(5-hexenylloxy)-4'(4)-methoxy- α -methylstilbene,

4(4')-(7-octenylloxy)-4'(4)-methoxy- α -methylstilbene and

4(4')-(10-undecenylloxy)-4'(4)-methoxy- α -methylstilbene (n-O).

All compounds were prepared by the etherification of MHMS with the corresponding bromoalkene or chloroalkene. An example of this procedure is given below. Freshly cut sodium (0.096 g, 4.17×10^{-3} mole) was dissolved in 20 ml of absolute ethyl alcohol. After the sodium was completely dissolved, MHMS (1.0 g, 4.17×10^{-3} mole) was added to the reaction mixture. The ethyl alcohol was then removed by using a rotavapor to form the sodium salt of MHMS, and dried N-methyl-2-pyrrolidinone (20 ml) was added to the same flask. When the sodium salt was completely dissolved, 11-chloro-1-undecene (0.785 g, 4.17×10^{-3} mole) was added to the reaction mixture. The reaction mixture was stirred at 110°C under nitrogen atmosphere overnight, cooled, and poured into water. The resulted precipitate was filtered, washed with dilute NaOH aqueous solution, water and dried in vacuum. The product was recrystallized from methanol to yield 1.4 g (86%) of white crystals. Table V summarizes the chemical shifts of all

synthesized compounds. Table VI presents the thermal transitions of the same compounds.

Synthesis of Copolysiloxanes (P-n-S and P-n1/n2-S)

The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. A general synthetic procedure used for the synthesis of P-n-S and P-n1/n2-S (i.e., copolysiloxanes containing two dissimilar spacers) is described below. 1.0 g (10 mole % excess versus Si-H groups present in polysiloxane) of the olefinic derivative (n-O) was dissolved in 100 ml of dry, freshly distilled toluene together with the proper amount of poly(methylhydrosiloxane). The reaction mixture was heated to 110°C under nitrogen, and 100 µg dicyclopentadienylplatinum (II) chloride catalyst (14) 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 all the Si-H groups were consumed. The white polymers were separated by precipitation into methanol, and were purified by several reprecipitations from chloroform solution into methanol and then were dried under vacuum. In order to avoid the contamination of the resulting polymers with polydimethylsiloxane from silicon grease or silicon oil, only teflon tape and teflon gaskets were used in the assemblage of the hydrosilation equipment. Tables VII and VIII summarize the thermal transitions

of both P-n-S and P-n1/n2-S.

Over the entire manuscript, including Tables, monomer and polymer samples are going to be labeled with the letter A or B in between paranthesis, following the short name of the compound. A and B will always refer to sample A or sample B of starting MHMS, i.e., P-n-S(A) or P-n-S(B).

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolymethacrylates (P-n-MA) and Copolyacrylates (P-n-AC)

Scheme 1 describes the synthesis of the mixture containing 4-methoxy-4'-hydroxy- α -methylstilbene and 4-hydroxy-4'-methoxy- α -methylstilbene, as well as the preparation of the methacrylates and acrylates containing two, three, six, eight and eleven methylenic units in the flexible spacer. The expansions of the aromatic regions of the ¹H-NMR spectra in Figures 1 and 2 allow the determination of the ratio between the two constitutional isomers for samples A and B. It is essential to use acetone as an NMR solvent in order to separate all the aromatic resonances. Sample A is less soluble than sample B, and it always contains an about 1/2 (mole/mole) ratio of 4-methoxy-4'-hydroxy- α -methylstilbene to

4-hydroxy-4'-methoxy- α -methylstilbene (Figure 1). Sample B contains an 2/1 ratio of 4-methoxy-4'-hydroxy- α -methylstilbene to 4-hydroxy-4'-methoxy- α -methylstilbene (Figure 2).

Both samples of MHMS were characterized by differential scanning calorimetry. Two typical DSC scans are presented in Figure 3. Sample A exhibits a sharp melting at 135°C, followed by a broad melting at 154°C, while sample B exhibits a broad melting centered at 160°C. A brief examination of Figure 3 concludes that the melting at the lower temperature is mostly due to the 4-hydroxy-4'-methoxy- α -methylstilbene isomer, while the melting at higher temperature is due to the 4-methoxy-4'-hydroxy- α -methylstilbene isomer.

The synthesis of methacrylates (n-MA) and acrylates (n-AC) is also outlined in Scheme 1. The characterization of the intermediary compounds and of the monomers is presented in Tables I and II. It is difficult to fully understand the phase behavior of both sets of monomers since they undergo thermal induced polymerization during their characterization by both DSC and optical polarization microscopy. At the same time, the thermal characterization of the n-O is also difficult because all compounds exhibit both mesomorphic and multiple crystalline transitions which are overlapped.

Table III summarizes the thermal characterization of the polymethacrylates. Indifferent of the thermal history and

preparation history of the polymer sample, i.e., as precipitated from solution and then dried, or after several heating and cooling scans in the DSC instrument, the DSC thermograms of these polymers are perfectly reproducible. All of them exhibit only two transitions: a glass transition temperature followed by a liquid crystalline mesophase, and the isotropization transition. Only the polymethacrylate containing eleven methylenic units in the flexible spacer exhibits a smectic mesophase. The other polymethacrylates present nematic mesophases. The polymethacrylate and the polyacrylate containing eight methylenic units in the spacer present both a nematic and a smectic mesophase.

The assignment of the polymers mesophases was made by comparing the isotropization enthalpies calculated from the DSC thermograms (Table III) (29), and by observing their mesomorphic textures on the hot stage of the optical polarized microscope (25, 26). Figure 4 presents representative heating and cooling DSC thermograms for both P-8-MA(A) and P-8-AC(A). While P-11-MA(A) and P-11-AC(A) exhibit focal-conic fan-shape textures (24) typical to smectic C (S_c) mesophases (Figure 4 a, b), P-11-S(A) and P-11-S(B) present a schlieren smectic texture which is also characteristic for S_c mesophases (Figure 4 c) (25, 26). Nevertheless, the isotropization enthalpies for all three polymers containing eleven methylenic units in the flexible

spacer are below the values expected for smectic liquid crystalline mesophases (Table III). The isotropization enthalpies for smectic polymers are usually higher than 0.85 kcal/m.r.u. (29). The polymers containing eight and less than eight methylenic units in the flexible spacer present isotropization enthalpies within the range of nematic mesophases and at the same time exhibit typical nematic textures. Some representative nematic textures exhibited by the polymers containing eight methylenic units in the spacer are presented in Figure 6, while Figure 7 presents representative textures for the nematic polymers containing six methylenic units in the spacer. P-8-MA and P-8-AC are the first examples of nematic polymers containing eight methylenic units in the flexible spacer. Previous examples of nematic polymers would always have less than six methylenic units in the flexible spacer (3, 4). At the same time, the polymers containing six, eight and eleven methylenic units in the flexible spacer are between the very few examples of polymers containing such long spacers and do not exhibit side-chain crystallization (3, 4).

The homologues polyacrylates present for the same spacer length, the same type of mesophase as the corresponding polymethacrylates. Table V summarizes the phase transitions and the thermodynamic parameters of the polyacrylates. Only the polyacrylate containing eleven methylenic units in the flexible

spacer exhibits a slightly different thermal behavior from that of the corresponding polymethacrylate. Both polymers present a smectic C mesophase. While P-11-MA(A) and P-11-MA(B) do not present side-chain crystallization, P-11-AC(A) exhibits three melting transitions and a single crystallization transition, indifferent of the preparation or thermal histories of the sample (Table IV). The three melting transitions exhibited by P-11-AC(A) are assumed to be due to the individual isomers of HMS (two of them) and due to their eutectic mixture (the third one). A more detailed discussion on these multiple meltings is going to be presented in the subchapter on polysiloxanes.

The major conclusion which starts to emerge from these two sets of experiments is that although a more flexible backbone does not affect the type of mesophase formed, it allows a higher degree of freedom to the mesogenic units. This behavior gives rise to the side-chain crystallization of the mesogenic units in the case of polyacrylate containing eleven methylenic units in the spacer. At least for the polymer-pair polymethacrylate-polyacrylate, the more flexible polyacrylate combined with a long spacer containing eleven methylenic units, gives the highest degree of decoupling.

Figure 8 plots the glass transition, melting and isotropization temperatures, all as a function of the number of methylenic units in the spacer, for both polyacrylates and

polymethacrylates. All these data were collected from the heating scans of the DSC thermograms. It is well documented that phase transitions, particularly melting and liquid crystalline transitions are strongly molecular weight dependent up to a certain molecular weight, for both main chain (21, 30) and side-chain liquid crystalline polymers (8, 31). Therefore, a quantitative comparison of these polymers is difficult to be made at this time, since the molecular weights of the polyacrylates are lower than those of the polymethacrylates (Table III and IV). At the same time, while the molecular weights of the polymethacrylates seem to be above the limit where they influence the phase transitions, the molecular weights of polyacrylates are below this limit. In addition, the composition of these polymers, which in fact are copolymers of the two constitutional isomeric side-groups, is not very uniform. Nevertheless, glass transition temperatures are not so drastic affected by molecular weight differences as melting and liquid crystalline transitions are (8, 21, 30, 31). A brief examination of Figure 8 shows that the glass transition temperatures of both polymers are decreasing with the increase in the spacer length until they reach a plateau for polymers having eight and more than eight methylenic units in the spacer. It is interesting to remember that while the glass transition of atactic polymethylmethacrylate is 110°C, the glass transition temperature of atactic polymethylacrylate is 10°C. A

simple inspection of Figure 8 shows that the glass transition temperature of both P-n-MA and P-n-AC are within less than 10°C difference, particularly when the spacer contains more than six methylenic units. This result points toward the conclusion that the glass transition temperature of the polymers containing long spacers is mostly controlled by the flexible side-group, and that the main chain behaves as a simple liquid which does or does not dissolve the side groups. We can speculate that the side-chain crystallization is depressed in polymer systems where the backbone is miscible with the polymer side groups. It could be that the difference of one methyl group existing between the polymethacrylate and the polyacrylate backbones makes the first one enough paraffinic in character, so that it is miscible with the side groups. The reverse of this situation occurs for the case of the polyacrylate containing eleven methylenic units in the spacer. Therefore, the side-chain crystallization in this system might have been helped not only by the more flexible backbone but also by its less paraffinic character which depresses the miscibility between the main chain and the side-groups.

Synthesis and Characterization of Copolysiloxanes (P-n-S)

The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. The olefinic intermediary derivatives, n-O, were

characterized by DSC and their thermal transitions are presented in Table VI. Their thermal behavior is affected by the different ratio between the two constitutional isomers in the initial MHMS mixture and therefore, a quantitative characterization of these mixtures can not be obtained at this time. Nevertheless, we can mention that all of them exhibit either monotropic or enantiotropic liquid crystalline mesophases.

The thermal transitions and the thermodynamic parameters of the polysiloxanes are presented in Table VII. All polysiloxanes exhibit the same type of enantiotropic liquid crystalline mesophases as the corresponding polymethacrylates and polyacrylates i.e., the polymers containing eight and less than eight methylenic units in the flexible spacer are nematics while the one with eleven methylenic units is smectic C. Some representative mesomorphic textures are presented in Figures 5, 6 and 7. Although the type of liquid crystalline mesophase exhibited by these polymers is not dependent on the polymer backbone nature, the textures exhibited by these polymers is strongly dependent on the polymer backbone nature. Not only the type of texture but also the mobility of the texture is strongly influenced by the polymer main chain nature. The mobility of the mesophase increases with the increase of the polymer main chain flexibility and for the same polymer chain it decreases with the decrease of the spacer length. For example, in the case of

polymers containing less than six methylenic units in the spacer, only the polysiloxanes can give characteristic textures. The other polymers exhibit very viscous mesophases which could not give rise to characteristic textures even after long periods of annealing. For the polymers containing six or more than six methylenic units in the flexible spacer, the polysiloxanes reach equilibrated textures after very short annealing times, while the polymethacrylates and polyacrylates are requiring substantially longer annealing times (Figures 5, 6 and 7).

The other major difference between the behavior of polysiloxanes and of the other polymers consists in their ability to give rise to side-chain crystallization. All polysiloxanes undergo side-chain crystallization indifferent of the thermal history of the sample and the length of their spacer. The polysiloxanes containing three, five and six methylenic units in the spacer present a single melting transition, while the polysiloxanes containing six, eight and eleven methylenic units in the spacer exhibit three melting transitions and a single crystallization process.

Figure 9 presents some representative heating and cooling DSC thermograms of the P-11-S(A) and of the P-11-S(B). The heating scan of P-11-S(A) (Figure 9, A) presents three melting endotherms followed by a S_c mesophase and the isotropization transition. The first melting seems to be followed by a recrystallization

exotherm. The cooling scan of the same sample exhibits a slightly supercooled (4°C only) isotropization transition, followed by a single crystallization exotherm. Multiple endotherms observed on the heating scan which give a single supercooled crystallization exotherm on the cooling scan are usually assigned to melting and respectively crystallization transitions (21). The overall enthalpy change associated with T_{m1} , T_{m2} and T_{m3} is smaller than the enthalpy change of crystallization (T_c) (Table VII), and this behavior supports kinetically controlled processes like melting and crystallization. Liquid crystalline transitions of low degree of order mesophases (i.e., nematic, smectic A and smectic C) are usually thermodynamically controlled, as is the case for the S_c phase exhibited by P-11-S(A) (Figure 9, A and B, and Table VII). At the same time, the enthalpies of melting associated with T_{m1} , T_{m2} and T_{m3} from samples P-11-S(A) and P-11-S(B) are proportional to the ratio between the two constitutional isomers of MHMS present in sample A and B, i.e., T_{m1} to 4-hydroxy-4'-methoxy- α -methylstilbene, T_{m3} to 4-methoxy-4'-hydroxy- α -methylstilbene, while T_{m2} to their eutectic mixture (Table VII). This result is supporting the idea that these meltings might be due to the individual constitutional isomers and their eutectic mixture. If this assumption is correct, it demonstrates that in the case of polysiloxanes, the degree of decoupling is much higher than in the case of

polyacrylates, and the degree of decoupling in polyacrylates is higher than that in polymethacrylates. These results also support the idea that the decoupling increases with the increase in the spacer length, but it is not complete, since in no case, the glass transition temperature of the LCP is identical to that of the parent unsubstituted backbone. It could be that the higher degree of decoupling achieved by polysiloxane is not only the consequence of its highly flexible backbone but also the consequence of the high immiscibility between the polysiloxane backbone and its side-groups. Additional research is required to support all these assumptions.

Figure 10 presents the plot of thermal transitions of the P-n-S as a function of number of methylenic units in the flexible spacer "n". Before going into any quantitative discussion we have to mention that the extent of hydrosilation reaction was considered by following the disappearance of the Si-H absorption in the IR or of the Si-H resonance in the ¹H-NMR spectra as a function of the reaction time. Although this is a general analytical method used to demonstrate that the hydrosilation reaction is complete (32), this method is not necessarily correct since it does not measure the amount of new compound formed. Since hydrosilation is accompanied by a number of side reactions (33, 34), until the real hydrosilation conversion is measured, the composition of polysiloxanes has to

be considered only in a qualitative way. Nevertheless, even so, a quick inspection of Figures 8 and 10 shows that not only the glass transition temperatures of P-n-S are lower than of the P-n-MA and P-n-AC, but also the isotropization temperatures of P-n-S are higher than of P-n-MA and P-n-AC. As we have already mentioned in the previous subchapter, since the molecular weights of the P-n-AC are very low, they can not be considered in a quantitative manner. Since the molecular weights of P-n-MA and P-n-S are suspected to be above the molecular weights of the molecular weight-phase transition plateau, these two polymer sets are more suitable to be compared, and they definitively show that more flexible backbones give rise to higher isotropization temperatures.

Synthesis and Characterization of Copolysiloxanes (P-n1/n2-S)

As it has been demonstrated by the experimental results from the previous subchapters, the constitutional isomerism of the mesogenic groups depress the side-chain crystallization process only for polymer systems having rigid polymer backbones i.e., polymethacrylates. For more flexible polymer backbones, like for the case of polyacrylates, the side-chain crystallization process can be avoided only when the spacer has less than eleven methylenic units. In the case of polysiloxanes, side-chain

crystallization takes place indifferent of the length of the flexible spacer.

An additional tool useful to depress the degree of order in side-chain liquid crystalline polymers would be by synthesizing copolymers containing different spacer lengths and identical mesogenic units. In order to investigate the possibility of decreasing the degree of order in polysiloxanes containing two different spacer lengths, we have synthesized three copolysiloxanes according to the reaction avenue presented in Scheme 3. It is obvious from this Scheme that these copolymers contain in fact four different structural units i.e., each spacer length has two constitutional isomers of the mesogenic group.

We will discuss their thermal behavior based on two representative examples. The first one refers to a copolymer containing a 1/1 mole ratio between the two spacers, the first spacer containing three methylenic units, and the second spacer containing six methylenic units i.e., P-3/6-S(A/A). Representative heating and cooling scans of the DSC thermograms of both P-6-S(A) and P-3/6-S(A/A) are presented in Figure 11. Figure 12 presents the heating and cooling scans of P-3-S(A). While P-6-S(A) exhibits two melting endotherms and a single crystallization exotherm (Table VII, Figure 11), P-3-S(A) presents a single melting and a single crystallization (Table VII, Figure 12). The resulting P-3/6-S(A/A) copolymer (Figure 11, Table VIII) presents

only a melting and a crystallization transition, and as expected a nematic mesophase. The P 6/11 S(A/A) copolymer exhibits an almost similar behavior as the parent homopolymers. All three polymers present two meltings, a crystallization, and a nematic mesophase (Table VIII).

The most interesting but at the same time not unexpected result was obtained for a copolymer containing two highly dissimilar spacer lengths i.e., three and respectively eleven methylenic units (P-3/11-S(A/A)). Figure 12 presents representative heating and cooling DSC thermograms for P-3-S(A) and P-3/11-S(A/A). The heating and cooling DSC thermograms of P-11-S(A) are available in Figure 9. Although P-11-S(A) presents three meltings and P-3-S(A) only one melting (Figures 9, 11 and Table VII), the resulting P-3/11-S(A/A) copolymer does not undergo side-chain crystallization (Table VIII, Figure 12). This result is expected in view of the previous data from our laboratory concerning the highly depressed rate of crystallization of main chain liquid crystalline random copolyethers based on 4,4'-dihydroxy- α -methylstilbene and dissimilar flexible spacers (21, 30, 35). Quite rewarding is the fact that P-3/11-S(A/A) presents a nematic mesophase. In fact as we have already mentioned, all copolysiloxanes reported in Table VIII present nematic mesophases which reach thermodynamically equilibrated textures within short annealing times. A

representative behavior of the nematic texture exhibited by P-6/11-S(A/A) is presented in Figure 13. Both the textures and the evolution in time of the texture during the isothermal treatment of the other copolymers from Table VIII are similar to those in Figure 13.

Although a quantitative conclusion of this work requires the synthesis of the individual constitutional isomeric monomers based on 4-hydroxy-4'-methoxy- α -methylstilbene and 4-methoxy-4'-hydroxy- α -methylstilbene, the qualitative results obtained through this research have led to the following conclusion. The present results are supporting our previous conclusion (12) that the type of mesophase obtained for a certain mesogenic unit is dictated by the spacer length, and seems to be independent on the nature of polymer backbone. Nevertheless, for the same mesogenic unit and spacer length, the nature of the polymer backbone dictates the overall number of phase transitions exhibited by the LCP, and apparently controls the degree of decoupling. Constitutional isomeric mesogenic units attached as side-groups to polymeric backbones, depress both the degree of order in the mesophase (i.e., provide lower enthalpy changes associated with liquid crystalline transitions than expected) and the rate of side-chain crystallization. This last point is particularly true for rigid backbones. Noncrystallizable LCP based on very flexible backbones can be prepared by

copolymerization of monomers containing highly dissimilar spacer lengths. Last but not least, the use of constitutional isomers of mesogenic units, provides not only a simple novel technique to tailor phase transitions in side-chain LCP but also a tool to obtain at least qualitative information concerning the degree of decoupling of the side-groups from the main chain. A quantitative picture of this research is going to be obtained by the synthesis of the individual constitutional isomeric monomers.

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FIGURE CAPTIONS

Figure 1: 200 MHz ^1H -NMR spectrum of: A) MHMS(A) ($(\text{CD}_3)_2\text{CO}$, TMS);
B) an expansion of the aromatic region of MHMS(A)

Figure 2: 200 MHz ^2H -NMR spectrum of: A) MHMS(B) ($(\text{CD}_3)_2\text{CO}$, TMS);
B) an expansion of the aromatic region of MHMS(B)

Figure 3: Normalized DSC thermograms of: A) MHMS(A); MHMS(B)

Figure 4: Normalized DSC thermograms of: A) P-8-MA(A), heating scan; B) P-8-MA(A), cooling scan; C) P-8-AC(A), heating scan; D) P-8-AC(A), cooling scan

Figure 5: Typical optical polarized micrographs (magnification, 300X) of the S_c textures of: A) P-11-MA(A), after 1 hr at 116°C; B) P-11-AC(A), after 1 hr at 79°C; C) P-11-S(A), after 24 hr at 118.5°C

Figure 6: Typical optical polarized micrographs (magnification, 300X) of the nematic textures of: A) P-8-MA(A), after 1 hr at 105°C; B) P-8-AC(A), after 1 hr at 95°C; C) P-8-S(A), after 1 hr at 108.4°C

Figure 7: Typical optical polarized micrographs (magnification, 300X) of the nematic textures of: A) P-6-MA(A), after 1 hr at 112°C; B) P-6-AC(A), after 2 min at 92.2°C; C) P-6-AC(A), after 30 min at 92.2°C; D) P-6-S(A), after 30 min at 89°C

Figure 8: Thermal transitions of P-n-MA and P-n-AC as a function of number of methylenic units "n" in the spacer

Figure 9: Normalized DSC thermograms of: A) P-11-S(A), heating

scan; B) P-11-S(A), cooling scan; C) P-11-S(B), heating scan; D) P-11-S(B), cooling scan

Figure 10: Thermal transitions of P-n-S as a function of number of methylenic units "n" in the spacer

Figure 11: Normalized DSC thermograms of: A) P-6-S(A), heating scan; B) P-6-S(A), cooling scan; C) P-6/11-S(A/A), heating scan; D) P-6/11-S(A/A), cooling scan

Figure 12: Normalized DSC thermograms of: A) P-3-S(A), heating scan; B) P-3-S(A), cooling scan; C) P-3/11-S(A/A), heating scan; D) P-3/11-S(A/A), cooling scan

Figure 13: Typical optical polarized micrographs (magnification, 300X) of the nematic texture of P-6/11-S(A/A):
A) after 10 seconds at 114.7°C; B) after 3 min at 114.7°C; C) after 15 min at 114.7°C; D) same as C), cooled to 110.5°C; E) after 30 min at 114.7°C; F) after 24 hr at 110°C

SCHEMES

Scheme 1: Synthesis of Copolyethacrylates (P-n-MA) and

and Copolyacrylates (P-n-AC)

Scheme 2: Synthesis of Copolysiloxanes (P-n-S)

Scheme 3: Synthesis of Copolysiloxanes (P-n1/n2-S)

Table I. Characterization of 4(4')-(ω-Hydroxyalkanyloxy)-4'(4)-methoxy-α-methylstilbene (n-A)

Compound	Conversion (%)	m.p. (°C)	200M Hz ¹ H-NMR (CDCl ₃ , δ, ppm) ^{a)}
11-A (A)	86	118-122	1.31-1.80 (m, -(CH ₂) ₉); 2.24 (s, CH ₃ -C=); 3.64 (t, -CH ₂ O-); 3.83 (s, CH ₃ O-); 3.97 (t, -CH ₂ OPh); 6.70 (s, Ph-CH=); 6.86-7.44 (m, 8 aromatic protons).
8-A (A)	45	109-112	1.26-1.83 (m, -(CH ₂) ₆); 2.26 (s, CH ₃ -C=); 3.66 (t-CH ₂ O-); 3.84 (s, CH ₃ O-); 3.99 (t, -CH ₂ OPh); 6.70 (s, Ph-CH=); 6.86-7.46 (m, 8 aromatic protons).
6-A (A)	55	114-119	1.47-1.83 (m, -(CH ₂) ₄); 2.24 (s, CH ₃ -C=); 3.54 (t, -CH ₂ O-); 3.81 (s, CH ₃ O-); 4.01 (t, -CH ₂ OPh); 6.74 (s, Ph-CH=); 6.87-7.49 (m, 8 aromatic protons).
3-A (B)	79	122-127	1.97 (m, -CH ₂ -); 2.24 (s, CH ₃ -C=); 3.74 (t, -CH ₂ O-); 3.83 (s, CH ₃ O-); 4.17 (t, -CH ₂ OPh); 6.81 (s, Ph-CH=); 6.96-7.56 (m, 8 aromatic protons).
2-A (A)	57	126-130	2.23 (s, CH ₃ -C=); 3.81 (s, CH ₃ O-); 3.87 (t, -CH ₂ O-); 4.09 (t, -CH ₂ OPh); 6.73 (s, Ph-CH=); 6.90-7.51 (m, 8 aromatic protons).

a) Chemical shifts for n-A prepared from MHMS sample A or B are identical.

Table II. Characterization of Methacrylates (n-MA) and Acrylates (n-Ac)

Compound	Conversion	m.p. T ₁ (°C) ²	T ₁ (°C) ²	200M Hz ¹ H-NMR (CDCl ₃ , δ, ppm) ^a
11-MA (A)	79	60	85	1.34-1.80 (m, -(CH ₂) ₉); 1.93 (s, CH ₃ -C-COO); 2.24 (s, CH ₃ -C=); 3.82 (s, CH ₃ O-); 3.97 (t, -CH ₂ OPh); 4.15 (t, -CH ₂ OOC); 5.53 and 6.08 (2s, CH ₂ =); 6.72 (s, Ph-CH=); 6.86-7.47 (m, 8 aromatic protons).
8-MA (A)	56	47	--	1.37-1.80 (m, -(CH ₂) ₆); 1.94 (s, CH ₃ -C-COO); 2.24 (s, CH ₃ -C=); 3.83 (s, CH ₃ O-); 3.97 (t, -CH ₂ OPh); 4.14 (t, -CH ₂ OOC); 5.54 and 6.10 (2s, CH ₂ =); 6.71 (s, Ph-CH=); 6.87-7.44 (m, 8 aromatic protons).
6-MA (A)	75	22	28	1.45-1.83 (m, -(CH ₂) ₄); 1.94 (s, CH ₃ -C-COO); 2.24 (s, CH ₃ -C=); 3.81 (s, CH ₃ O-); 3.96 (t, -CH ₂ OPh); 4.16 (t, -CH ₂ OOC); 5.54 and 6.10 (2s, CH ₂ =); 6.72 (s, Ph-CH=); 6.85-7.46 (8 aromatic protons).
3-MA (B)	41	47	55	1.97 (s, CH ₃ -C-COO); 2.20 (m, -CH ₂ -); 2.26 (CH ₃ -C=); 3.84 (s, CH ₃ O-); 4.11 (t, -CH ₂ OPh); 4.39 (t, -CH ₂ OOC); 5.59 and 6.14 (2s, CH ₂ =); 6.74 (s, Ph-CH=); 6.90-7.49 (m, 8 aromatic protons).
2-MA (A)	30	68	81	1.94 (s, CH ₃ -C-COO); 2.23 (s, CH ₃ -C=); 3.74 (s, CH ₃ O-); 4.16 (t, -CH ₂ OPh); 4.41 (t, -CH ₂ OOC); 5.4 and 6.03 (2s, CH ₂ =); 6.56 (s, Ph-CH=); 6.74-7.31 (8 aromatic protons).
11-AC (A)	47	71	--	1.31-1.81 (m, -(CH ₂) ₉); 2.26 (s, CH ₃ -C=); 3.86 (s, CH ₃ O-); 4.00 (t, -CH ₂ OPh); 4.19 (t, -CH ₂ OOC); 5.83-6.49 (m, CH ₂ =CH-); 6.76 (s, Ph-CH=); 6.91-7.51 (8 aromatic protons).
8-AC (A)	62	75	--	1.40-1.83 (m, -(CH ₂) ₆); 2.26 (s, CH ₃ -C=); 3.84 (s, CH ₃ O-); 4.00 (t, -CH ₂ OPh); 4.19 (t, -CH ₂ OOC); 5.80-6.47 (m, CH ₂ =CH-); 6.74 (s, Ph-CH=); 6.90-7.47 (m, 8 aromatic protons).
6-AC (A)	63	66	--	1.50-1.81 (m, -(CH ₂) ₄); 2.26 (s, CH ₃ -C=); 3.84 (s, CH ₃ O-); 4.00 (t, -CH ₂ OPh); 4.20 (t, -CH ₂ OOC); 5.79-6.46 (m, CH ₂ =CH-); 6.71 (s, Ph-CH=); 6.87-7.46 (m, 8 aromatic protons).

(see continuation)

Table II (continued)

3-AC (B)	73	63	71	2.17 (m, $-\text{CH}_2^-$); 2.26 (s, $\text{CH}_3-\overset{\text{I}}{\text{C}}=$); 3.86 (s, $\text{CH}_3\text{O}-$); 4.10 (t, $-\text{CH}_2\text{OPh}$); 4.40 (t, $-\text{CH}_2\text{OOC}$); 5.81-6.49 (m, $\text{CH}_2=\text{CH}-$); 6.73 (s, $\text{Ph}-\text{CH}=\text{}$); 6.91-7.49 (m, 8 aromatic protons).
2-AC (B)	45	86	101	2.24 (s, $\text{CH}_3-\overset{\text{I}}{\text{C}}=$); 3.81 (s, $\text{CH}_3\text{O}-$); 4.23 (t, $-\text{CH}_2\text{OPh}$); 4.53 (t, $-\text{CH}_2\text{OOC}$); 5.83-6.50 (m, $\text{CH}_2=\text{CH}$); 6.73 (s, $\text{Ph}-\text{CH}=\text{}$); 6.89-7.46 (m, 8 aromatic protons)

a) Chemical shifts for n-MA and n-AC prepared from MHMS sample A or B are identical.

Table III: Thermal Transitions and Thermodynamic Parameters of Polymethacrylates (P-n-MA).

		Thermal Transitions, ($^{\circ}\text{C}$) and Thermodynamic Parameters, $\Delta\text{H}(\text{Kcal/mru}^*), \Delta\text{S}(\text{cal/mru}^*.\text{K})$							
Polymer	Spacer	GPC**		Tg	Heating		Cooling		
		$\text{Mn} \times 10^{-3}$	$\overline{\text{Mw/Mn}}$		Tl	Tl	Tl	Tl	
					$\Delta\text{Hl}/\Delta\text{Sl}$	$\Delta\text{Hl}/\Delta\text{Sl}$	$\Delta\text{Hl}/\Delta\text{Sl}$	$\Delta\text{Hl}/\Delta\text{Sl}$	
P-11-MA(A)	C11	15.2	2.17	14	--	118	110	--	
					--/--	1.03/2.64	1.04/2.72	--/--	
P-8-MA(A)	C8	45.2	1.60	21	54	113	107	47	
					0.06/0.17	0.24/0.62	0.22/0.58	0.06/0.18	
P-6-MA(A)	C6	15.6	2.17	23	--	113	108	--	
					--/--	0.26/0.66	0.24/0.62	--/--	
P-3-MA(B)	C3	9.4	2.54	49	--	100	94	--	
					--/--	0.11/0.29	0.11/0.30	--/--	
P-2-MA(A)	C2	20.8	2.33	82	--	114	109	--	
					--/--	0.11/0.28	0.11/0.29	--/--	

* mru = mole of repeat units.

** polystyrene standard.

Table IV: Thermal Transitions and Thermodynamic Parameters of Polyacrylates (P-n-AC).

		Thermal Transitions, (°C) and Thermodynamic Parameters, $\Delta H(\text{Kcal/mru}^*), \Delta S(\text{cal/mru}^* \cdot ^\circ\text{K})$						
Polymer	Spacer	GPC**		Heating		Cooling		
		$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Tg	T _{m1} , T _{m2} , T _{m3} $\Delta H_m/\Delta S_m$	T _i $\Delta H_i/\Delta S_i$	T _i $\Delta H_i/\Delta S_i$	T _c $\Delta H_c/\Delta S_c$
P-11-AC(A)	C11	6.6	1.32	9	53,70,78 2.48/--	103 0.48/1.28	95 0.48/1.30	20 0.14/0.48
P-8-AC(A)	C8	7.7	1.27	9	64**** 0.02/0.06	97 0.17/0.46	92 0.17/0.47	59**** 0.02/0.06
P-6-AC(A)	C6	7.5	1.27	16	-- --/--	93 0.10/0.27	89 0.10/0.27	-- --/--
P-3-AC(B)	C3	5.6	1.45	31	-- --/--	69 0.02/0.06	64 0.02/0.06	-- --/--
P-2-AC(B)	C2	4.6	1.24	52	-- --/--	68 0.02/0.06	---*** --/--	-- --/--

* mru = mole of repeat units.

** polystyrene standard.

*** Transition overlaps with glass transition.

**** T_m, T_c = T_i.

Table V. Characterization of Vinyl Derivatives (n-0)

Compound	200 MHz ¹ H-NMR (CDCl ₃ , δ, ppm)
11-0 (A)	2.24(s, CH ₃ -C=); 3.83(s, CH ₃ O-); 4.57(d, -CH ₂ O-); 5.37 and 6.08 (m, H ₂ C=CH-); 6.73(s, =CH-Ph); 6.88 to 7.47(m, 8 aromatic protons).
8-0 (A)	1.91 to 2.31(m, 2 -CH ₂ - and CH ₃ -C=); 3.83(s, CH ₃ O-); 4.0(t, -CH ₂ O-); 5.04 and 5.86(m, H ₂ C=CH-); 6.71(s, =CH-Ph); 6.87 to 7.44(m, 8 aromatic protons).
6-0 (A)	1.56 to 2.20(m, 3 -CH ₂ -); 2.25(s, CH ₃ -C=); 3.84(s, CH ₃ O-); 4.0(t, -CH ₂ O-); 5.01 and 5.84(m, H ₂ C=CH-); 6.71(s, =CH-Ph); 6.88 to 7.48(8 aromatic protons).
5-0 (A)	1.43 to 2.14(m, 5 -CH ₂ -); 2.24(s, CH ₃ -C=); 3.83(s, CH ₃ O-); 4.00(t, -CH ₂ O-); 5.00 and 5.88(m, H ₂ C=CH-); 6.74(s, =CH-Ph); 6.88 to 7.48(8 aromatic protons).
3-0 (A)	1.33 to 2.07(m, 8 -CH ₂ -); 2.26(s, CH ₃ -C=); 3.83(s, CH ₃ O-); 3.98(t, -CH ₂ O-); 4.97 and 5.84(m, H ₂ C=CH-); 6.73(s, =CH-Ph); 6.88 to 7.48(8 aromatic protons).

Table VI: Thermal Transitions of vinyl derivatives(n-O).

Compound	Thermal Transitions				
	Heating		Cooling		
	T1	T2	T1	T2	T1
11-O(A)	84	102	88	85	71
8-O(A)	80	95	79	77	68
6-O(A)	75	--	58	51	38
5-O(A)	75	--	49	46	42
3-O(A)	85	--	70	58	55

Table VII: Thermal Transitions and Thermodynamic Parameters of Polysiloxanes (P-n-S)

Polymer	S _{icer}	Heating					Cooling				
		T _{m1}	T _c	T _{m2}	T _{m3}	T ₁	T ₁	T ₁	T _c	T _c	
T _g	$\Delta H_{m1}/\Delta S_{m1}$	$\Delta H_c/\Delta S_c$	$\Delta H_{m2}/\Delta S_{m2}$	$\Delta H_{m3}/\Delta S_{m3}$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_c/\Delta S_c$	$\Delta H_c/\Delta S_c$		
P-11-S(A)	C11	-11	54	59	71	78	107	102	33		
			0.74/2.26	0.07/0.21	--/--	0.71/--**	0.50/1.32	0.51/1.36	1.34/4.38		
P-11-S(B)	C11	-10	45	53	74	82	125	121	36		
			0.09/0.28	0.10/0.31	--/--	1.57/--**	0.48/1.21	0.50/1.27	1.39/4.50		
P-8-S(A)	C8	-7	53	55	80	--	110	107	34		
			0.57/1.76	0.77/2.35	1.62/4.64	--/--	0.18/0.47	0.18/0.47	0.96/3.14		
P-6-S(A)	C6	0	57	61	79	--	114	111	36		
			0.88/2.67	0.61/1.83	0.93/2.65	--/--	0.13/0.32	0.14/0.36	1.02/3.29		
P-6-S(B)	C6	-2	57	--	--	--	98	95	35		
			1.13/3.41	--/--	--/--	--/--	0.10/0.27	0.10/0.27	0.98/3.20		
P-5-S(A)	C5	6	72	--	--	--	110	107	52		
			1.21/3.50	--/--	--/--	--/--	0.10/0.26	0.11/0.30	1.10/3.37		
P-3-S(A)	C3	20	78	--	--	--	119	116	63		
			0.88/2.50	--/--	--/--	--/--	0.10/0.24	0.10/0.25	0.85/2.54		

* mru = mole of repeat units.

** overlapped transition.

Table VIII: Thermal Transitions and Thermodynamic Parameters of Copolysiloxanes (P-n1/n2-S).

		Thermal Transitions, (°C) and Thermodynamic Parameters, ΔH(Kcal/mru*), ΔS(cal/mru*.°k)					
Polymer	Spacer	Heating			Cooling		
		T _g	T _{m1} ΔH _{m1} /ΔS _{m1}	T _{m2} ΔH _{m2} /ΔS _{m2}	T _i ΔH _i /ΔS _i	T _i ΔH _i /ΔS _i	T _c ΔT _c /ΔS _c
P-3/6-S(A/A)	C3:C6=1:1	-11	59 0.70/2.10	-- --/--	111 0.11/0.29	105 0.13/0.33	35 0.57/1.84
P-6/11-S(A/A)	C6:C11=1:1	-8	51 --/--	61 0.81/--**	118 0.35/0.89	113 0.34/0.88	10 0.31/1.09
P-3/11-S(A/A)	C3:C11=1:1	-5	-- --/--	-- --/--	112 0.28/0.73	108 0.28/0.75	-- --/--

* mru = mole of repeat units.

** overlapped transitions.

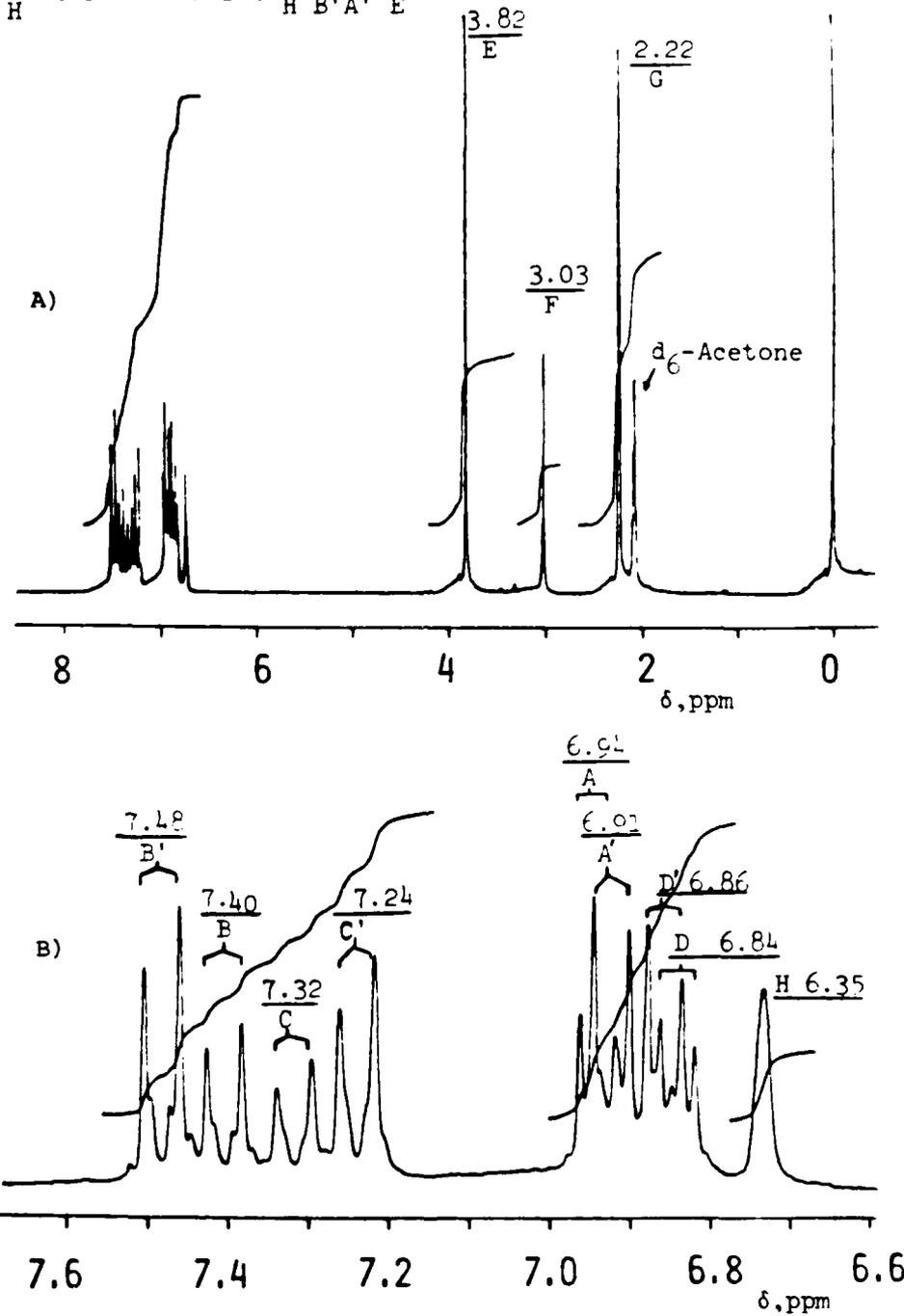
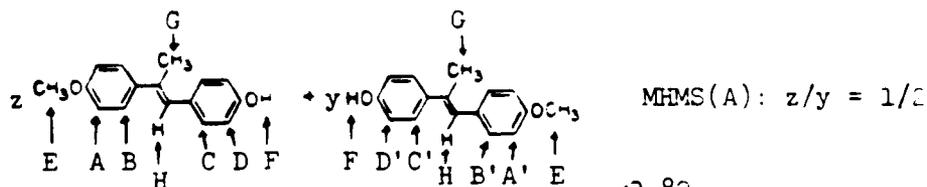


Figure 1

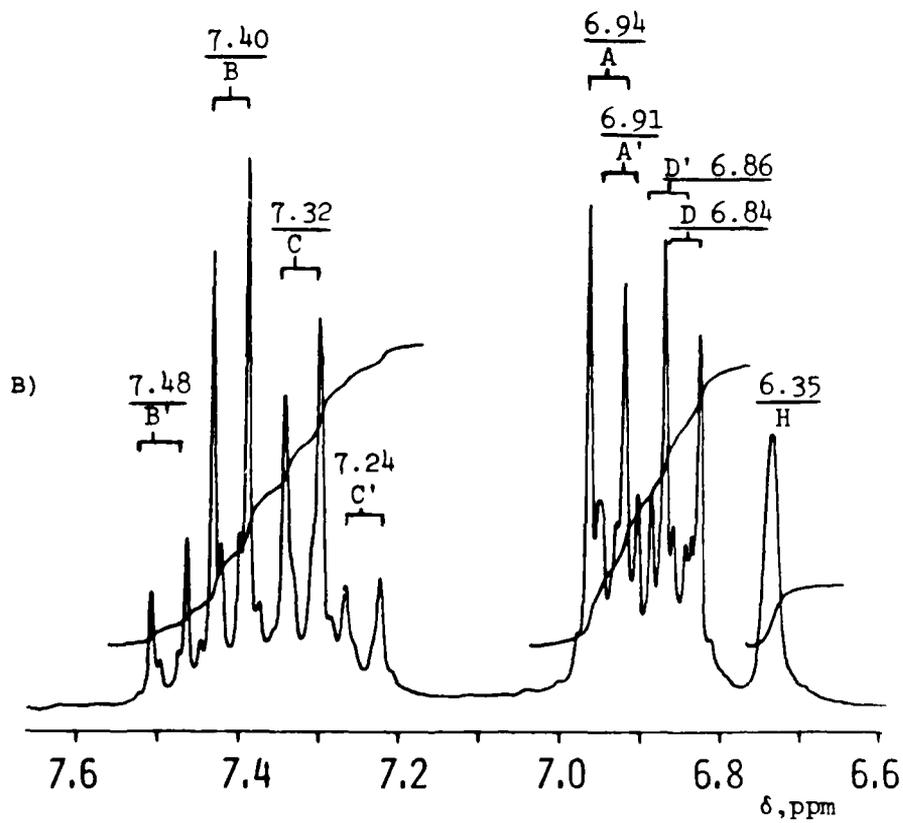
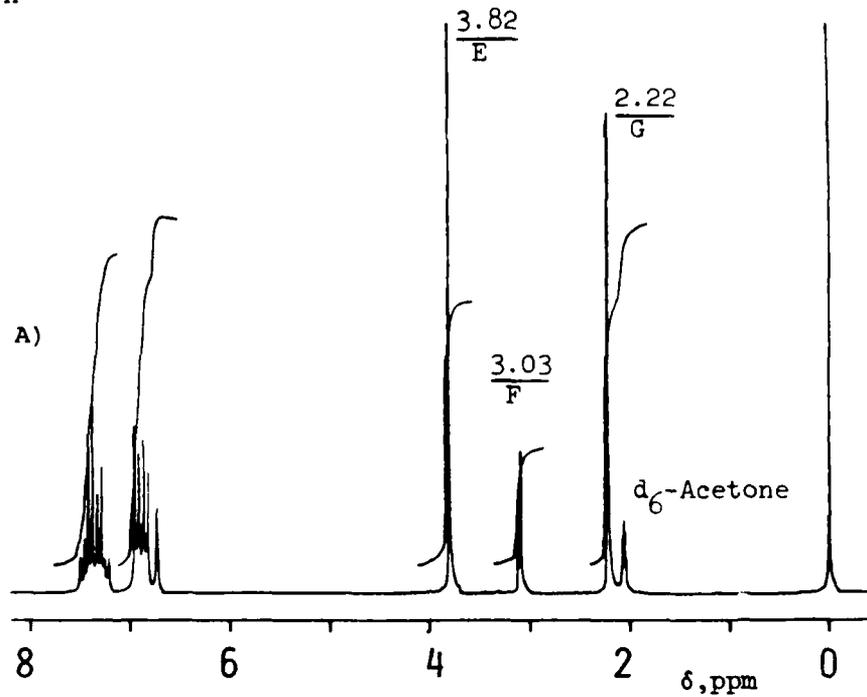
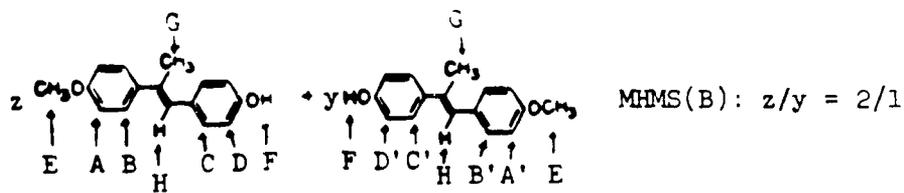


Figure 2

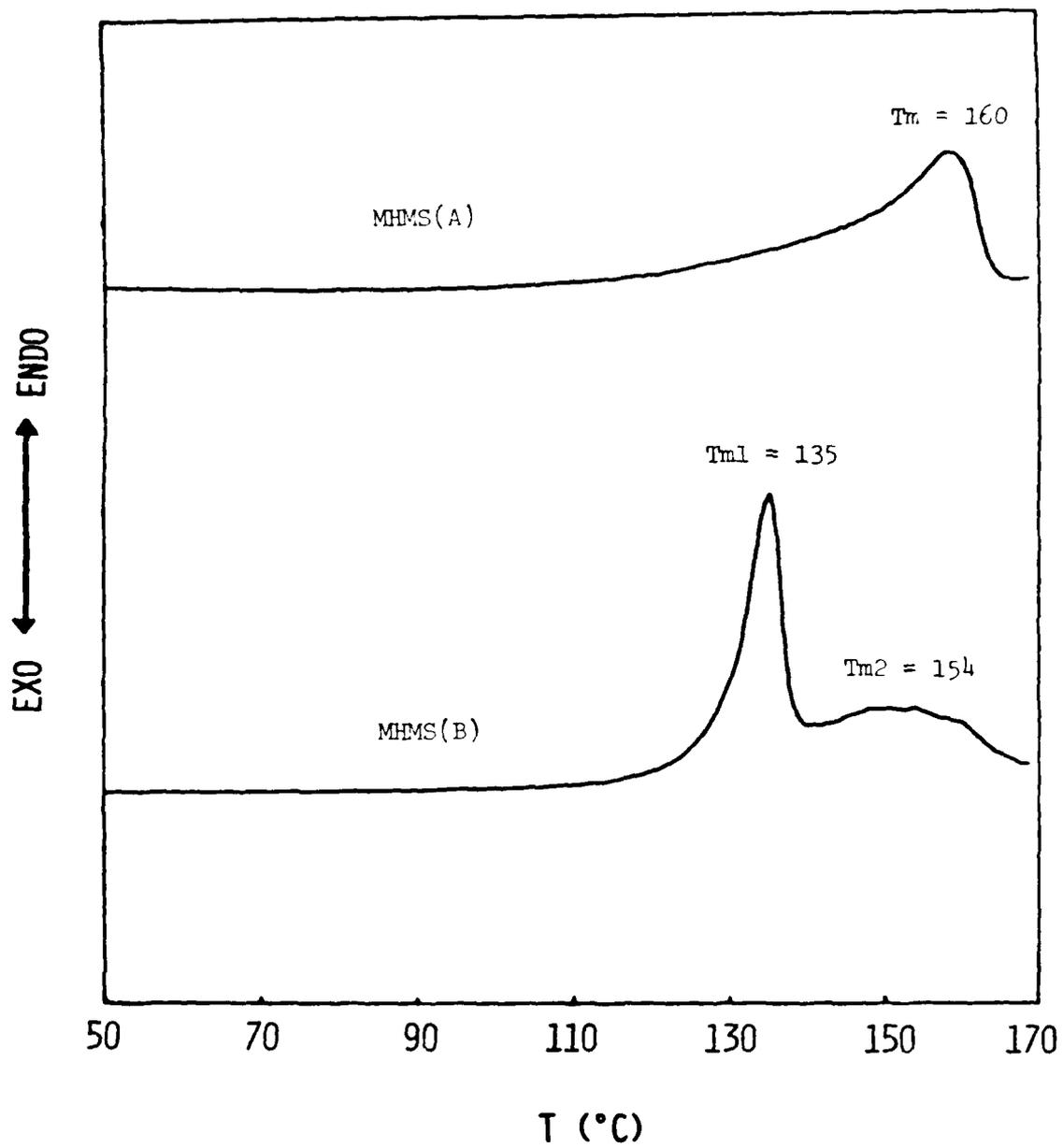


Figure 3

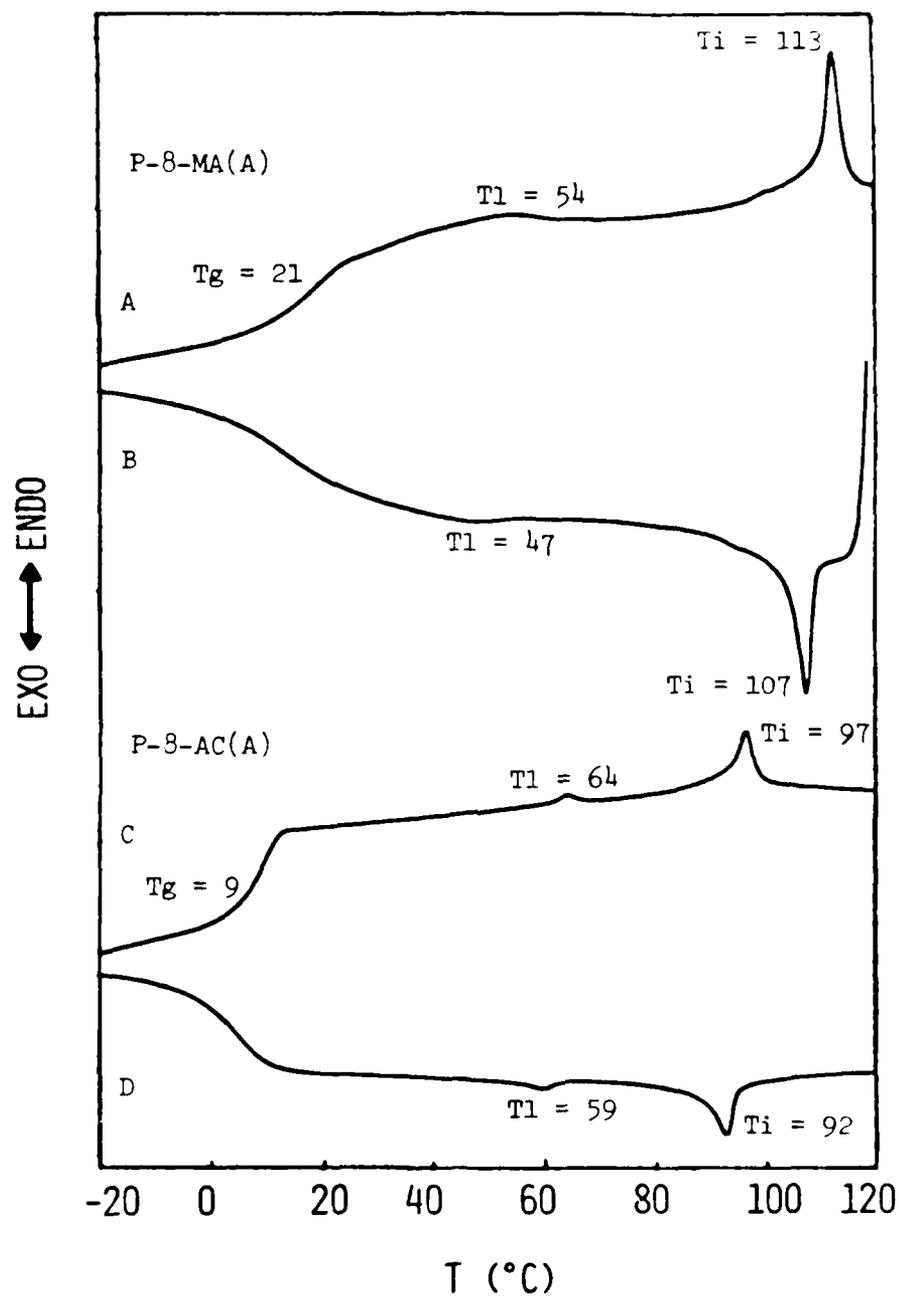


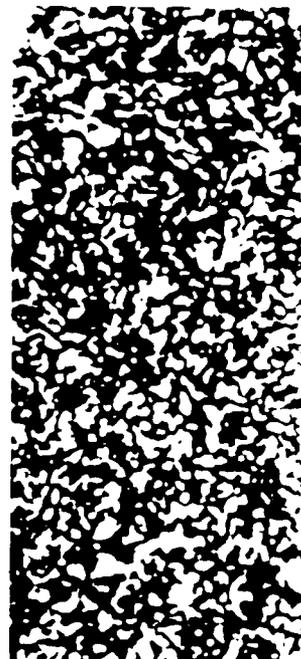
Figure 4



A)



B)



C)

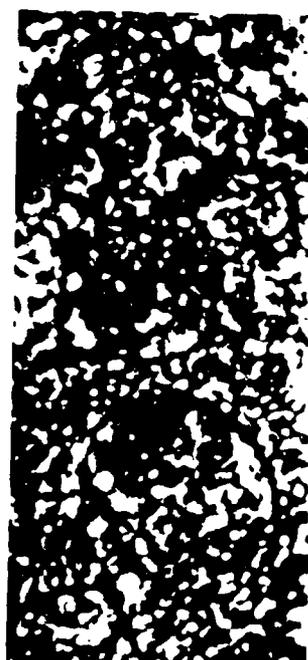
Figure 5



A)



B)



C)

Figure 6



A)



B)



C)



D)

Figure 7

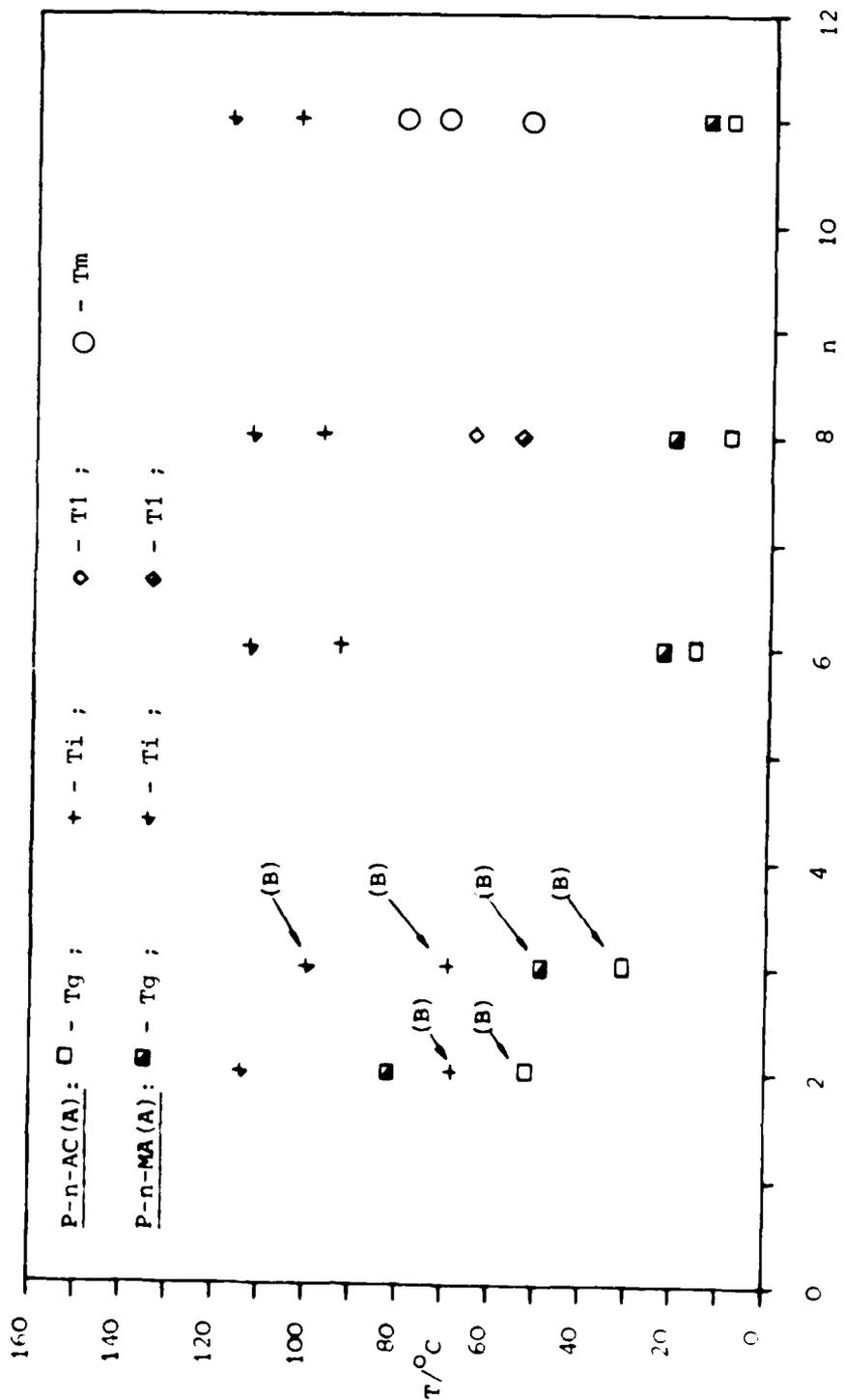


Figure 8

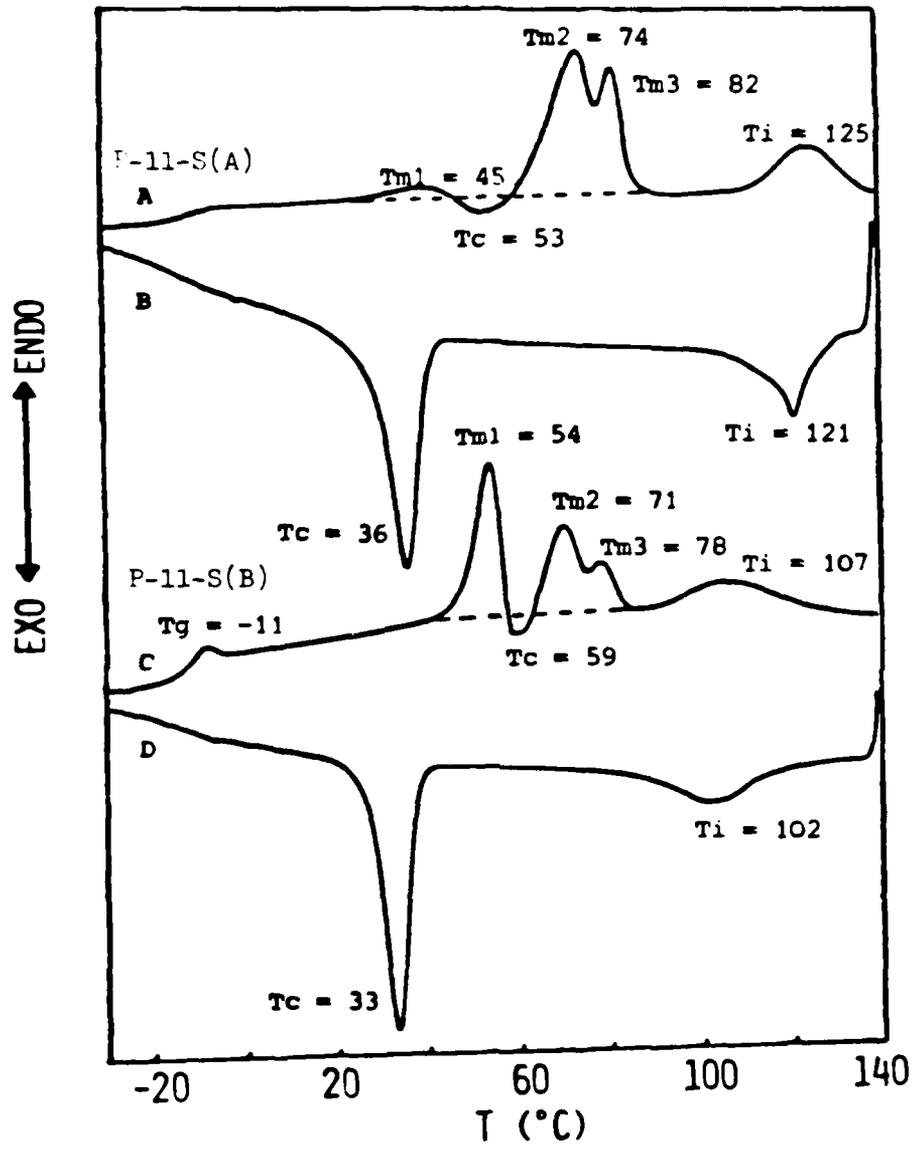


Figure 9

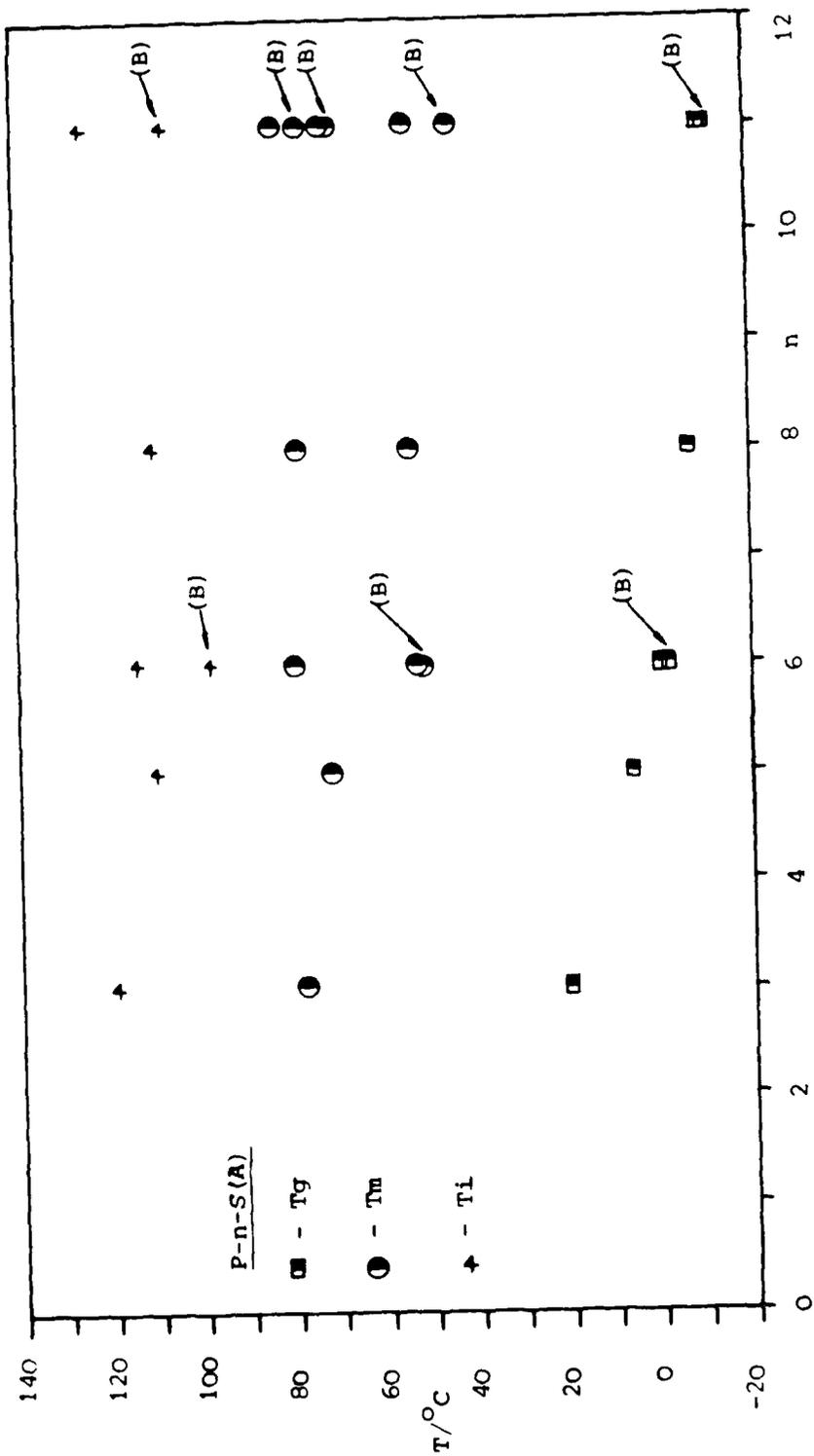


Figure 10

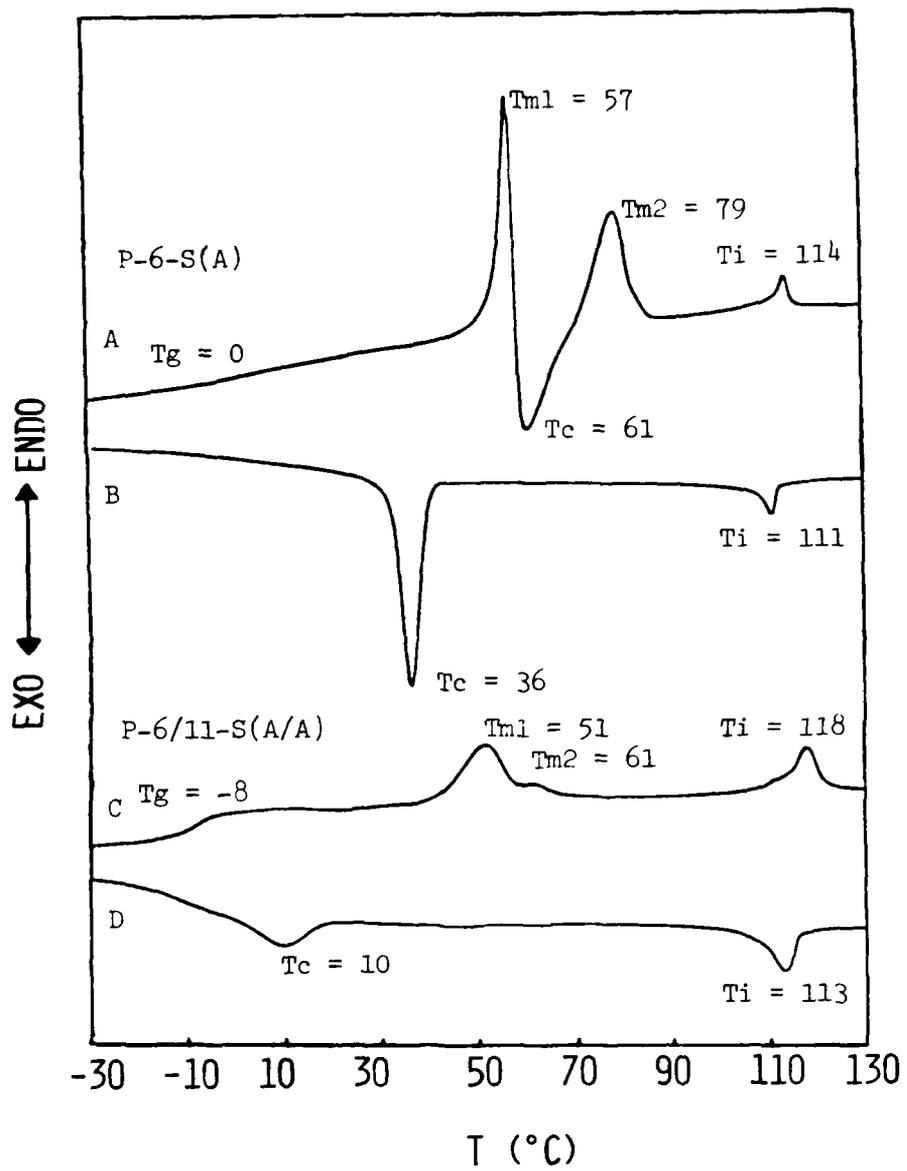


Figure 11

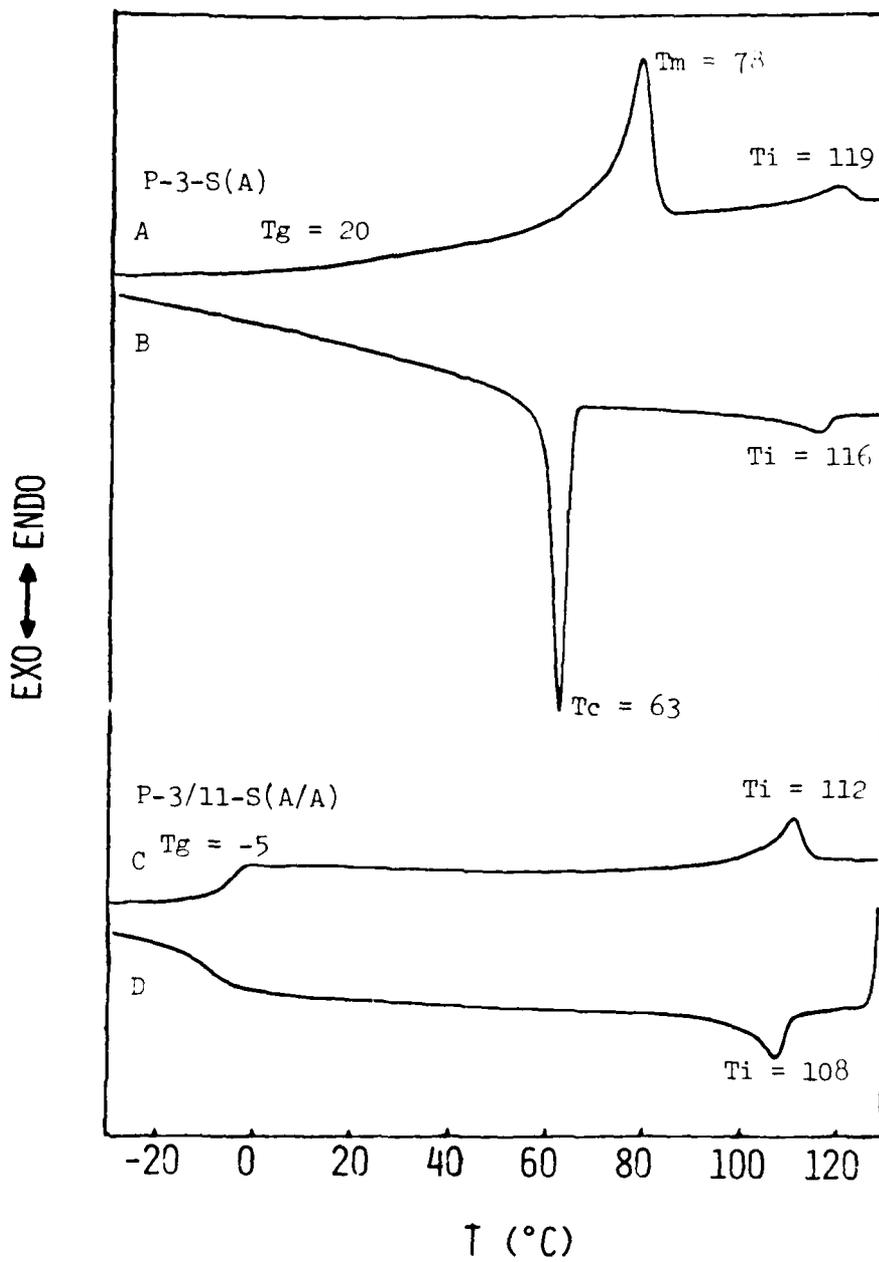
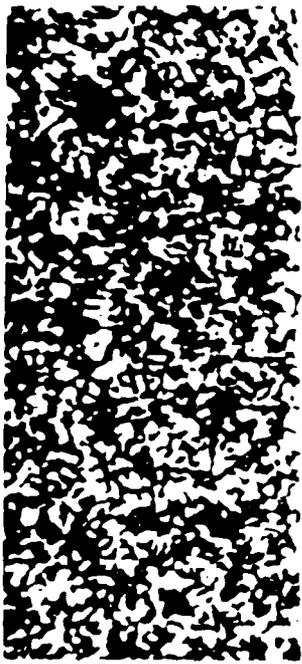


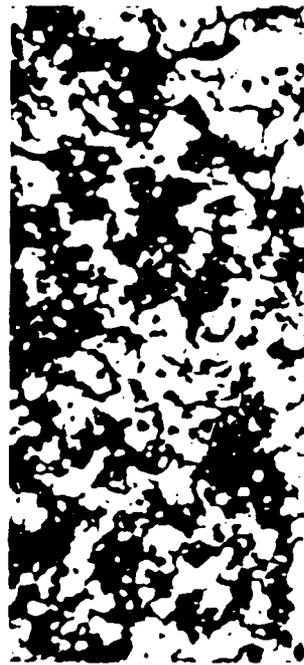
Figure 12



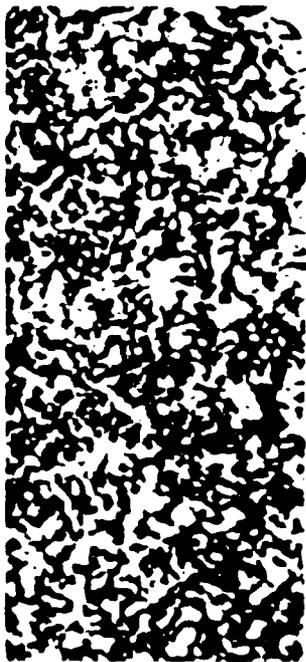
A)



B)



C)



D)

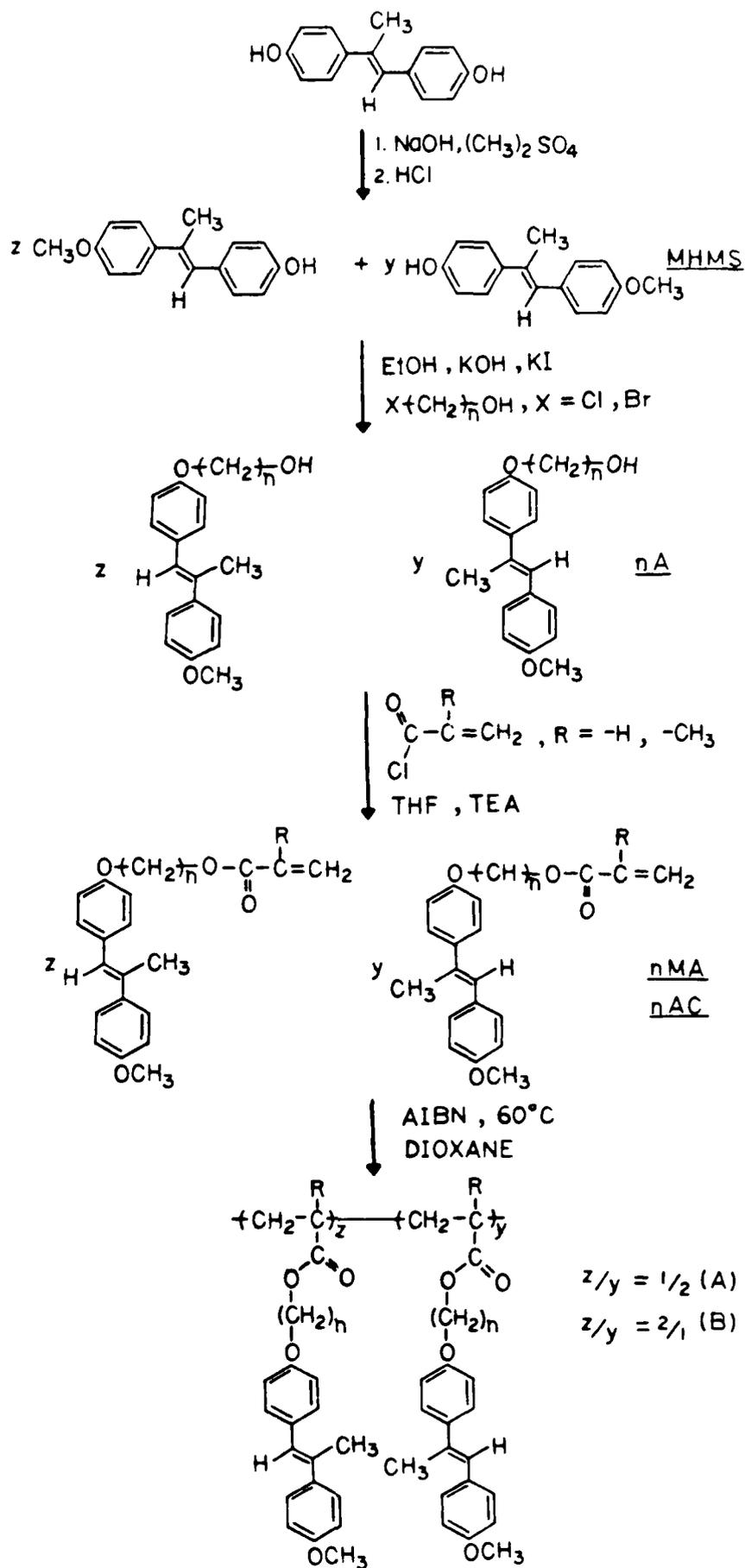


E)

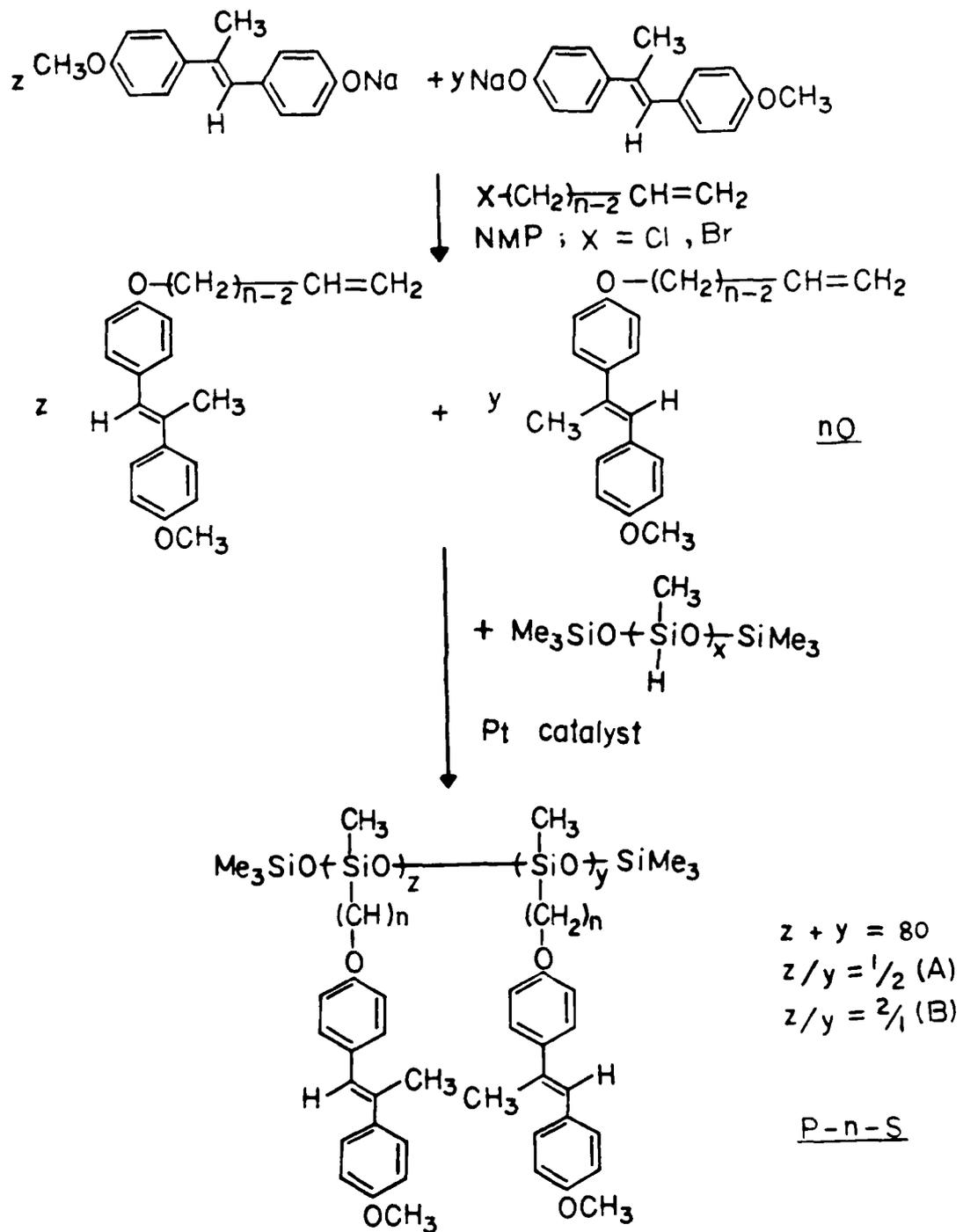


F)

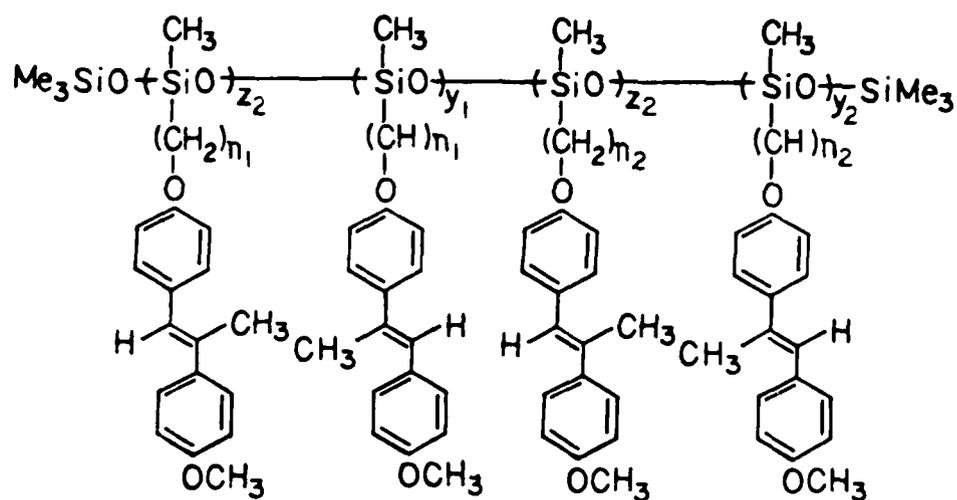
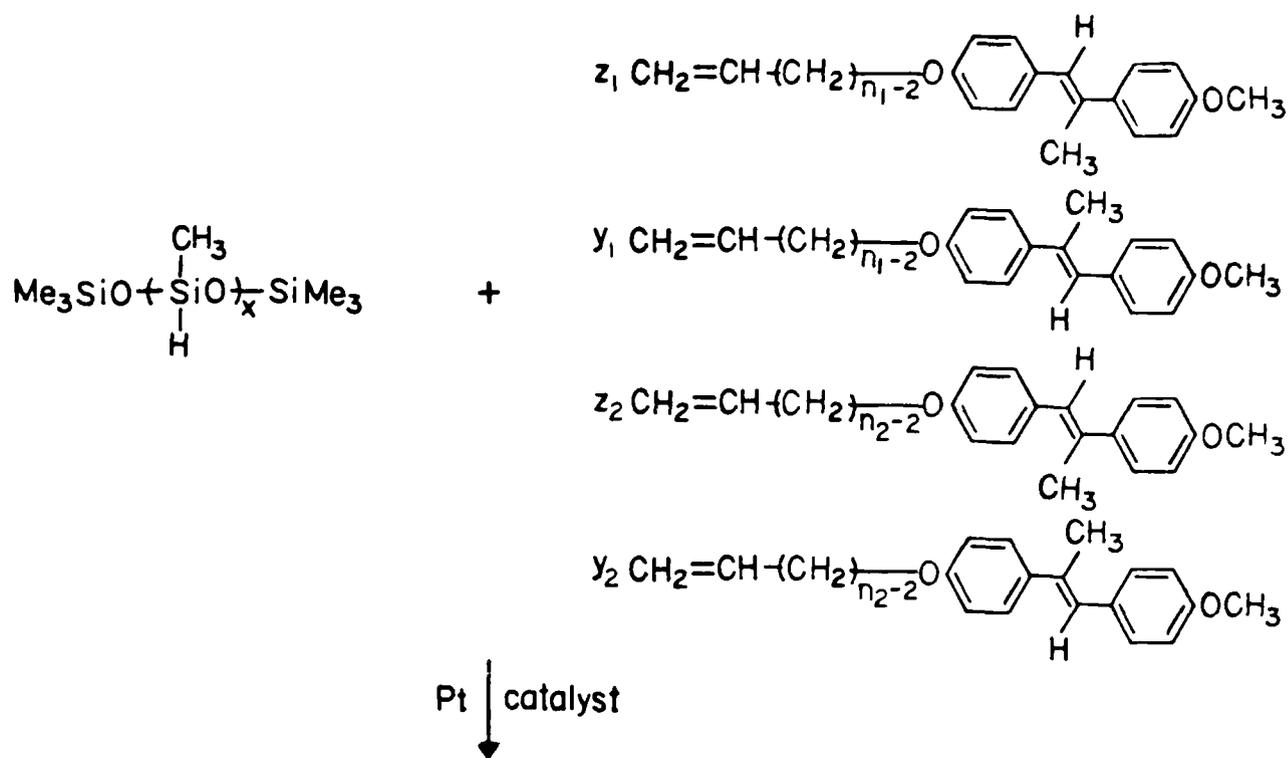
Figure 13



Scheme 1



Scheme 2



$$z_1 + z_2 = z$$

$$y_1 + y_2 = y$$

$$z/y = 1/2 \text{ (A)}$$

$$z/y = 2/1 \text{ (B)}$$

$$z + y = 80$$

Scheme 3

END

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