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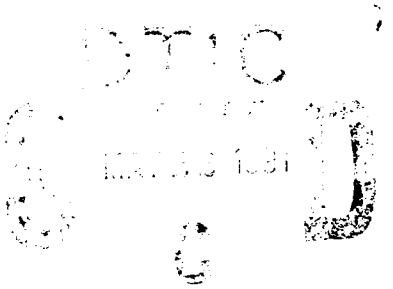

Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 13. Synthesis and Living Cationic Polymerization of 4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(ω-Oxyalkyl-1-Vinyl Ether)Biphenyl with Undecanyl and Hexyl Alkyl Groups

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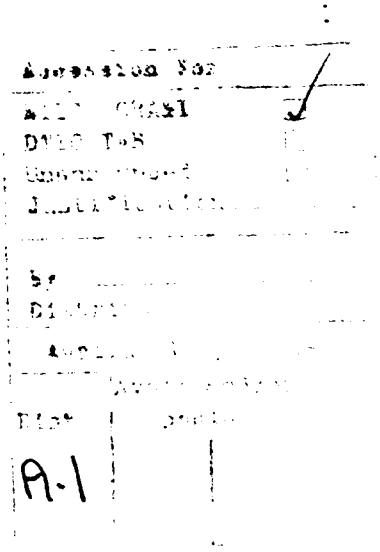

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ABSTRACT

The synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(11-oxyundecanyl-1-vinyl ether)biphenyl (13-11) and 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(6-oxyhexyl-1-vinyl ether)biphenyl (13-6) are described. Polymers with degrees of polymerization from four to twenty six and polydispersities equal and lower than 1.10 were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. When determined from first heating and cooling DSC scans, poly(13-11)s exhibit monotropic s_A, s_C* and s_X (unidentified) mesophases over the entire range of molecular weights. When determined from second and subsequent heating and first and subsequent cooling scans, poly(13-11)s with degrees of polymerization equal to ten and lower than ten exhibit enantiotropic s_A, s_C* and s_X mesophases, and crystallization on the heating scan, while those with higher degrees of polymerization exhibit enantiotropic s_A, s_C* and s_X mesophases only. Regardless of the thermal history of the sample, poly(13-6) exhibits an enantiotropic s_A and the polymers with degrees of polymerization higher than twelve also an enantiotropic s_X mesophase.

Keywords: chiral vinyl ether, living cationic polymerization, chiral smectic C.

INTRODUCTION

Liquid crystalline polymers exhibiting chiral mesophases, i.e., cholesteric[1] and chiral smectic C (s_C*)[2] are of both theoretical and technological interests. Liquid crystals exhibiting chiral smectic A (s_A*) mesophases were only recently discovered[3] and to our knowledge, polymers exhibiting s_A* mesophases were not yet reported. Side chain liquid crystalline polymers exhibiting s_C* mesophases were reported from several different laboratories.[2,4-15] However, there is very little understanding of the molecular design of side chain liquid crystalline polymers displaying s_C* mesophases, and of the influence of various architectural parameters of these polymers on their dynamics.[2,4-15] The ability to synthesize side chain liquid crystalline polymers by a living polymerization technique would provide a very useful praparative tool which gives access to polymers with narrow molecular weight distribution and controllable molecular weight.

Group transfer polymerization of mesogenic methacrylates can be used to prepare side chain liquid crystalline polymers with narrow molecular weight distribution and controllable molecular weights.[16,17] However, this polymerization does not tolerate functional groups sensitive to the nucleophilic growing species and can be used mostly for the polymerization of methacrylates. Cationic polymerization can be used to polymerize

under living conditions mesogenic vinyl ethers containing a large variety of functional groups,[18,19] especially with the initiating system $CF_3SO_3H/S(CH_3)_2$.[20]

The goal of this paper is to describe the synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(11-oxyundecanyl-1-vinyl ether)biphenyl (13-11) and 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(6-oxyhexyl-1-vinyl ether) biphenyl (13-6). The mesomorphic behavior of poly(13-11) and poly(13-6) will be discussed as a function of molecular weight.

EXPERIMENTAL

Materials

4-Hydroxybiphenyl (97%), dimethylsulfate (99%+), HBr (48% in H_2O), 9-borabicyclo[3.3.1]nonane (9-BBN dimer, crystalline, 98%), 11-bromoundecan-1-ol (98%), n-butyl vinyl ether (98%), tetra-n-butylammonium hydrogen sulfate (TBAH) (all from Aldrich), 1,10-phenanthroline (anhydrous, 99%), palladium (II) diacetate (both from Lancaster Synthesis), acetyl chloride (99%) and S(-)-2-methyl-1-butanol (95%) (both from Fluka) were used as received. Methylene chloride (Fisher) was purified by washing with concentrated sulfuric acid several times until the acid layer remains colorless, then with water, dried over anhydrous $MgSO_4$, refluxed over calcium hydride and freshly distilled under nitrogen before each use. Dimethyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN and then distilled under nitrogen. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1320 infrared spectrophotometer. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven and a Nelson Analytical 900 series integrator data station. A set of two Perkin-Elmer PL gel columns of $5x10^2$ and 10^4 Å with $CHCl_3$ as solvent (1ml/min) were used. The measurements were made at 40°C using the UV detector. Polystyrene standards were used for the calibration plot. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument. Absolute number average molecular weights were determined by ^{1}H-NMR spectroscopy by analyzing the chain ends of the resulting polymers. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks. In all cases, heating and cooling rates were 20°C/min unless specified. Glass transition temperatures (Tg) were

read at the middle of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. A Carl-Zeiss optical polarized microscope (magnification 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transition and to analyze the anisotropic textures.

Synthesis of Monomers

Monomers were synthesized as outlined in Scheme I

4-Methoxybiphenyl (2)

4-Hydroxybiphenyl (127.8 g, 0.75 mol) was dissolved in 2,250 ml of 1.5 N sodium hydroxide solution at 55°C. Dimethyl sulfate (189 g, 1.5 mol) was added slowly so that the temperature did not exceed 60°C. The temperature was then raised to 70°C for 30 minutes and then the reaction mixture was allowed to cool to room temperature. The resulting white precipitate was filtered and recrystallized from 95% ethanol to yield 68.5 g (50%) of white crystals. Purity: 99.8% (HPLC). mp, 87.0-87.5°C (lit. 21a, mp, 89.0°C· lit. 21b, mp, 80.5°C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.81 (s, 3 protons, -O-CH_3), 6.92(d, 2 aromatic protons, o to -OCH_3), 7.22 (d, 2 aromatic protons, m to -O-CH_3), 7.35 (m, 2 aromatic protons, o to -PhOCH_3), 7.47 (m, 3 aromatic protons, m and p to -PhOCH_3).

4-Acetyl-4'-(Methoxy)Biphenyl (3)

4-Methoxybiphenyl (2) (56 g, 0.303 mol) was dissolved in 500 ml dry methylene chloride in a 2,000 ml three necks round bottom flask, equipped with dropping funnel and condenser. The solution was cooled to 0-2°C. Anhydrous aluminium chloride (48.4 g, 0.36 mol) was added quickly to give a green solution. Acetyl chloride (28.5 g 0.363 mol) was then added during 20-30 minutes, and the reaction mixture was refluxed for two hours. Ice cooled concentrated HCl (300 ml) was added to the cooled mixture to decompose the yellow-green complex. Then 200 ml of water were added and the mixture was heated to remove most of the methylene chloride. A light yellow-brown solid separated from the reaction mixture. The resulting solid was washed twice with diethyl ether (200 ml each time) to remove the isomeric 3-acetyl-4'-methoxybiphenyl, which is soluble in diethyl ether. The solid was then recrystallized from isopropyl alcohol (24 ml/gram) to yield 64 g (93%) of colorless flakes. Purity: 99.5% (HPLC). mp, 153-154 °C (lit. 21b, mp, 153-154°C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.61 (s, 3 protons, -$COCH_3$), 3.88 (s, 3 protons, -OCH_3), 7.00 (m, 2 aromatic protons, o to -OCH_3), 7.58 (d, 2 aromatic protons, m to -OCH_3), 7.64 (d, 2 aromatic protons, m to -$COCH_3$), 7.98 (d, 2 aromatic protons, o to -$COCH_3$).

4-(Carboxylic Acid)-4'-(Methoxy)Biphenyl (4)

A sodium hypobromite solution, prepared at 0-5°C by adding bromine (34 ml, 0.659 mol) very slowly into a solution of sodium hydroxide (95.2 g, 2.38 mol) in 450 ml of water, was added slowly to a solution of 4-acetyl-4'-(methoxy)biphenyl (3) (34 g, 0.15 mol) in 1,100 ml of 1,4-dioxane during one hour. The temperature of the reaction mixture was allowed to raise to 35-40°C. After stirring for an additional 15 minutes, the sparingly soluble sodium salt solution was treated with enough sodium bisulfite (52.5 g, 0.505 mol) to destroy the excess hypobromite. The hot solution was then acidified to yield 29 g (84.5%) 4-(carboxylic acid)-4'-(methoxy)biphenyl of sufficient purity to be used in the reduction step. mp, 253-254°C (lit. 22, mp, 258°C). ^{1}H-NMR (d_6-acetone, TMS, δ, ppm): 3.86(s, 3, protons, -O$\underline{CH_3}$), 7.05 (m, 2 aromatic protons, o to -OCH_3), 7.68 (d, 2 aromatic protons, m to -OCH_3), 7.75 (d, 2 aromatic protons, m to -COOH), 8.08 (d, 2 aromatic protons, o to -COOH).

4-(Carboxylic Acid)-4'-(Hydroxy)Biphenyl (10)

4-(Carboxylic acid)-4'-(methoxy)biphenyl (4) (29 g, 0.127 mol) was dissolved in 1,160 ml of boiling acetic acid. A solution of 48% hydrobromic acid (230 ml, 2.03 mol) was added and the reaction mixture was heated at reflux temperature for 12-13 hours. The reaction mixture was then poured into 3,000 ml of water, and allowed to cool to room temperature. The resulting precipitate was separated, washed with water and dried to yield 27 g (99%) of crude solid product. The product was purified by dissolving in methanol, and treating the solution with activated carbon to give a colorless solution, which was poured into water to yield 25 g (91%) of white powder. mp, 293-294°C (lit. 23. mp, 293-294°C). ^{1}H-NMR (d_6-acetone, TMS, δ, ppm): 3.03 (s, 1 protons, -O$\underline{H}$), 6.98 (d, 2 aromatic protons, o to -OH), 7.58 (d, 2 aromatic protons, m to -OH), 7.71 (d, 2 aromatic protons, m to -COOH), 8.07 (d, 2 aromatic protons, o to -COOH). IR (nujol, KBr plate): 3,300-2,400 cm^{-1} (υ, -OH of -COOH), 1,670 cm^{-1} (υ, -CO-).

S(-)-2-Methyl-1-Butyl Tosylate (6)

S(-)-2-Methyl-1-butanol (44 g, 0.5 mol) was added slowly to a solution of p-toluenesulfonyl chloride (190.6 g, 1 mol) in 300 ml of dry pyridine at 0°C.[24] The reaction mixture was stirred overnight at room temperature. The resulting solution was poured into 300 ml of water and extracted with diethyl ether. The ether layer was dried over $MgSO_4$ and the diethyl ether was removed on a rotary evaporator to yield 120 g (99%) of colorless oil. Purity: 99% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.85 (m, 6 protons, -$CH(C\underline{H_3})CH_2C\underline{H_3}$), 1.02-1.39 (m, 2 protons, -CH-$C\underline{H_2}CH_3$), 1.61 (m, 1 proton, -$CH_2C\underline{H}(CH_3)CH_2$-), 2.40 (s, 3 protons -Ph-$C\underline{H_3}$), 3.83 (m, 2 protons -$OC\underline{H_2}$-), 7.22(d, 2 aromatic protons, o to -CH_3), 7.71 (d, 2 aromatic protons, m to -CH_3).

1,10-Phenanthroline Palladium (II) Diacetate

To a stirred solution of 1.783 g (7.94 mmol) palladium (II) diacetate in 60 ml dry benzene was added a solution of 1.5 g (8.32 mmol) 1,10-phenanthroline in 70 ml of benzene during 30 minutes. The mixture was stirred for 4 hours and the yellow precipitate was filtered and washed with benzene and petroleum ether to yield 3.2 g (99%) of a yellow solid. mp, 233-234°C (lit. 25, mp, 234°C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.16 (s, 6 protons, -OCO(CH_3)$_2$), 7.77 (m, 2 aromatic protons, m to N), 7.99 (s, 2 aromatic protons, 5,6 positions in the middle ring), 8.56-8.67 (m, 4 aromatic protons, o to N).

11-Bromoundecanyl-1-Vinyl Ether (9-11)[19c]

A solution of 8 g (0.23 mol) 11-bromo-1-undecanol, 0.418 g (1.03 mmol) 1,10-phenanthroline palladium (II) diacetate, 20 ml dry chloroform and 85 ml butyl vinyl ether was heated to reflux overnight (12-14 hours). The resulting light yellow solution, obtained after gravity filtration, was distilled on a rotary evaporator to remove the excess butyl vinyl ether and chloroform. The remaining yellow oil was purified by column chromatography (silica gel, CH_2Cl_2 as eluent) to yield 8.1 g (92%) of light yellow oil. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.27-1.81(m, 18 protons -OCH$_2$-(CH$_2$)$_9$-), 3.38 (t, 2 protons, -CH$_2$-Br), 3.64 (t, 2 protons, =CHOCH$_2$-), 3.96 (d, 1 protons, =CH$_2$, trans), 4.14 (d, 1 proton, =CH$_2$, cis), 6.39-9.51 (m, 1 proton, =CH-O-).

6-Bromohexanyl-1-Vinyl Ether (9-6)

9-6 was synthesized by the same procedure as the one used for in the synthesis of 9-11. 6-Bromohexan-1-ol (12 g, 66.3 mmol) and 1,10-phenanthroline palladium (II) diacetate (0.872 g, 2.16 mmol), 20 ml dry chloroform and 177 ml butyl vinyl ether were heated to reflux overnight. The resulting product was purified to produce 12.2 g (89%) of a light yellow oil. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.42-1.84 (m, 8 protons, -OCH$_2$-(CH$_2$)$_4$), 3.38 (t, 2 protons, -CH$_2$-Br), 3.65 (t, 2 protons, =CH-OCH$_2$-), 3.93 (d, 1 proton, =CH$_2$, trans), 4.14 (d, 1 proton, =CH$_2$ cis), 6.38-9.49 (m, 1 proton, =CH-O-).

4-(Potassium Carboxylate)-4'-(Hydroxy)Biphenyl (11)

4-(Carboxylic acid)-4'-(hydroxy)biphenyl (10) (20 g, 0.293 mol) was dissolved in 500 ml methanol. The solution was titrated with a solution of 1M KOH in CH_3OH using phenolphthalein as indicator. The solution was then poured into 1,500 ml of diethyl ether to give a white precipitate. The precipitate was filtered and dried to yield 20.2 g (96%) of product. The formation of potassium carboxylate was confirmed by IR. After complete reaction, the carbonyl peak of the carboxylic acid at 1,670 cm^{-1} was shifted down to 1,585 cm^{-1} due to the more single bond character of the carbonyl group of the potassium carboxylate.

4-{[S(-)-2-Methyl-1-Butyloxycarbonyl} 4'-(Hydroxy)Biphenyl (12)

To a solution of 4-(potassium carboxylate)-4'-(hydroxy)biphenyl (11) (20.2 g, 0.08 mol) and 4 g of TBAH in 300 ml of dry DMSO was added 20.1 g (0.0826 mol) of 2-(S)-methyl-1-butyl tosylate (6). After stirring at 60°C for 20 hours, the clear light yellow solution was poured into 1,200 ml of water. The resulting precipitate was filtered. The crude product was dissolved in 400 ml of methanol to give a light brown solution, which was treated with activated carbon to produce a colorless solution. The white solid, obtained after the solvent was distilled, was recrystallized from a mixture of methanol and water (1.25/1.0, v/v) to yield 22.1 g (98.2%) of crystals. Purity: 99.0% (HPLC). mp, 115.8°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.02 (m, 6 protons, -CH($C\underline{H}_3$)-$CH_2C\underline{H}_3$), 1.33-1.49 (m, 2 protons, -CH-$C\underline{H}_2CH_3$), 1.90 (m, 1 proton, -C<u>H</u>-), 4.24 (m, 2 protons, -O$C\underline{H}_2$-), 5.18 (s, 1 proton, -O<u>H</u>), 6.98 (d, 2 aromatic protons, o to -OH), 7.56 (d, 2 aromatic protons, m to -OH), 7.63 (d, 2 aromatic protons, m to -COO-), 8.11 (d, 2 aromatic protons, o to -COO-).

4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(11-Oxyundecanyl-1-Vinyl Ether)Biphenyl (13-11)

To a mixture of potassium carbonate (5.9 g, 0.0378 mol) and 90 ml of acetone were added 4.3 g (0.015 mol) of 12. After stirring for 2 hours at 60°C, the mixture turned yellow. Then, 11-bromoundecanyl-1-vinyl ether (4.0 g, 0.014 mol) and 5 ml of dry DMSO were added and the reaction mixture was stirred for 20 hours at 60°C. The reaction mixture was poured into 250 ml of water to give a white precipitate, which was extracted with chloroform. The chloroform solution was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator. The resulting solid was recrystallized from methanol to yield 5.2 g (75%) of monomer 13-11. Purity: 97% (HPLC). The monomer was further purified by column chromatography (silica gel, CH_2Cl_2 as eluent) to give 4.3 g (62%). Purity: 99.9% (HPLC). mp, 48.0°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.99 (m, 6 protons, -CH($C\underline{H}_3$)$CH_2C\underline{H}_3$), 1.29 (m, 16 protons, -OCH2$CH_2(C\underline{H}_2)_7$-, and -$CHC\underline{H}_2$-CH_3), 1.63 (m, 2 protons, -$C\underline{H}_2CH_2$-OPh-), 1.78 (m, 3 protons, =CH-O$CH_2C\underline{H}_2$-, and -$CH_2C\underline{H}(CH_3)CH_2$-), 3.64 (t, 2 protons, =CH-O$C\underline{H}_2$-), 3.98 (m, 3 protons, -$C\underline{H}_2$-OPh and =$C\underline{H}_2$ trans), 4.13-4.17 (m, 3 protons -COO$C\underline{H}_2$- and =$C\underline{H}_2$ cis), 6.40-6.51 (m, 1 proton =C<u>H</u>O-), 6.96 (d, 2 aromatic protons, o to -O$(CH_2)_9$-), 7.54 (d, 2 aromatic protons, m to -O$(CH_2)_9$-), 7.60 (d, aromatic protons, m to -COO-), 8.07 (d, 2 aromatic protons, o to -COO-).

4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(6-Oxyhexyl-1-Vinyl Ether)Biphenyl (13-6)

13-6 was synthesized by the same procedure as the one used for the preparation of 13-11. Starting with 5 g (0.0176 mol) of 12, 3.646 g (0.0176 mol) of 9-6 and 6.9 g of potassium carbonate, 5.5 g (76%) of 13-6 was obtained. Purity: 99% (HPLC). mp,

38.5°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.97 (m, 6 protons, -CH($C\underline{H}_3$)CH_2-$C\underline{H}_3$), 1.29 (m, 2 protons, -CH$C\underline{H}_2CH_3$), 1.46 (m, 4 protons, =CHO$CH_2CH_2(C\underline{H}_2)_2$-$CH_2$-), 1.65 (m, 2 protons, -$C\underline{H}_2CH_2$OPh-), 1.78 (m, 3 protons, -O$CH_2C\underline{H}_2$-, and -CH_2-$C\underline{H}$(CH_3)CH_2-), 3.65 (t, 2 protons, =CH-O$C\underline{H}_2$-), 3.96 (m, 3 protons, =$C\underline{H}_2$ trans, and -$C\underline{H}_2$-OPh), 4.14-4.18 (m, 3 protons =$C\underline{H}_2$ cis, and -COO$C\underline{H}_2$-), 6.40-6.51 (m, 1 proton =C$\underline{H}$O-), 6.96 (d, 2 aromatic protons, o to -O$(CH_2)_6$-), 7.50 (d, 2 aromatic protons, m to -O-$(CH_2)_6$-), 7.58 (d, aromatic protons, m to -COO-), 8.06 (d, 2 aromatic protons, o to -COO-).

Cationic Polymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hour. All glassware was dried overnight at 180°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt % of the solvent volume and the dimethyl sulfide concentration was 20 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_o/[I]_o$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The filtered polymers were dried, and precipitated from methylene chloride solution into methanol several times until GPC traces showed no traces amount of unreacted monomer. The polymerization results are summarized in Tables I and II. Although polymer yields are lower than expected due to losses during the purification process, conversions are almost quantitative in all cases.

RESULTS AND DISCUSSION

In the area of low molar mass liquid crystals there are some empirical rules which can be used to design compounds displaying chiral smectic C (s_C^*) mesophases.[26] Such rules are not available for the design of side chain liquid crystalline polymers exhibiting s_C^* phases.[2-15] A classic example comes from our laboratory where repeated attempts to synthesize side chain liquid crystalline polymers exhibiting s_C^* mesophases led to polymers exhibiting a s_A mesophase.[24,27] Therefore, we decided to perform a series of systematic investigations aimed to derive some empirical rules useful for the molecular engineering of side chain liquid crystalline polymers exhibiting s_C^* mesophases. In some previous publications, we have reported the synthesis and characterization of some polymers containing various polymer backbones and spacer length, and side groups derived from 4-[S(-)-2-methyl-1-butoxy]-4'-(hydroxy)-α-methylstilbene.[15,27c] The

influence of polymer backbones, spacer length and mesogenic group length on the ability to generate a S_C^* mesophase was discussed.

In the first part of this paper we will discuss the synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(11-oxyundecanyl-1-vinyl ether)biphenyl (13-11) and 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(6-oxyhexyl-1-vinyl ether)biphenyl (13-6). In the second part, we will discuss their mesomorphic behavior.

Scheme I outlines the synthesis of vinyl ethers 13-11 and 13-6. The cationic polymerization of both monomers was initiated with the system $CF_3SO_3H/S(CH_3)_2$ and was performed at 0°C in CH_2Cl_2.[19,20] The polymerization mechanism is described in Scheme II. It is essential that the monomers used in these polymerization experiments are completely free of protonic impurities. In order to achieve this degree of purity, after the purification by conventional techniques, the monomer is purified by passing through a chromatographic column containing silica gel and using methylene chloride as eluent. Polymerization results are summarized in Tables I and II. In both Tables, conversions are less than quantitative due to polymer losses during the purification process. However, at the end of the polymerization, HPLC and GPC traces showed that the monomer conversion was about 100%. Although the molecular weights determined by GPC and reported in Tables I and II are relative to polystyrene standards, they demonstrate that the ratio of $[M]_o/[I]_o$ provides a very good control of the polymer molecular weight. In addition, all polydispersities of poly(13-11)s and poly(13-6)s are equal or lower than 1.10. Absolute number average molecular weights and degrees of polymerization were determined by 200 MHz ^{1}H-NMR spectroscopy. A representative ^{1}H-NMR spectrum together with its protonic assignments is presented in Figure 1. Degrees of polymerization were determined by measuring the ratio of the doublet at δ = 6.97 ppm versus the broad triplet at δ = 4.64 ppm. The degrees of polymerization determined by NMR are summarized in Table I and II and unexpectedly, especially for the case of poly(13-11), they agree quite well with the results obtained by GPC. Figure 2 presents the plots of Mn determined by GPC and NMR and Mw/Mn versus $[M]_o/[I]_o$ obtained for the polymerizations of 13-11 (Figure 2a) and 13-6 (Figure 2b). These plots demonstrate that within this range of molecular weights both monomers polymerize through a living polymerization mechanism. As expected, the plots of absolute and relative Mn versus $[M]_o/[I]_o$ provide different slopes (Figure 2b).

Figure 3 presents the DSC traces of poly(13-11)s with various degrees of polymerization. As we can observe from this figure, the DSC curves of the first heating scan (Figure 3a) differ from those of the second heating scan (Figure 3c). However, second and subsequent heating scans exhibit identical DSC traces. First and subsequent

cooling scans also exhibit identical DSC traces (Figure 3b). On the first heating scan all polymers exhibit a glass transition temperature followed by a crystalline phase which melts into a s_A mesophase. The s_A-isotropic transition temperature has a stronger dependence on molecular weight than that of the melting transition temperature (Figure 3a, Table I). On the cooling DSC scans all poly(13-11)s exhibit an isotropic-s_A followed by s_A-s_C* and s_C*-s_X phase transitions (Figure 3b). The nature of the s_X phase was not identified. On the second heating scan the phase behavior of poly(13-11)s is strongly dependent on the molecular weight of the polymer (Figure 3c). Poly(13-11)s with degrees of polymerization equal and lower than 10 undergo the transition from s_A to s_C* phase followed by crystallization through endothermic and exothermic peaks. The crystalline phase melts into a s_A phase (Figure 3c, Table I). Poly(13-11) with DP=4 has an additional exothermic peak on the second heating scan (Figure 3c). This peak is due to the completion of the s_X phase formation. The endotherm due to s_X-s_C* and the exotherm of s_C*-k phase transitions are overlapped (Figure 3c). Therefore, Poly(13-11)s with degrees of polymerization equal and lower than 10 exhibit very narrow enantiotropic s_X, s_C* and s_A mesophases and a crystallization on the heating scan when their data are collected from the second DSC scans. Poly(13-11)s with degrees of polymerization higher than 10 do not crystallize on the heating scan (Figure 3c). Subsequently, their DSC traces show very distinct transitions from s_X to s_C* and from s_C* to s_A mesopnases. Therefore, when the thermal transitions of these polymers are collected from second and subsequent heating and first and subsequent cooling DSC traces, they exhibit a quite broad enantiotropic s_C* phase (Figure 3b, c, Table I). However, if these polymers are annealled within their s_C* phase below the melting transition temperatures determined from the first heating scan (Figure 3a, c), they crystallize. This means that under equilibrium condition, poly(13-11)s exhibit an enantiotropic s_A and a monotropic s_C* mesophase. The difference between the behavior of low and high molecular weight poly(13-11)s is determined by the difference between the crystallization ability of these two series of polymers. The low molecular weight polymers exhibit a high rate of crystallization and therefore, can crystallize on the second heating scan, while the higher molecular weight polymers have a much lower rate of crystallization and subsequently, they do not crystallize on the second heating scan. This represents a classic example of "polymer effect" which shows how the kinetically controlled crystallization process affects the stability of a thermodynamically controlled mesophase. Similar examples of this behavior are available both from our[16,19] and from other laboratories.[18] The thermal transition temperatures collected from Figure 3 are summarized in Table I and plotted in Figure 4a (data from the first heating scan), Figure 4b (data from the first cooling scan) and Figure 4c (data from the second heating scan). Figure 5 presents

representative optical polarized micrographs of the s_A and s_C* phases exhibited by poly(13-11)s. The s_A mesophase displays a focal conic-texture (Figure 5a). The s_A-s_C* phase transition is accompanied by the formation of equidistant lines on the focal conic texture.[5b,10,12,15]

The DSC traces of the first and second heating and of the first cooling scans of poly(13-6)s with various molecular weights are presented in Figure 6a,b,c. Over the entire range of molecular weights, these polymers exhibit an enantiotropic s_A phase. Polymers with degrees of polymerization equal and higher than 17 exhibit also an enantiotropic s_X phase. The only difference between the first and second or subsequent heating scans consists of the fact that the enthalpy changes of the s_X-s_A phase transition temperatures from the second heating and first cooling scans are lower than those from the first heating scans (Table II). This is due to the close proximity of the s_X phase to the glass transition of poly(13-6)s. Due to this proximity, the s_X phase is kinetically controlled. A similar behavior was observed with other polymers.[16,19] The phase transition temperatures collected from the first and second heating scans are plotted in Figure 7a, while those from the first cooling scan in Figure 7b. As we can observe both from Figure 6a and 6b, the slopes of the dependences of s_X-s_A and s_A-s_X transition temperatures versus the degree of polymerization are steeper than the slope of the dependence of Tg versus degrees of polymerization. Consequently, poly(13-6)s with degrees of polymerization lower than 17 exhibit a virtual s_X mesophase. These results can be explained by using the thermodynamic schemes published previously.[28] A general discussion on the polymer backbone effects on the phase behavior of side chain liquid crystalline polymers will be published elsewhere.[29] Some brief discussion on the same topic has been already published.[30,31] Additional experiments on the synthesis and characterization of side chain liquid crystalline polymers and copolymers with narrow molecular weight distribution, well defined molecular weights, and exhibiting s_C* mesophases are in progress. The availability of these well defined polymers will allow the elucidation of the influence of various parameters like molecular weight and polydispersity on the dynamics of the s_C* mesophases exhibited by side chain liquid crystalline polymers.

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REFERENCES AND NOTES

1. V. P. Shibaev and Ya. S. Freidzon, in "Side Chain Liquid Crystal Polymers", C. B. McArdle Ed., Chapman and Hall, New York, **1989**, p. 260.
2. P. LeBarny and J. C. Dubois, in "Side Chain Liquid Crystal Polymers", C. B. McArdle Ed., Chapman and Hall, New York, **1989**, p. 130.
3. J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, J. Am. Chem. Soc. **1989**, 111, 8119.
4. a) V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov and N. A. Plate, Polym. Bull. **1984**, 12, 299. b) V. P. Shibaev, M. V. Kozlovsky, N. A. Plate L. A. Beresnev and L. M. Blinov, Polym. Sci. USSR **1987**, 29, 1616. c) L. M. Blinov, V. A. Baikalov, M. J. Barnik, L. A. Beresnev, E. P. Pozhidayev and S. V. Yablonsky, Liq. Cryst. **1987**, 2, 121.
5. a) G. Decobert, F. Soyer and J. C. Dubois, Polym. Bull. **1985**, 14, 179. b) J. M. Guglielminetti, G. Decobert and J. C. Dubois, Polym. Bull. **1986**, 16, 411. c) J. C. Dubois, G. Decobert, P. LeBarny, S. Esselin, C. Friedrich and C. Noel, Mol. Cryst. Liq. Cryst. **1986**, 137, 349. d) G. Decobert, J. C. Dubois, S. Esselin and C. Noel, Liq. Cryst. **1986**, 1, 307. e) S. Esselin, L. Bosios, C. Noel, G. Decobert and J. C. Dubois, Liq. Cryst. **1987**, 2, 505. f) S. Esselin, C. Noel, G. Decobert and J. C. Dubois, J.Mol. Cryst. Liq. Cryst. **1988**, 155, 371.
6. a) R. Zentel, G. Reckert and B. Reck, Liq. Cryst., **1987**, 2, 83. b) S. Bualek and R. Zentel, Makromol. Chem. **1988**, 189, 797. c) H. Kapitza and R. Zentel, Makromol. Chem. **1988**, 189, 1793. d) S. Bualek, H. Kapitza, J. Meyer, G. F. Schmidt and R. Zentel, Mol. Cryst. Liq. Cryst. **1988**, 155, 47. e) S. U. Vallerien, R. Zentel, F. Kremer, H. Kapitza and E. W. Fischer, Makromol. Chem. Rapid Commun. **1989**, 10, 333. f) R. Zentel, H. Kapitza, F Kremer and S. U. Vallerien, in "Liquid Crystalline Polymer", R. A. Weiss and C. K. Ober Eds., ACS Symposium Series 435, Washington DC., **1990**, p. 207.
7. S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto and K. Kawasaki, Mol. Cryst. Liq. Cryst. **1988**, 155, 93.
8. N. Koide, K. Uehara and K. Iimura, Mol. Cryst. Liq. Cryst. **1988**, 157, 151.
9. T. Suzuki, T. Okawa, K. Ohnuma and Y. Sakon, Makromol. Chem. Rapid Commun. **1988**, 9, 755.
10. M. Dumon, H. T. Nguyen, M. Mauzac, C. Destrade, M. F. Achard and H. Gasparoux, Macromolecules **1990**, 23, 355.
11. D. M. Walba, P. Keller, D. S. Parmar, N. A. Clark and M. D. Wand, J. Am. Chem. Soc. **1989**, 111, 8273.

12. H. Kapitza, R. Zentel, R. J. Twieg, C. Nguyen, S. U. Vallerien, F. Kremer and C. G. Willson, Adv. Mater. **1990**, 2, 539.
13. T. Kitazume, T. Ohnogi and K. Ito, J. Am. Chem. Soc. **1990**, 112, 6608.
14. H. M. Colquhoun, C. C. Dudman, C. A. O'Makoney, G. C. Robinson and D. J. Williams, Adv. Mater. **1990**, 2, 139.
15. a) V. Percec and C. S. Wang, J. Macromol. Sci.-Chem., submitted b) V. Percec and C. S. Wang, J. Macromol. Sci.-Chem., submitted c) V. Percec, C. S. Wang, and M. Lee, Polym. Bull., in press
16. V. Percec, D. Tomazos and C. Pugh, Macromolecules **1989**, 22, 3259.
17. W. Kreuder, O. W. Webster and H. Ringsdorf, Makromol. Chem. Rapid Commun. **1986**, 7, 5.
18. a) T. Sagane and R. W. Lenz, Polym. J. **1988**, 20, 923. b) T. Sagane and R. W. Lenz, Polymer **1989**, 30, 2269. c) T. Sagane and R. W. Lenz, Macromolecules **1989**, 22, 3763.
19. a) J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Polym. Chem. Ed., **1986**, 24, 1363. b) R. Rodenhouse, V. Percec and A. E. Feiring, J. Polym. Sci. Polym. Lett. **1990**, 28, 345. c) V. Percec and M. Lee, J. Polym. Sci., Part A: Polym. Chem., in press d) V. Percec and M. Lee, Macromolecules, in press e) V. Percec and M. Lee, Polymer, in press f) V. Percec and M. Lee, Polym. Bull., in press g) H. Jonsson, V. Percec and A. Hult, Polym. Bull., in press h) V. Percec, A. Gomes and M. Lee, J. Polym. Sci., Polym. Chem., submitted i) V. Percec, C. S. Wang and M. Lee, Polym. Bull., in press
20. C. G. Cho, B. A. Feit and O. W. Webster, Macromolecules **1990**, 23, 1918.
21. a) S. H. Korzeniowski, L. Blum and G. W. Golcel, Tetrahedron Lett. **1977**, 22, 1871. b) G. W. Gray, J. B. Hartlay and B. Jones, J. Chem. Soc. **1955**, 1412.
22. W. S. Johnson, C. D. Gutsche and R. D. Offenhauer, J. Am. Chem. Soc. **1946**, 68, 1649.
23. L. F. Fisher and C. K. Bradsher, J. Am. Chem. Soc. **1936**, 58, 1738.
24. B. Hahn and V. Percec, Macromolecules **1987**, 20, 2961.
25. J. E. McKeon and P. Fitton, Tetrahedron **1972**, 28, 233.
26. a) G. W. Gray and J. W. Goodby, Mol. Cryst. Liq. Cryst., **1976**, 37, 157. b) G. W. Gray and J. W. Goodby, Mol. Cryst. Liq. Cryst., **1978**, 48, 127. c) D. Demus, H. Demus and H. Zaschke, Flussige Kristalle in Tabellen; I and II, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, **1974** and **1984**. d) D. M. Walba, C. S. Slater, W. N. Thurmes, N. A. Clark, M. A. Handsky and F. Supon, J. Am. Chem. Soc. **1986**, 108, 5210.

27. a) V. Percec and B. Hahn, Macromolecules **1989**, 22, 1588. b) B. Hahn and V. Percec, Mol. Cryst. Liq. Cryst. **1988**, 157, 125. c) V. Percec and B. Hahn, J. Polym. Sci., Part A: Polym. Chem. **1989**, 27, 2367. d) V. Percec, B. Hahn, M. Ebert and J. H. Wendorff, Macromolecules **1990**, 23, 2092. e) V. Percec and C. S. Wang, Macromolecular Reports, in press

28. a) V. Percec and A. Keller, Macromolecules **1990**, 23, 4347. b) A. Keller, G. Ungar and V. Percec, in "Advances in Liquid Crystalline Polymers", R. A. Weiss and C. K. Ober Eds., ACS Sympossium Series 435, Washington D. C. **1990**, p. 308

29. V. Percec, "Polymer Backbone Effects", invited lecture presented at the 13th International Liquid Crystal Conference, Vancouver, July 22-27, 1990; Mol. Cryst. Liq. Cryst., to be published

30. a) V, Percec, D. Tomazos and R. A. Willingham, Polym. Bull. **1989**, 22, 199. b) V. Percec and D. Tomazos, Polymer **1990**, 31, 1658.

31. V. Percec and C. Pugh, in "Side Chain Liquid Crystal Polymers", C. B. McArdle Ed., Chapman and Hall, New York, **1989**, p. 30

FIGURES AND SCHEME CAPTIONS

Scheme I: Synthesis of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(11-Oxyundecanyl Vinyl Ether)Biphenyl (13-11) and 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(6-Oxyhexyl Vinyl Ether)Biphenyl (13-6).

Scheme II: Cationic polymerization of 13-11 and 13-6.

Figure 1: 200 ^{1}H-NMR spectrum of poly(13-11) with theoretical DP = 4.

Figure 2: The dependence of the number average molecular weight (Mn) determined by GPC □ and by NMR ■ and of the polydispersity (Mw/Mn) of poly(13-11) by GPC (a) and poly(13-6) (b) on the $[M]_o/[I]_o$ ratio▲.

Figure 3: DSC traces displayed during the first heating scan (a), the first cooling scan (b) and the second heating scan (c) by poly(13-11) with different degrees of polymerization (DP) determined by GPC. DP is printed on the top of each DSC scan.

Figure 4: The dependence of phase transition temperatures on the degree of polymerization determined by GPC of poly(13-11). a) data from the first heating scan: ○-Tg; ■-T_k-s_A; □-Ts_A-i; b) data from the first cooling scan; □ -Ti-s_A; ▲-Ts_A-s_C*; ◆-Ts_C*-s_X; ●-Tg: c) data from the second heating scan: ○-Tg; ◇-Ts_X-s_C*; ■-T_k-s_A; △–Ts_C*-s_A; □-Ts_A-i.

Figure 5: Representative optical polarized micrographs (100x) of: a) the s_A mesophase displayed by poly(13-11) (DP=10) at 90°C on the cooling scan ; b) the s_C* mesophase displayed by poly(13-11) (DP=10) at 31°C on the cooling scan.

Figure 6: DSC traces displayed during the first heating scan (a), the first cooling scan (b) and the second heating scan (c) by poly(13-6) with different degrees of polymerization determined by GPC (DP). DP is printed on the top of each DSC scan.

Figure 7: The dependence of phase transition temperatures on the degree of polymerization of poly(13-6) (determined by GPC). a) data from the first heating (fh) and the second heating scan (sh): ○-Tg (fh); △-Ts_X-s_A (fh); □ -Ts_A-i (fh); ●-Tg (sh); ▲-Ts_X-s_A (sh); ■-Ts_A-i (sh); b) data from the first cooling scan: ■-Ti-s_A; ▲-Ts_A-s_X; ●-Tg.

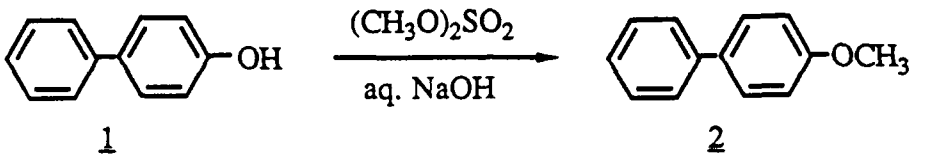
Table I. Cationic Polymerization of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(11-Oxyundecanyl Vinyl Ether)Biphenyl (13-11) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o$=0.208; $[(CH_3)_2S]_o/[I]_o$=20; polymerization time, 1hr) and Characterization of the Resulting Polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	$[M]_o/[I]_o$	Polymer yield(%)	$Mnx10^{-3}$ GPC	Mw/Mn GPC	DP NMR	DP NMR	phase transitions (°C) and corresponding enthalpy changes (kJ/mru) heating	cooling
1	4	88	1.8	1.07	4	5	g -1.4 k 52 8 (19.8) s_A 92.1 (6.23) i	i 84.4 (6.10) s_A 42.9 (0.121) sC^*
							g -3.1 s_X 5.8 (1.05) s_X 13.4 (-0.71) sC^* 26.4 (1.30) k	-0.11 (3.76) s_X -8.1 g
							32.7 (-1.17)[a] k 47.5 (10.2) s_A 91.5 (6.14) i	
2	7	93	3.0	1.10	6	6	g 4.2 k 56.8 (18.1) s_A 104.8 (6.14) i	i 97.5 (5.85) s_A 44.9 (0.142) sC^* 6.1
							g 1.2 s_X 15.5 (2.72) sC^* 31.7 (-) k 37.4 (-0.627)[a] k 48.4	(2.59) s_X -1.7 g
							(4.01) s_A 104.5 (5.89) i	
3	10	90	4.7	1.08	10	10	g 6.9 k 56.2 (16.8) s_A 108.7 (6.02) i	i 102.5 (5.81) s_A 46.3 (0.159) sC^*
							g 5.2 s_X 19.4 (2.63) sC^* 35.2 (-) k 38.2 (-0.418)[a] k 48.3	9.5 (2.72) s_X 1.8 g
							(1.42) s_A 108.5 (5.77) i	
4	14	90	6.7	1.09	14	12	g 10.1 k 56.8 (15.4) s_A 114.4 (5.56) i	i 108.4 (5.43) s_A 47.1 (0.180) sC^*
							g 6.8 s_X 20.8 (2.13) sC^* 51.1 (0.142) s_A 114.3 (5.56) i	12.7 (2.01) s_X 5.1 g
5	18	93	8.2	1.08	17	18	g 11.1 k 57.2 (12.9) s_A 118.6 (5.68) i	i 112.3 (5.35) s_A 48.4 (0.159) sC^*
							g 8.2 s_X 24.9 (2.09) sC^* 52.2 (0.159) s_A 118.1 (5.56) i	15.6 (2.05) s_X 7.9 g
6	23	91	11.5	1.07	24	24	g 10.5 k 60.4 (15.0) s_A 119.8 (5.56) i	i 113.8 (5.31) s_A 48.2 (0.159) sC^*
							g 9.5 s_X 24.0 (2.09) sC^* 52.3 (0.121) s_A 119.7 (5.27) i	15.7 (2.09) s_X 7.5 g
7	30	92	12.1	1.10	26	26	g 11.5 k 62.2 (15.5) s_A 122.8 (5.60) i	i 115.4 (5.14) s_A 48.8 (0.142) sC^*
							g 10.1 s_X 26.1 (2.34) sC^* 53.3 (0.142) s_A 121.8 (5.23)	16.7 (2.59) s_X 7.9 g

[a] crystallization during heating

Table II. Cationic Polymerization of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(6-Oxyhexyl Vinyl Ether)Biphenyl (13-6) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o$=0.244; $[(CH_3)_2S]_o/[I]_o$=20; polymerization time, 1hr) and Characterization of the Resulting Polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	$[M]_o/[I]_o$	Polymer yield(%)	$Mnx10^{-3}$ GPC	Mw/Mn GPC	DP NMR	DP NMR	phase transitions (°C) and corresponding enthalpy changes (kJ/mru) heating	cooling
1	5	70	2.9	1.04	6	6	g 2.4 s_A 90.8 (4.39) i	i 83.5 (4.51) s_A -4.1 g
							g 1.3 s_A 90.4 (4.47) i	
2	8	78	3.9	1.09	10	9	g 8.2 s_A 95.9 (4.60) i	i 87.7 (4.43) s_A -0.5 g
							g 7.5 s_A 95.5 (4.56) i	
3	12	87	5.0	1.06	12	15	g 16.9 s_A 103.2 (4.51) i	i 95.1 (4.60) s_A 8.8 g
							g 14.2 s_A 102.6 (4.56) i	
4	18	86	6.9	1.07	17	18	g 20.1 s_X 40.1 (0.920) s_A 106.9 (4.47) i	i 99.8 (4.51) s_A 29.9 (0.794) s_X 13.5 g
							g 19.3 s_X 38.6 (0.418) s_A 106.6 (4.68) i	
5	23	91	7.5	1.10	19	23	g 25.9 s_X 45.6 (1.630) s_A 108.5 (4.47) i	i 101.2 (4.60) s_A 38.3 (0.501) s_X 18.2 g
							g 24.1 s_X 46.7 (0.209) s_A 108.3 (4.56) i	
6	30	85	10.0	1.09	25	31	g 29.3 s_X 49.7 (1.05) s_A 111.7 (4.72) i	i 102.4 (4.72) s_A 48.1 (0.418) s_X 21.4 g
							g 27.9 s_X 58.0 (0.418) s_A 110.3 (4.47) i	



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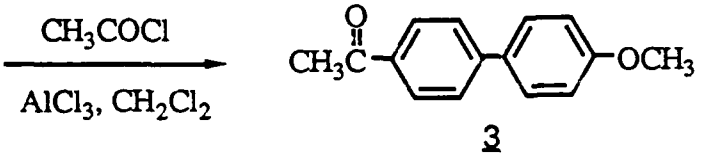

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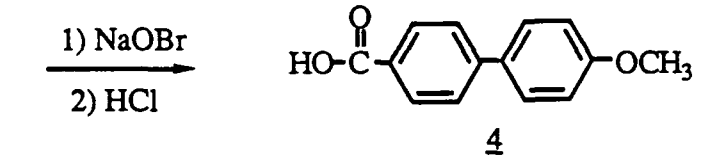
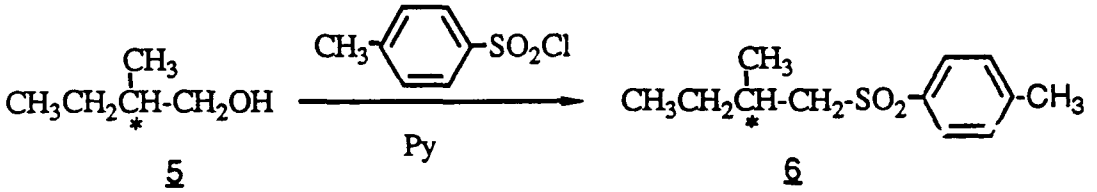
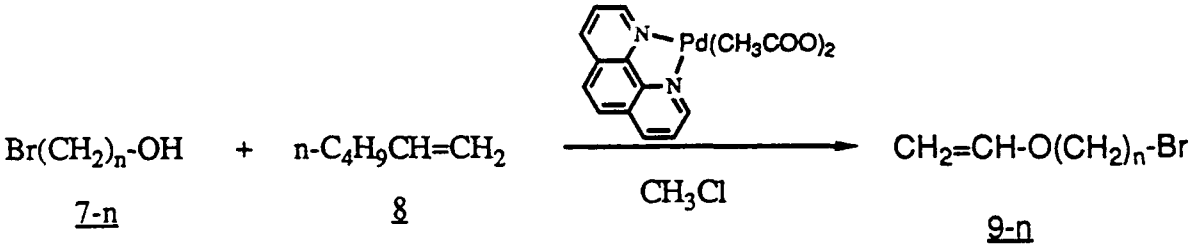


3 → 4

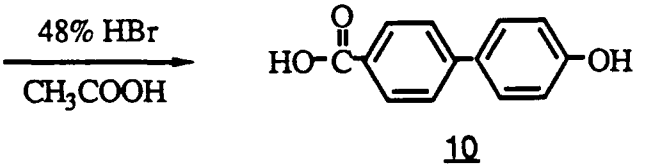


5 → 6

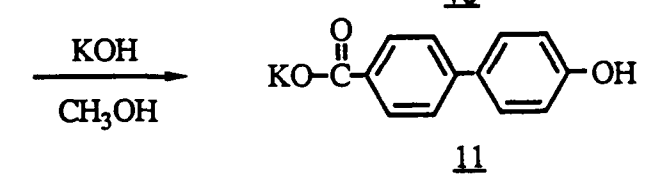


Br(CH2)n-OH + n-C4H9CH=CH2 → CH2=CH-O(CH2)n-Br

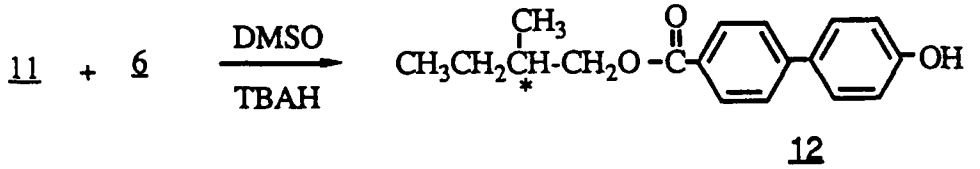
7-n (n=6, 11) + 8 → 9-n



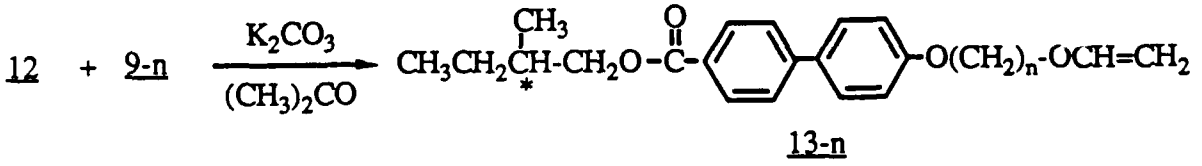
4 → 10



10 → 11

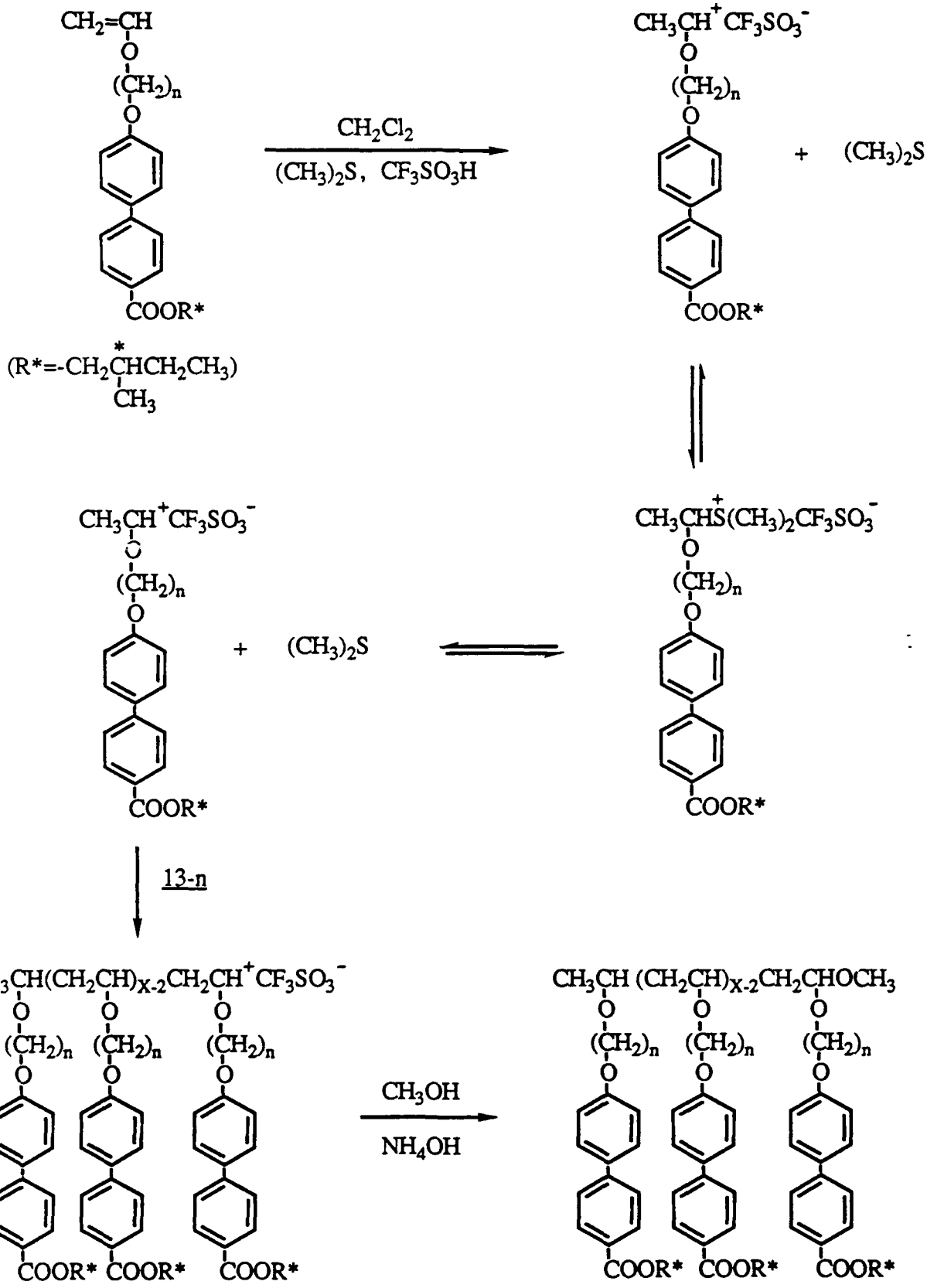


11 + 6 → 12



12 + 9-n → 13-n

Scheme I


CH2=CH
O
(CH2)n
O
COOR*
(R*=-CH2CHCH2CH3)
CH3
CH2Cl2
(CH3)2S, CF3SO3H
CH3CH+CF3SO3-
+ (CH3)2S
CH3CHS+(CH3)2CF3SO3-
13-n
CH3CH(CH2CH)X-2CH2CH+CF3SO3-
CH3OH
NH4OH
CH3CH (CH2CH)X-2CH2CHOCH3

Scheme II

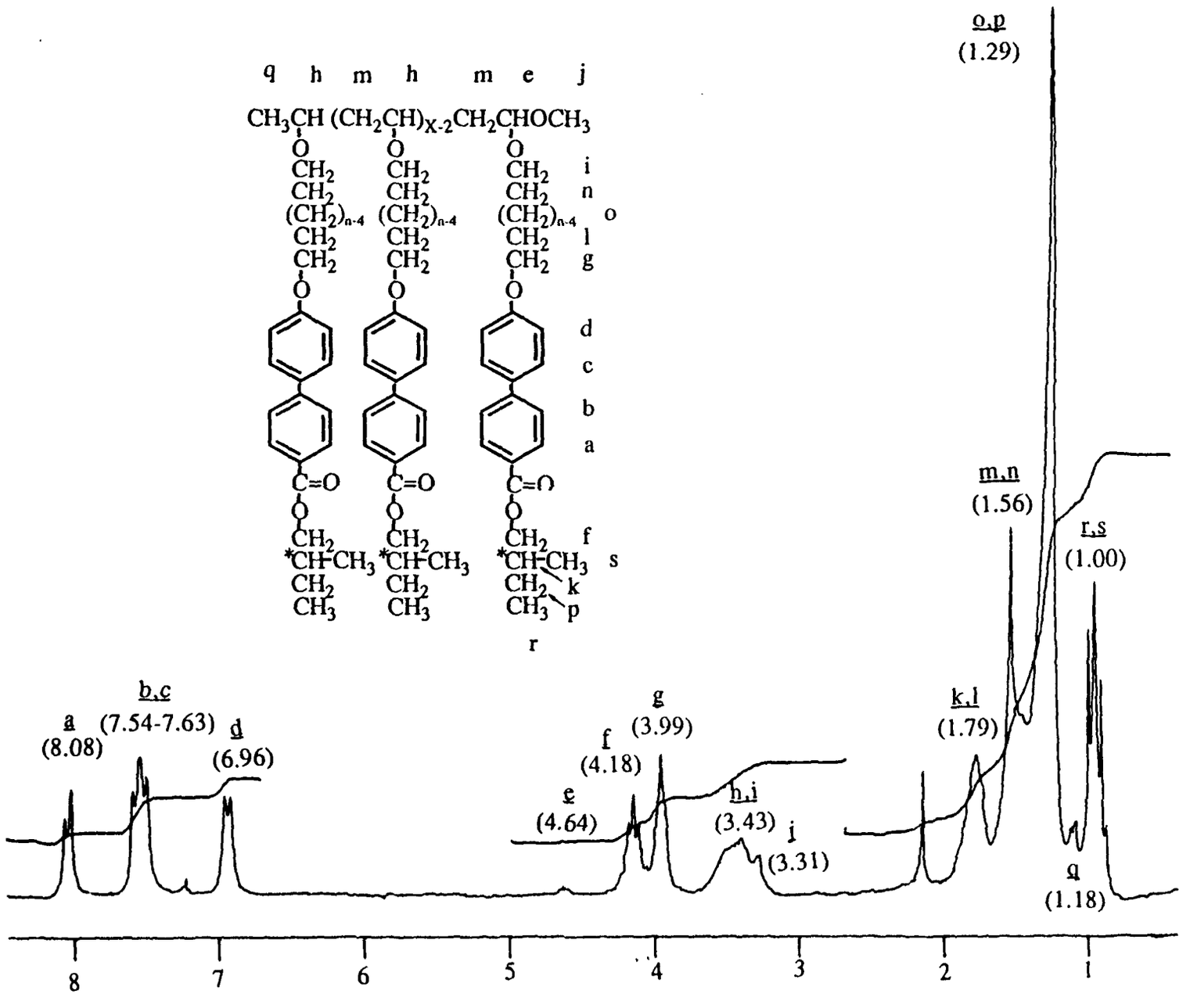

q h m h m e j
CH3CH (CH2CH)X-2CH2CHOCH3
i n o l g d c b a f s k p r
o,p (1.29)
m,n (1.56)
r,s (1.00)
k,l (1.79)
g (3.99)
f (4.18)
e (4.64)
h,i (3.43)
j (3.31)
q (1.18)
b,c (7.54-7.63)
a (8.08)
d (6.96)
8
7
6
5
4
3
2
1

Figure 1

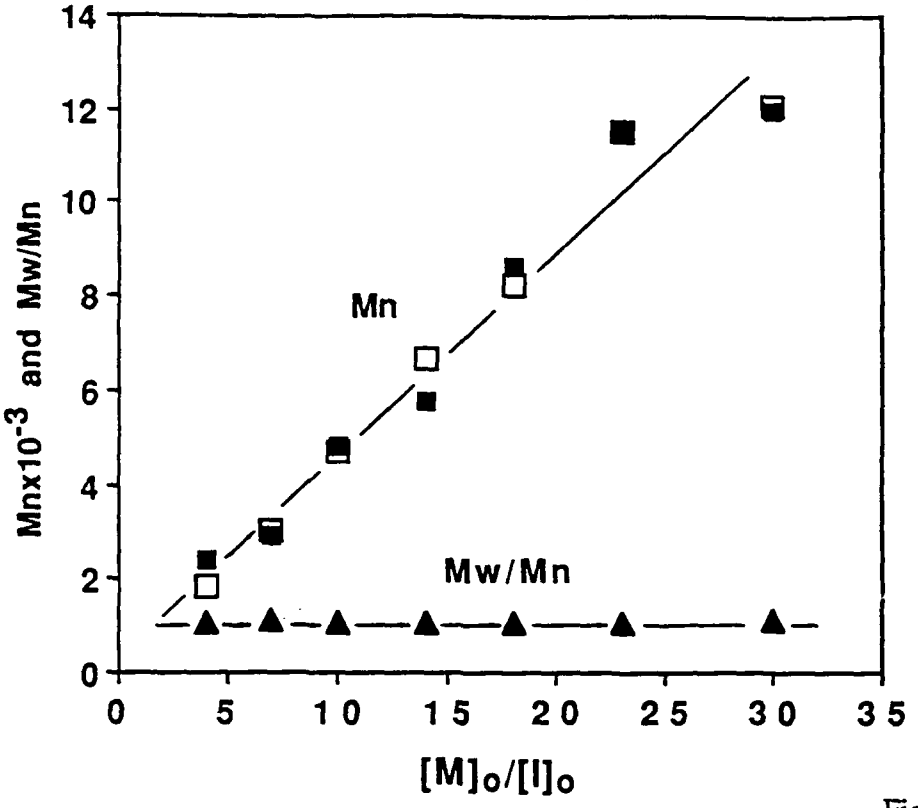


Figure 2a

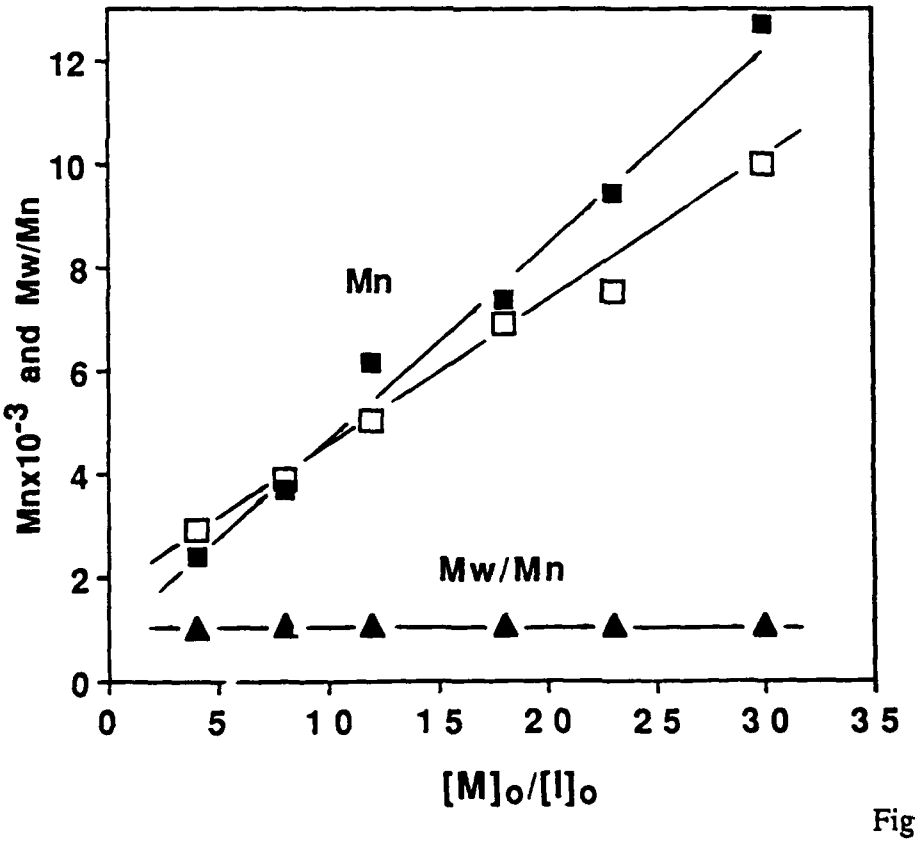


Figure 2b

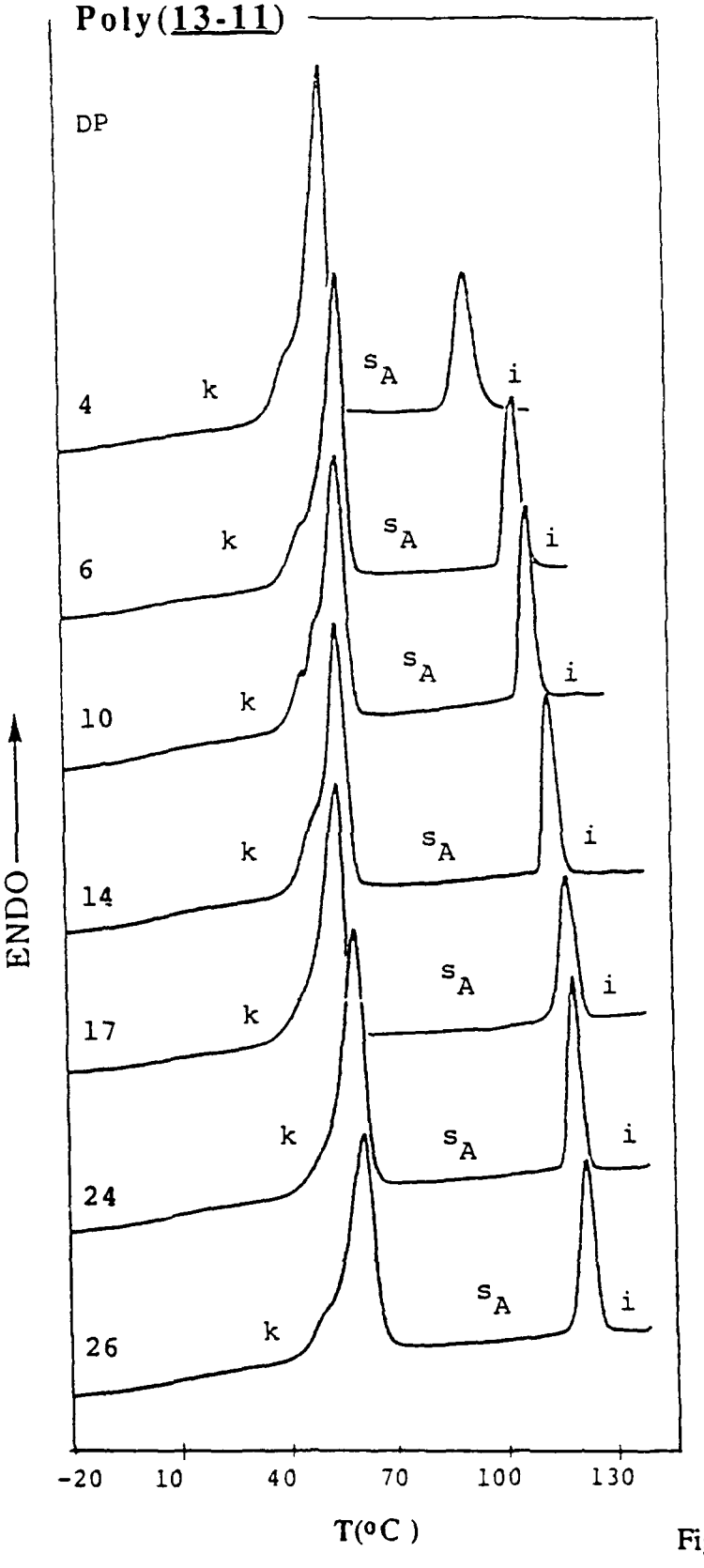


Figure 3a

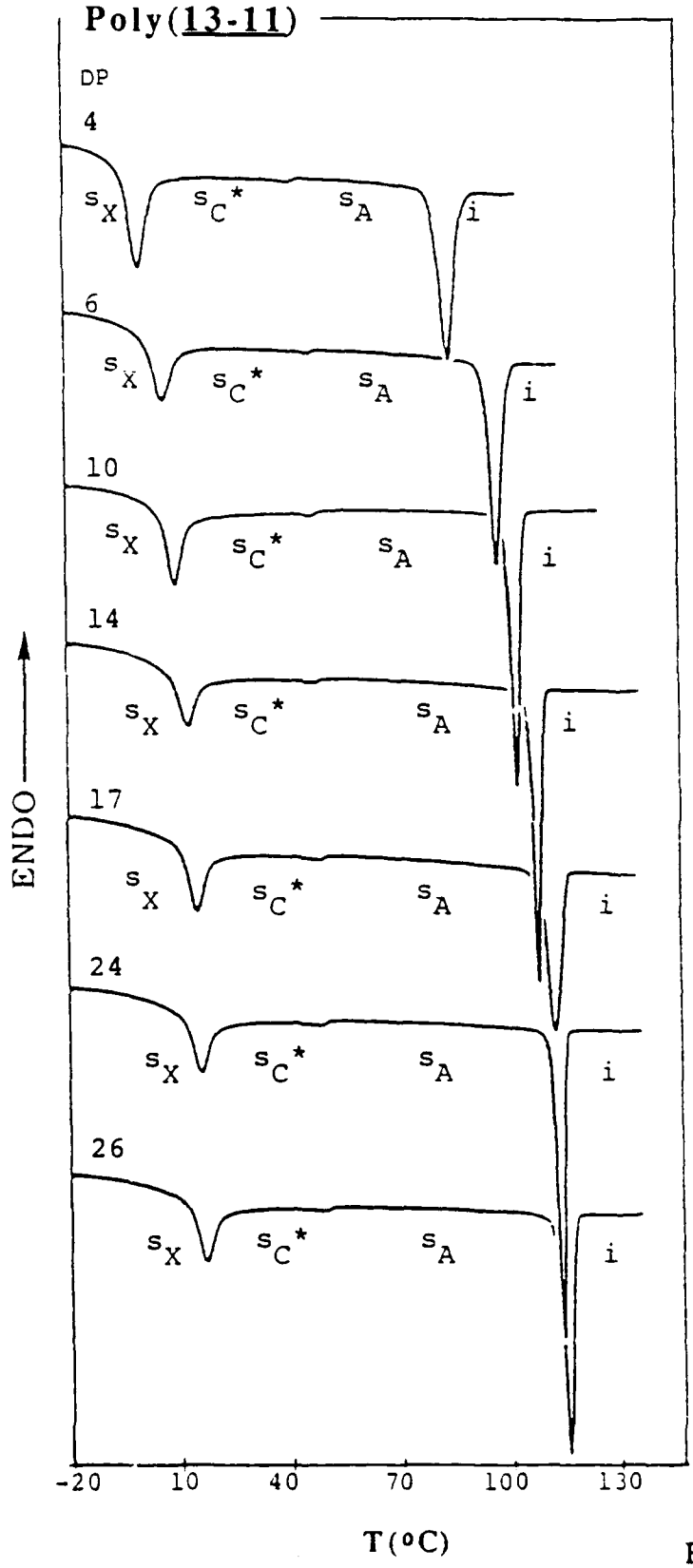


Figure 3b

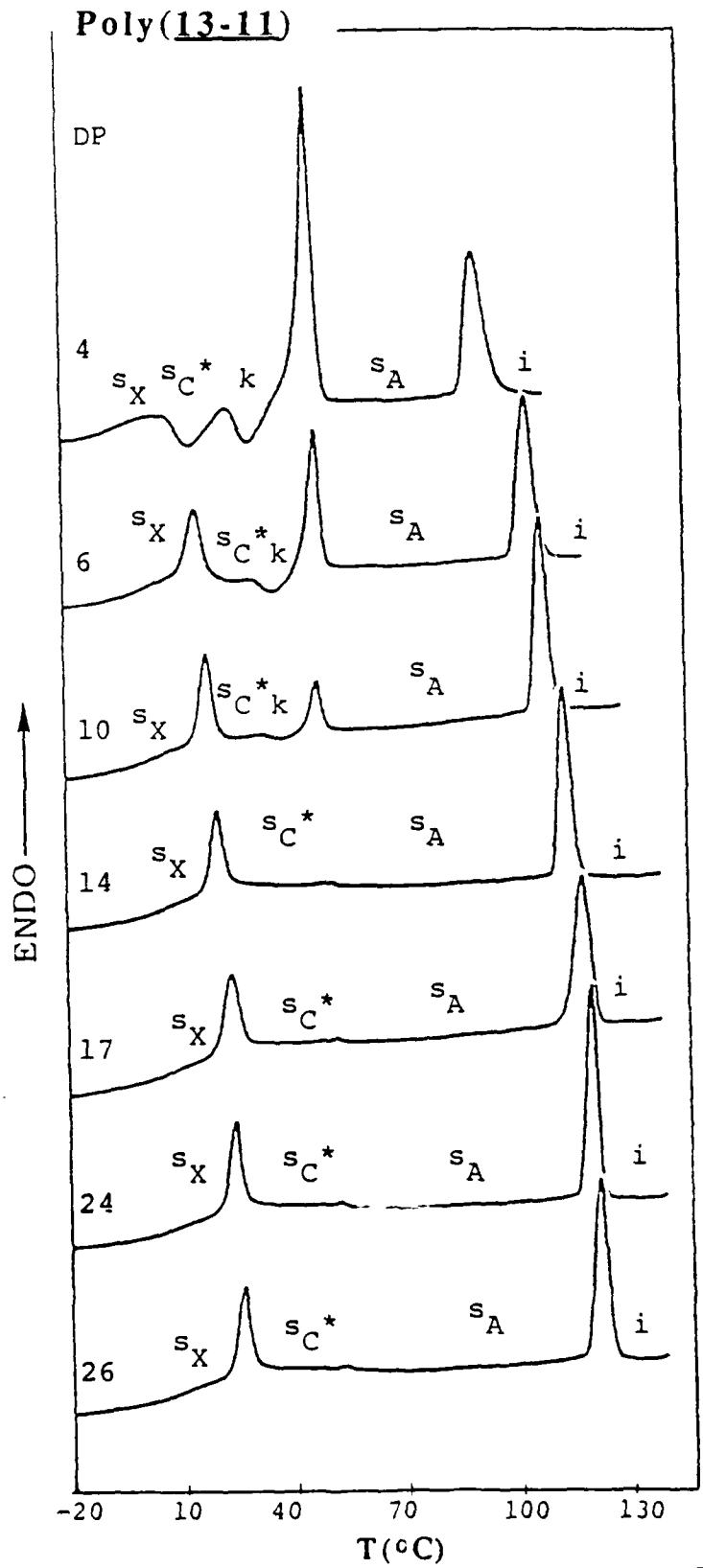

Poly(13-11)
DP
4
6
10
14
17
24
26
S_X
S_C^*
k
S_A
i
ENDO
-20
10
40
70
100
130
T(°C)

Figure 3c

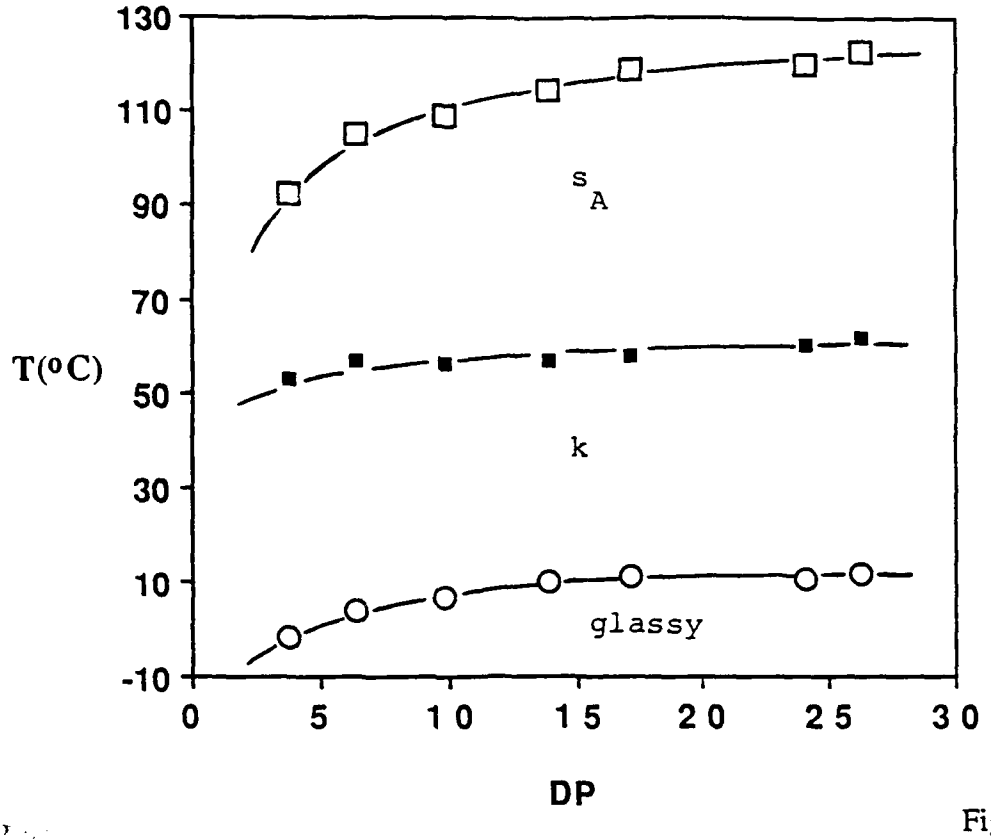


Figure 4a

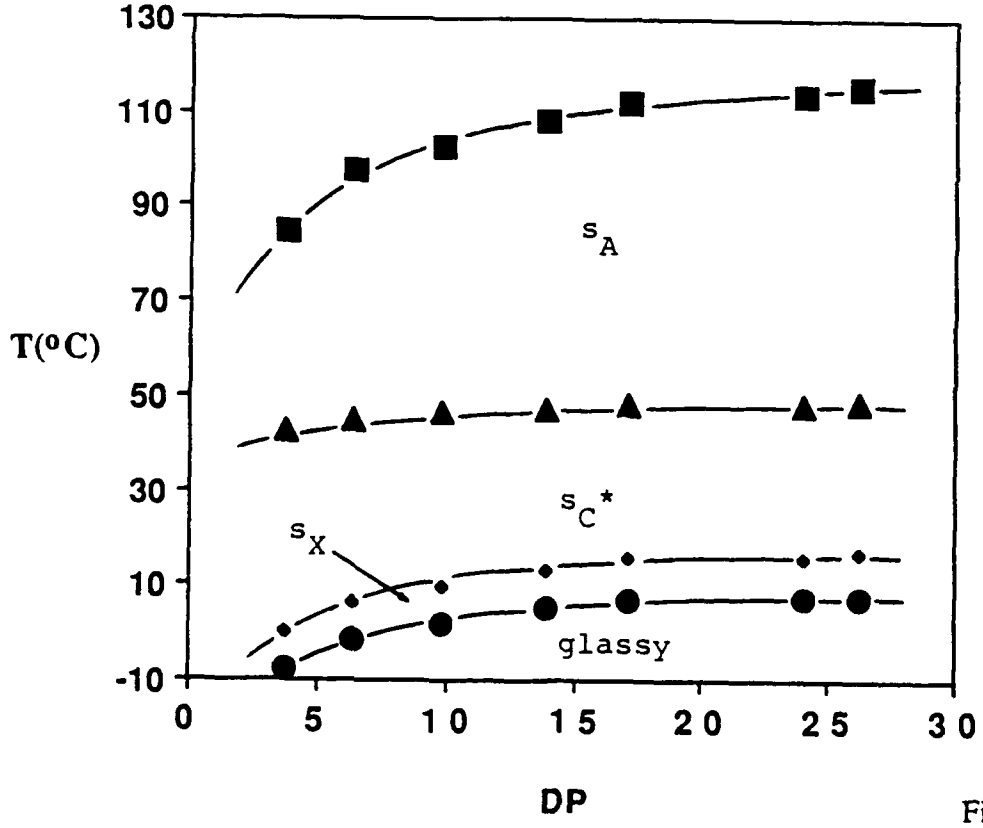


Figure 4b

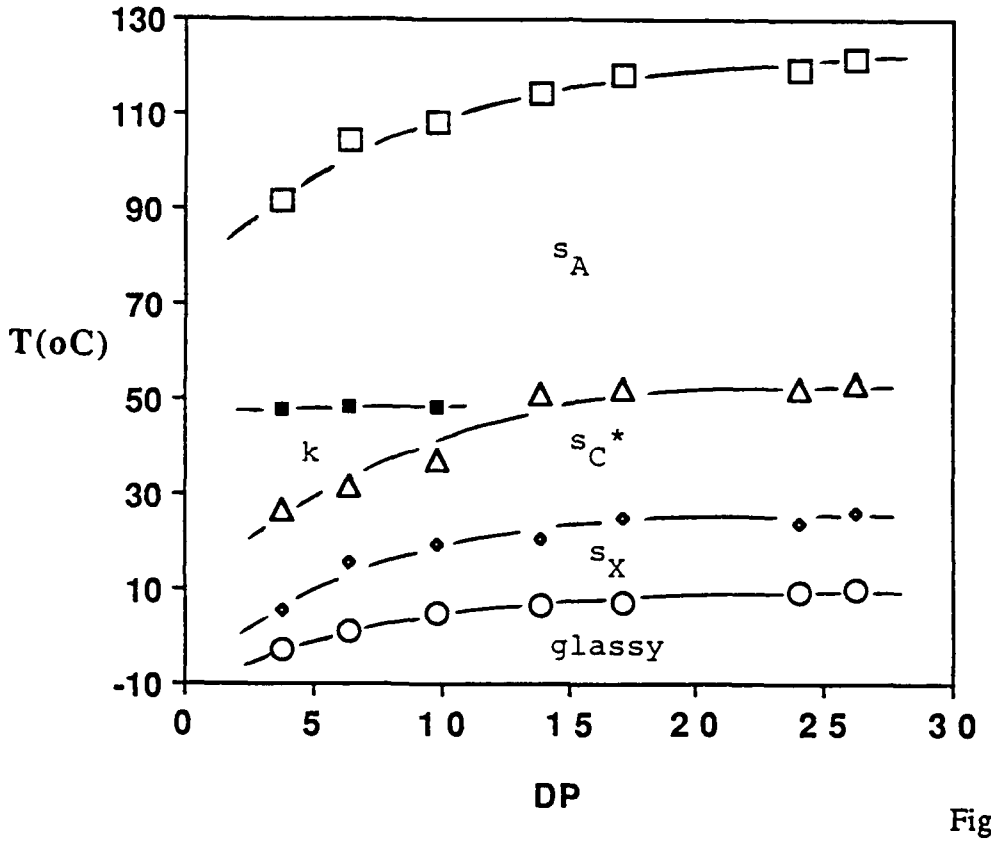


Figure 4c

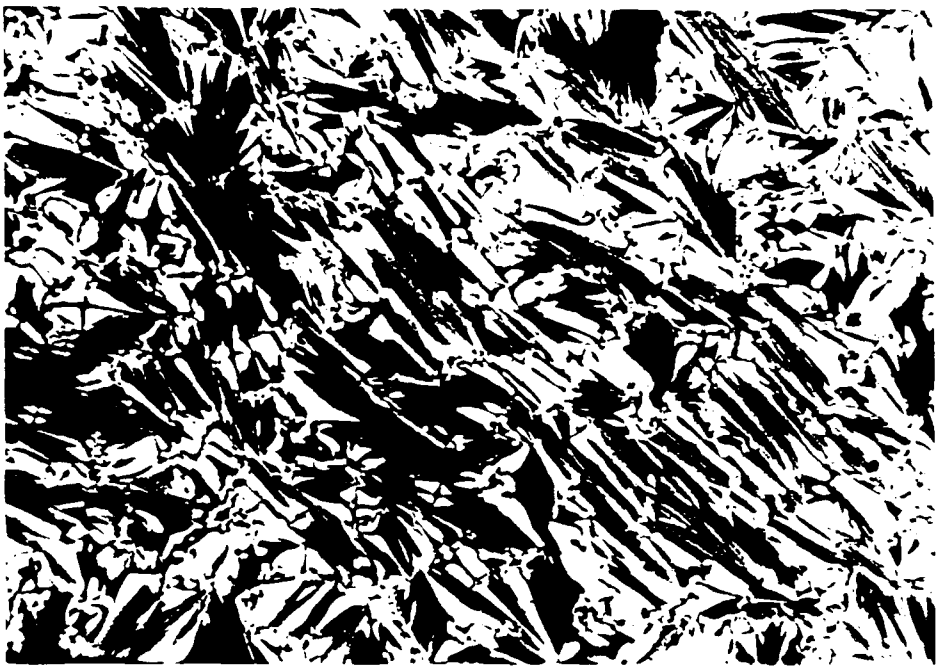


Figure 5a

Figure 5b

Poly(13-6)

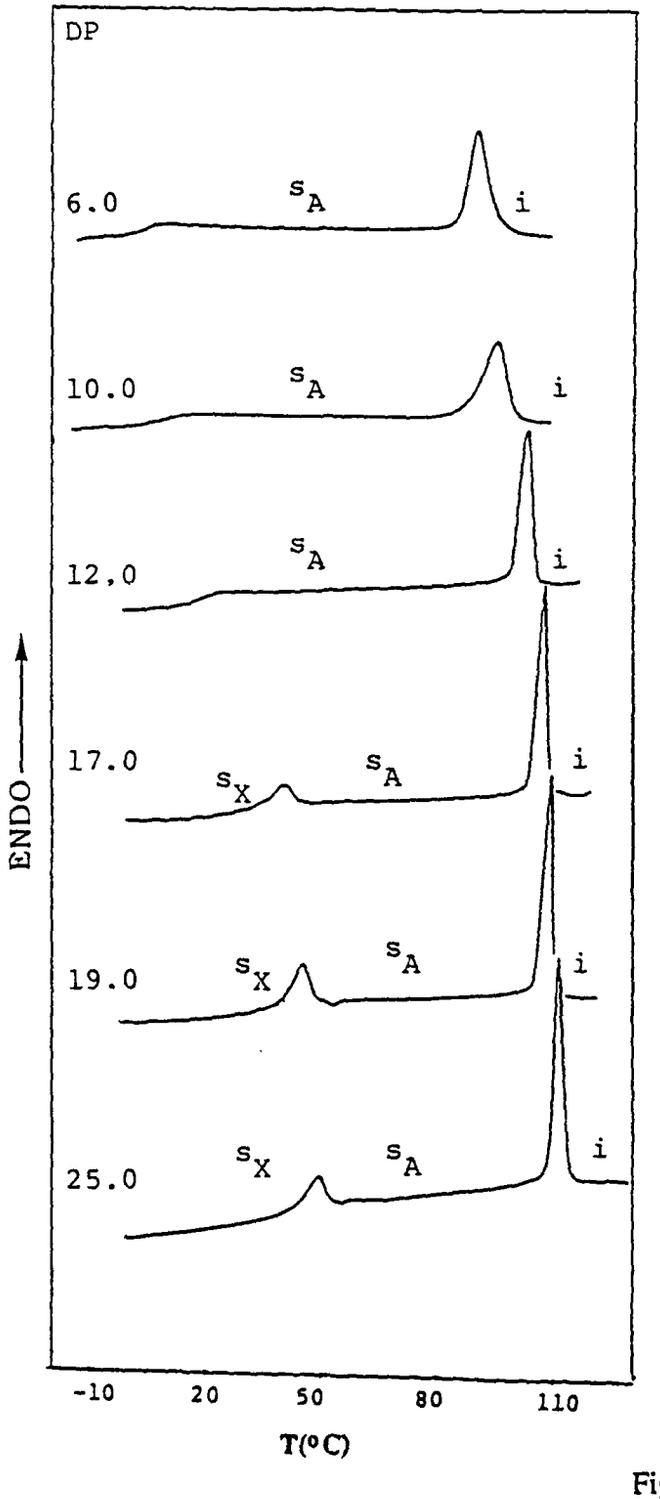


Figure 6a

Poly(13-6)

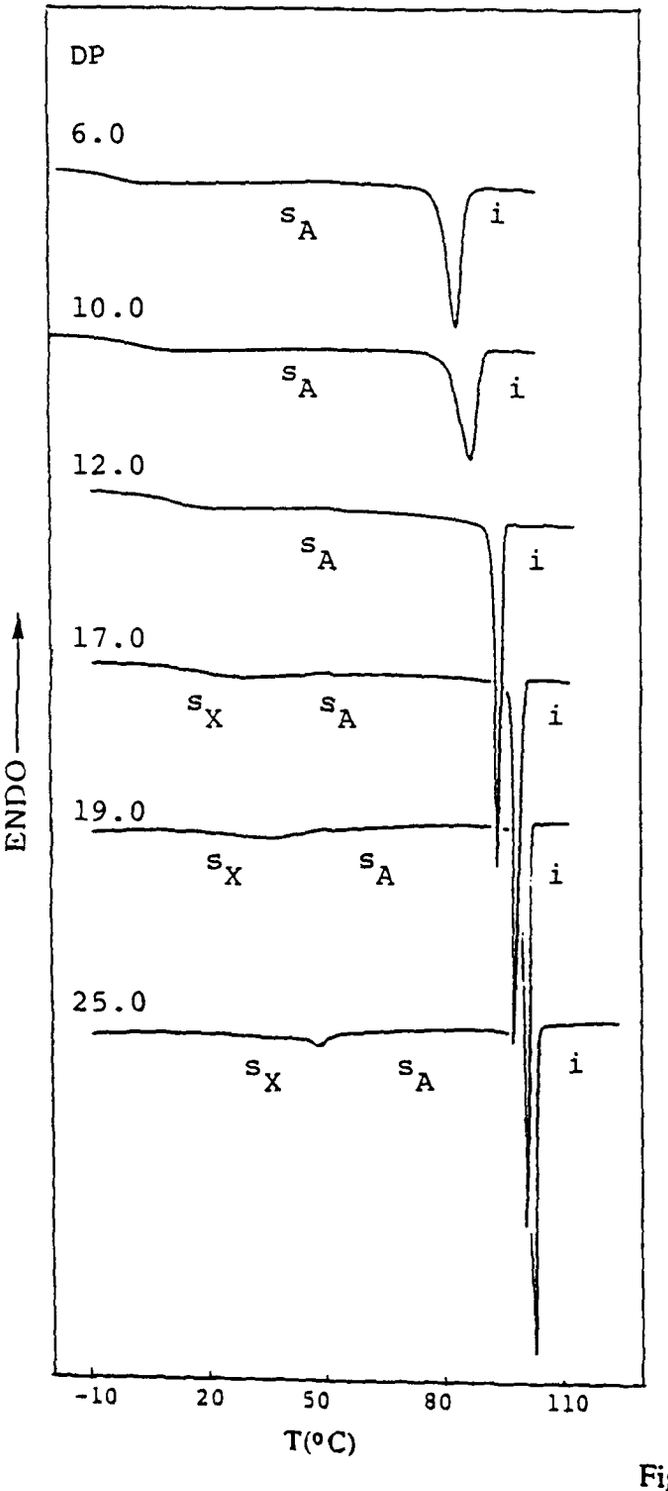


Figure 6b

Poly(13-6)

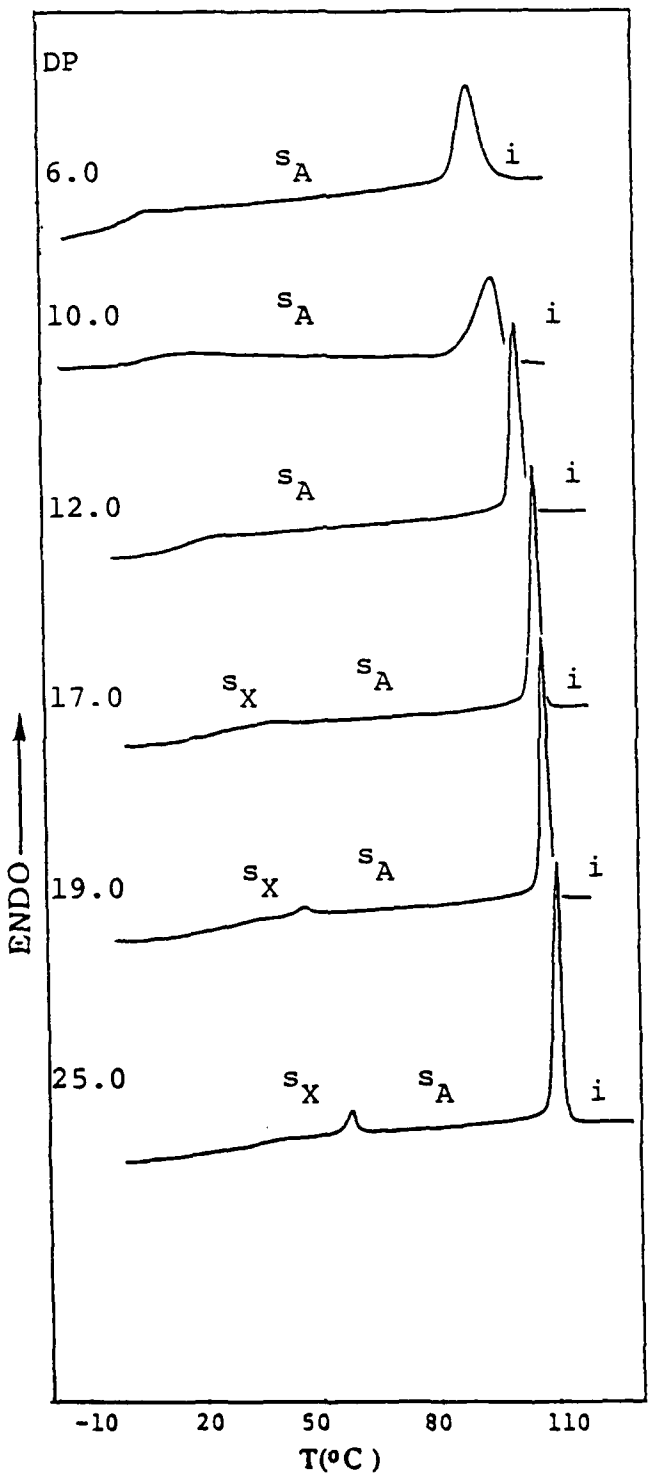


Figure 6c

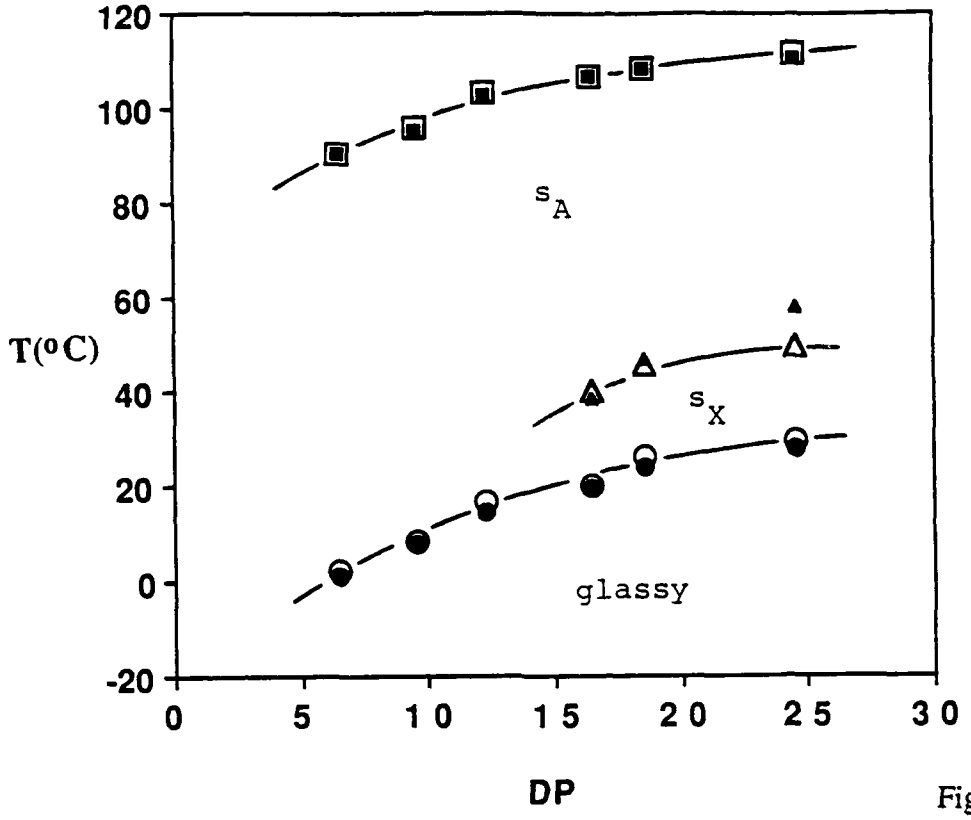


Figure 7a

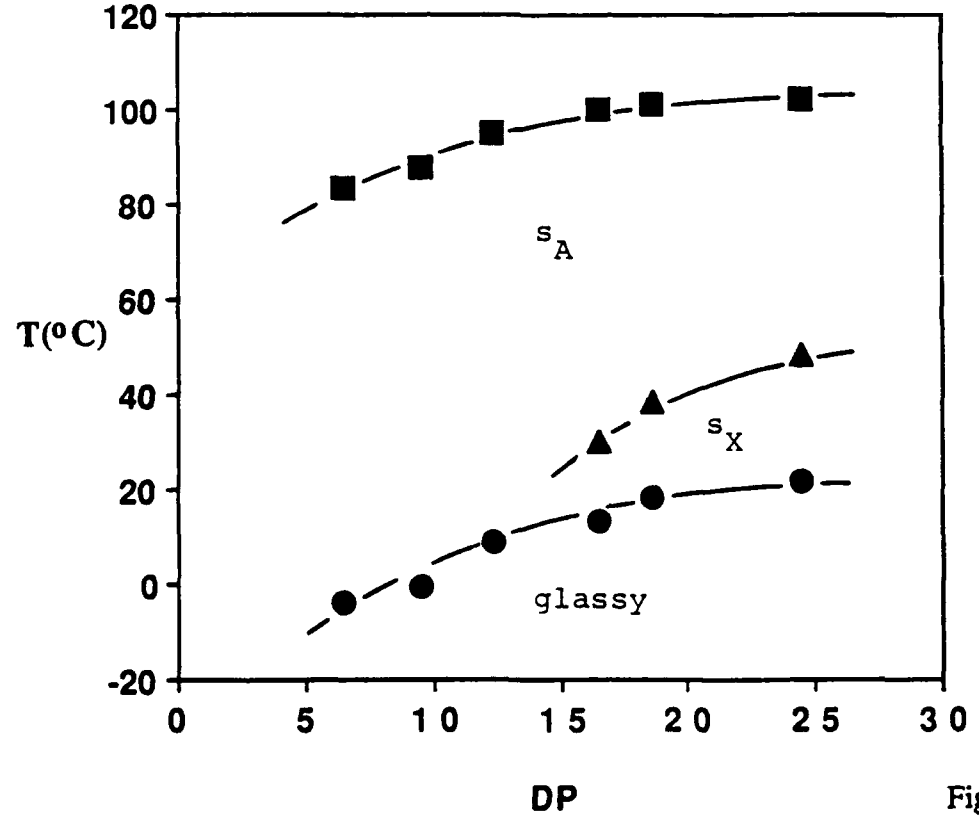


Figure 7b