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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization.16. Tailor-Made s_C^* Mesophase in Copolymers of 4-{[S-(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(ω-Oxyalkyl-1-Vinyl Ether)Biphenyl with Undecanyl and Octyl Alkyl Groups

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 16.[a] Tailor-Made s_C* Mesophase in Copolymers of 4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(ω-Oxyalkyl-1-Vinyl Ether)Biphenyl with Undecanyl and Octyl Alkyl Groups

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ABSTRACT

The synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(8-oxyoctyl-1-vinyl ether)biphenyl (14-8) are described. Poly(14-8) with degree of polymerization lower than 40 and polydispersities ≤ 1.15 were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscope. All polymers exhibit enantiotropic s_A and s_C* mesophases. Poly(14-8) with degrees of polymerization higher than 17 exhibit also an enantiotropic unidentified s_X mesophase. Copolymers of 14-8 with 4-{[S(-)-2-methyl-1-butyl] oxycarbonyl}-4'-(11-oxyundecanyl-1-vinyl ether)biphenyl (14-11) were synthesized to cover the entire range of composition at a degree of polymerization of 15. The phase bahavior of these copolymers was investigated and demonstrated a behavior similar to an ideal solution derived from the structural units of poly(14-8) and poly(14-11). This copolymerization experiment allowed the synthesis of copolymers exhibiting, depending on the composition, a s_C* mesophase from below 10°C to up to 50-80°C.

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

INTRODUCTION

Since the first examples of mesogenic vinyl ethers and liquid crystalline poly(vinyl ether)s were reported from our laboratory,[1] several research groups became actively engaged in the synthesis of mesomorphic poly(vinyl ether)s mainly because they can be polymerized by a living cationic mechanism.[2-4]

In the previous paper from this series we have reported the influence of molecular weight on the phase behavior of poly{ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s with alkyl groups from ethyl to undecanyl,[5] and of other functional mesogenic vinyl ethers.[6] The first series of liquid crystalline copolymers with constant molecular weight, narrow molecular weight distribution and various compositions were also prepared from mesogenic vinyl ethers.[6c,6e,7] These experiments have demonstrated that living cationic polymerization and copolymerization of mesogenic vinyl ethers provides a quantitative approach to the molecular design of side chain liquid crystalline polymers exhibiting uniaxial nematic, various smectic,[5,7a-d] chiral smectic C (s_C*),[6g] and reentrant nematic[7e] mesophases.

Liquid crystalline polymers exhibiting chiral mesophases, i.e., cholesteric and chiral smectic C (s_C*),[9] are of both theoretical and technological interests. Liquid crystals exhibiting chiral smectic A (s_A*) mesophases were only recently discovered[10] 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.[6g-22] 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.[6g,9-22]

In a previous paper from this series we have described the synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(11-oxyundecanyl-1-vinyl ether)biphenyl (14-11) and 4-{[S(-)-2-methyl-1-butyl]oxycarbonyl}-4'-(6-oxyhexyl-1-vinyl ether)biphenyl (14-6).[6g] The mesomorphic behavior of poly(14-11) and poly(14-6) was discussed as a function of molecular weight. Only poly(14-11) exhibited a s_C* mesophase over a narrow range of temperatures.

The goal of this paper is to describe the synthesis and living cationic polymerization of 4-{[S(-)-2-methyl-1-butyl]oxycarboxyl}-4'-(8-octyl-1-vinyl ether)biphenyl (14-8) and living cationic copolymerization of 14-8 with 14-11. These experiments will provide a convenient access to the design of side chain liquid crystalline polymers and copolymers exhibiting a s_C* phase over a broad range of temperatures.

EXPERIMENTAL

Materials

4-Hydroxybiphenyl (97%), dimenthylsulfate (99%+), HBr (48% in H_2O), 8-bromooctanoic acid (97%), borane-tetrahydrofuran complex (1.0M solution in tetrahydrofuran, dimethyl sulfide (anhydrous, 99%+, packaged under nitrogen in sure/seal bottle), 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 argon before each use. 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. The thermal transition temperatures were measured by a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station. In all cases, the heating and cooling rates were 20°C/min. The transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. 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 verify the thermal transitions and to characterize the anisotropic textures. 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 5×10^2 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.

Synthesis of 4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(8-Octanyl-1-Vinyl Ether) Biphenyl (14-8) and 4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(11-Oxyundecanyl-1-Vinyl Ether) Biphenyl (14-11)

Both monomers 14-8 and 14-11 were synthesized according to the synthetic route outlined in Scheme I. Compounds 3, 4, 5, 6, 8, 13 and monomer 14-11 were synthesized as described previously.[6g]

8-Bromo-1-Octanol (10)

A solution of borane-THF complex (180 ml) was stirred in a 1000 ml three neck round bottom flask for half an hour in an ice bath under nitrogen. Then, a solution of 21.4 g (0.096 mol) of 8-bromooctanoic acid in 220 ml of dry THF was added dropwise during 4-5 hours[23]. After stirring for additional 3 hours in an ice bath, 10 ml H_2O followed by 120 ml saturated K_2CO_3 solution were slowly added to the reaction mixture. The THF solution was separated and the water layer was extracted with THF twice. The combined THF solution was dried over $MgSO_4$. After the THF was evaporated on a rotary evaporator, the resulting light yellow oil was distilled under vacumm. The portion distilling at 90-92°C/0.11 mmHg was collected to yield 16.0 g of a colorless liquid (80%).

^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.65 (t, 2H, $-O-C\underline{H}_2-$), 3.41 (t, 2H, $Br-C\underline{H}_2-$), 1.86 (m, 2H, $-O-CH_2-C\underline{H}_2-$), 1.57 (m, 2H, $Br-CH_2-C\underline{H}_2-$), 1.34 (m, 8H, $Br-CH_2CH_2-(C\underline{H}_2)_4-$).

8-Bromooctanyl-1-Vinyl Ether (12)

A solution of 8-bromo-1-octanol (10) (15.5 g, 0.0742 mol), 1,10-phenanthroline palladium (II) diacetate[24] (0.97 g, 2.39 mmol), butyl vinyl ether (190 ml) and 20 ml dry chloroform was refluxed overnight (12-14 hours)[5a,e]. The resulting light yellow solution, obtained after gravity filtration, was placed 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 element) to yield 16.36 g (94%) of a light yellow oil. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 6.49-6.38 (m, 1H, $CH_2=C\underline{H}O-$), 4.14 (d, 1H, cis $C\underline{H}_2=CHO-$), 3.93 (d, 1H, trans $C\underline{H}_2=CHO-$), 3.64 (t, 2H, $CH_2=CH-OC\underline{H}_2-$), 3.38 (t, 2H, $Br-C\underline{H}_2-$), 1.82 (m, 2H, $-OCH_2C\underline{H}_2-$), 1.61 (m, 2H, $Br-CH_2C\underline{H}_2-$), 1.27 (m, 8H, $Br-CH_2CH_2-(C\underline{H}_2)_4-$).

4-{[S(-)-2-Methyl-1-Butyl]Oxycarbonyl}-4'-(8-Oxyoctyl-1-Vinyl Ether)Biphenyl (14-8)

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 13. After stirring for 2 hours at 60°C, the mixture turned yellow. Then, 8-bromooctyl-1-vinyl ether (3.31 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 and was further purified by column chromatography (silica gel, CH_2Cl_2 as eluent) to give 2.2 g (36%) of white crystals. Purity: 99.9% (HPLC). Thermal transition temperatures (°C) are: k 37.6 s_A 53.3 i on heating, and i 49.2 s_A 30.2 s_C* -15.6 k on cooling (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.00 (m, 6 protons, $-CH(C\underline{H}_3)CH_2C\underline{H}_3$), 1.37 (m, 10 protons, $-OCH_2CH_2(C\underline{H}_2)_4-$, and $-CHC\underline{H}_2-CH_3$), 1.64 (m, 2 protons, $-C\underline{H}_2CH_2-OPh-$), 1.78 (m, 3 protons, $=CH-OCH_2C\underline{H}_2-$, and $-CH_2C\underline{H}(CH_3)CH_2-$), 3.69 (t, 2 protons, $=CH-OC\underline{H}_2-$), 4.01 (m, 3 protons, $-C\underline{H}_2-OPh$ and $=C\underline{H}_2$ trans), 4.18 (m, 3 protons $-COOC\underline{H}_2-$ and $=C\underline{H}_2$ cis), 6.43-6.50 (m, 1 proton $=C\underline{H}O-$), 6.98 (d, 2 aromatic protons, o to $-O(CH_2)_9-$), 7.56 (d, 2 aromatic protons, m to $-O(CH_2)_8-$), 7.62 (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. After the flask was filled with argon, freshly distilled dry methylene chloride was added through a syringe and the solution was cooled to 0°C. Dimethyl sulfide and triflic acid were then added carefully via a syringe[25]. The monomer concentration was about 10 wt % of the solvent volume and the dimethyl sulfide concentration was 10 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 unreacted monomer. The polymerization results are summarized in Tables I and II.

RESULT 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.[6g, 9-22] 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. Based on our previous experience on the molecular engineering of nematic and smectic phases, the first requirement for such an investigation would be to have available two homopolymers displaying the same mesophase and also to know the influence of molecular weight on their phase transition temperatures.[5,6] Copolymerization experiments can then be used to enlarge the thermal stability of a certain mesophase.[7]

The data presented in this manuscript will follow the same pattern. We have already information on the influence of molecular weight on the phase transitions of poly(14-11) which exhibits a s_C* phase.[6g] Therefore, the next step is to provide a second polymer for which we will have the same information. This polymer is poly(14-8).

Scheme I outlines the synthesis of 14-8. Experiment details for all intermediate steps were published elsewhere[6g]. The cationic polymerization of 14-8 was initiated with the system $CF_3SO_3H/S(CH_3)_2$ and was performed at 0°C in CH_2Cl_2.[25] 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 passed through a chromatographic column containing silica gel using methylene chloride as eluent. The polymerization mechanism is presented in Scheme II and the polymerization results of 14-8 are summarized in Table I. Polymer yields are lower than expected, due to the polymer loss during the purification process. Although the molecular weights determined by GPC reported in Table I 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 are equal or lower than 1.15. 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. The degrees of polymerization were determined by measuring the ratio of the doublet at $\delta = 6.92$ ppm versus the broad triplet at $\delta = 4.63$ ppm. The degrees of polymerization determined by both GPC and NMR are summarized in Table I. The number average molecular weights of poly(14-8) determined by both GPC and NMR and the M_w/M_n data are plotted in Figure 2 as a function of $[M]_o/[I]_o$ ratio. All three dependences are linear, demonstrating a living polymerization mechanism. The difference between the two slopes of the dependences of Mn versus $[M]_o/[I]_o$ is expected since one set of data (from NMR) is absolute while the other (from GPC) is relative.

Figure 3 presents the DSC traces of the first, second heating and first cooling scans. As observed from this figure, first and second heating scans are almost identical. Regardless of their degree of polymerization all poly(14-8)s exhibit enantiotropic s_A and s_C* mesophases. The assignment of these mesophases was confirmed by thermal optical polarized microscopy. Representative textures displayed by the s_A and s_C* mesophases are presented in Figure 4. Only poly(14-8)s with degrees of polymerization 13, 17 and 23 present an enantiotropic unidentified s_X mesophase. The lower molecular weight polymers do not show this s_X phase since this transition temperature overlaps the glass transition temperature and therefore, is strongly controlled by kinetics. Since even the s_X phase of the high molecular weight poly(14-8) is close to the glass transition temperature of the polymer, no representitive texture could be obtained for this phase. The dependences between various phase transition temperatures and the degree of polymerization of poly(14-8) are plotted in Figure 5. Poly(14-11)s exhibit in the first heating and cooling scans a crystalline phase, an enantiotropic s_A and a monotropic s_C* phase. In the second heating scan, due to the close proximity of the crystallization temperature to the polymer phase transition, the crystallization process does not take place and therefore, the polymers exhibit enantiotropic s_X, s_C* and s_A mesophases.[6g] In general, since crystallization is a kinetically controlled process while the formation of a mesophase is a thermodynamically controlled process, the crystallization process is different for various DSC scans while mesomorphic phase transitions are not.

The copolymerization of 14-11 with 14-8 is outlined in Scheme III and the results are summarized in Table II. Attempts were made to synthesize poly(14-8-co-14-11) X/Y (where X/Y refers to the mole ratio of the two structural units) copolymers with a degree of polymerization of about 15.

Figure 6 presents the DSC traces of poly(14-8-co-14-11) X/Y obtained during the first and second heating and first cooling scans. Poly(14-8-co-14-11) X/Y with X/Y = 1/9 to 6/4 exhibit enantiotropic s_C* and s_A mesophases. Therefore, the structural units of poly(14-8) and poly(14-11) are isomorphic in their s_A and s_C* mesophases but are not isomorphic in their s_X phases. Subsequently the s_X phases of poly(14-8) and poly(14-11) are different. Therefore, as expected from the results obtained with other copolymer systems[7], cationic copolymerization of 14-8 with 14-11 allowed the synthesis of copolymers with a low glass transition temperature and a very broad range for the s_C* mesophase. This can be best observed from Figure 7 which plots the phase behavior of poly(14-8-co-14-11) as a function of copolymer composition.

These copolymerization experiments demonstrate the ability to engineer s_C* mosophases by living cationic copolymerization experiments. Such experiments will allow a quantitative investigation of the dynamics of s_C* paramaters versus various structural variants of the polymer and thus will contribute to the molecular engineering of ferroelectric liquid crystalline elastomers[9b] with well defined architecture.

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REFERENCES

1. a) J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **29**, 327. b) V. Percec and D. Tomazos, *Polym. Bull.*, 1987, **18**, 239. c) V. Percec, *Makromol. Chem., Macromol. Symp.*, 1988, **13/14**, 397.

2. 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.
3. S. G. Kostromin, N. D. Cuong, E. S. Garina and V. P. Shibaev, *Mol. Cryst. Liq. Cryst.*, 1990, **193**, 177.
4. a) V. Heroguez, A. Deffieux and M. Fontanille, *Makromol. Chem., Macromol. Symp.*, 1990, **32**, 199. b) V. Heroguez, M. Schappacher, E. Papon and A. Deffieux, *Polym. Bull.*, 1991, **25**, 307.
5. a) V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci.: Part A: Polym. Chem.*, 1991, **29**, 327. b) V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 1017. c) V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 2780. d) V. Percec, M. Lee and C. Ackerman, *Polymer*, in press. e) V. Percec and M. Lee, *J. Macromol. Sci.-Chem.*, 1991, **A28**, 651.
6. a) V. Percec, A. Gomes and M. Lee, *J. Polym. Sci.: Part A: Polym. Chem.*, in press. b) H. Jonsson, V. Percec and A. Hult, *Polym. Bull.*, 1991, **25**, 115. c) R. Rodenhouse and V. Percec, *Adv. Mater.*, 1991, **3**, 101. d) R. Rodenhouse and V. Percec, *Polym. Bull.* 1991, **25**, 47. e) R. Rodenhouse, V. Percec and A. E. Feiring, *J. Polym. Sci: Part C: Polym. Lett.*, 1990, **28**, 345. f) V. Percec, C. S. Wang and M. Lee, *Polym. Bull.*, in press. g) V. Percec, Q. Zheng and M. Lee, J. *Mater. Chem.*, in press.
7. a) V. Percec and M. Lee., *Polymer*, in press. b) V. Percec and M. Lee, *Polym. Bull.*, 1991, **25**, 123. c) V. Percec and M. Lee, *Polym. Bull.*, 1991, **25**, 131. d) V. Percec and M. Lee, *Macromolecules*, in press. e) V. Percec and M. Lee, *J. Mater. Chem.*, in press.
8. 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.
9. a) P. LeBarny and J. C. Dubois, in "*Side Chain Liquid Crystul Polymers*", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 130. b) J. H. Wendorff, *Angew. Chem., Int. Ed., Engl.*, 1991, **30**, 405, and references cited therein.
10. J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *J. Am. Chem. Soc.* 1989, **111**, 8119.
11. 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.

12. 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, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 371.
13. 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 Polymers*", R. A. Weiss and C. K. Ober Eds., ACS Symposium Series 435, Washington DC., 1990, p. 207.
14. a) S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto and K. Kawasaki, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 93. b) H. Endo, S. Hachiya, S. Uchida, K. Hashimoto and K. Kawasaki, *Liq. Cryst.*, 1991, **9**, 635
15. N. Koide, K. Uehara and K. Iimura, Mol. Cryst. Liq. Cryst., **1988**, 157, 151.
16. T. Suzuki, T. Okawa, K. Ohnuma and Y. Sakon, *Makromol. Chem. Rapid Commun.*, 1988, **9**, 755.
17. M. Dumon, H. T. Nguyen, M. Mauzac, C. Destrade, M. F. Achard and H. Gasparoux, *Macromolecules*, 1990, **23**, 355.
18. D. M. Walba, P. Keller, D. S. Parmar, N. A. Clark and M. D. Wand, *J. Am. Chem. Soc.* 1989, **111**, 8273.
19. H. Kapitza, R. Zentel, R. J. Twieg, C. Nguyen, S. U. Vallerien, F. Kremer and C. G. Willson, *Adv. Mater.* 1990, **2**, 539.
20. T. Kitazume, T. Ohnogi and K. Ito, *J. Am. Chem. Soc.* 1990, **112**, 6608.
21. a) H. J. Cole, H. F. Gleeson, G. Scherowsky and A. Schliwa, *Mol. Cryst. Liq. Cryst.*, 1990, **7**, 117 and 125. b) H. M. Colquhoun, C. C. Dudman, C. A. O'Makoney, G. C. Robinson and D. J. Williams, *Adv. Mater.*, 1990, **2**, 139.
22. a) V. Percec and C. S. Wang, *J. Macromol. Sci.-Chem.*, 1991, **A28**, 687.

b) V. Percec and C. S. Wang, *J. Macromol. Sci.-Chem.*, in press. c) V. Percec, C. S. Wang, and M. Lee, *Polym. Bull.*, 1991, **26**, 15.

23. N. M. Yoon, C. S. Pak, H. C. Brown, S. Krishnamurthy and T. P. Stocky, *J Org. Chem.*, 1973, **38**, 2786.

24. J. E. McKeon and P. Fitton, *Tetrahedron* , 1972, **28**, 233.

25. a) C. G. Cho, B. A. Feit and O. W. Webster, *Macromolecules*, 1990, **23**, 1918.
    b) C. H. Lin and K. Matyjaszewsky, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, 1990, **31(1)**, 599.

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) G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1990, **191**, 1. d) D. Demus, H. Demus and H. Zaschke, *Flussige Kristalle in Tabellen*, I and II, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1974 and 1984.
    e) 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.

FIGURES AND SCHEME CAPTIONS

Scheme I: Synthesis of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(11-Oxyundecanyl Vinyl Ether)Biphenyl (14-11) and 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(8-Octyl Vinyl Ether)Biphenyl (14-8).

Scheme II: Cationic polymerization of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(8-Octyl Vinyl Ether)Biphenyl (14-8).

Scheme III: Cationic copolymerization of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(11-Oxyundecanyl Vinyl Ether)Biphenyl (14-11) and 4-{[S(-)-2-Methyl-1-Butyl] oxycarbonyl}-4'-(8-Octyl Vinyl Ether)Biphenyl (14-8).

Figure 1: 200 MHz ^{1}H-NMR spectrum of poly(14-8) with theoretical DP = 8.

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(14-8) 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 second heating scan (b) and the first cooling scan (c) by poly(14-8) with different degrees of polymerization (DP) determined by GPC. DP is printed on the top of each DSC scan.

Figure 4: Representative optical polarized micrographs (100x) of: a) the s_A mesophase displayed by poly(14-8) (DP=23) at 102°C on the cooling scan ; b) the s_C^* mesophase displayed by poly(14-8) (DP=23) at 75°C on the cooling scan.

Figure 5: The dependence of phase transition temperatures on the degree of polymerization determined by GPC of poly(14-8). a) data from the first heating scan: ○ -Tg; ◇ -Ts_X-s_C^* △ -Ts_C^*-s_A □ -Ts_A-i; b) data from the second heating scan: ⊙ -Tg; ◆ -Ts_X-s_C^*; ◬ -Ts_C^*-s_A; ⊡ -Ts_A-i; c) data from the first cooling scan; ■ -Ti-s_A; ▲ -Ts_A-s_C^*; ◆ -Ts_C^*-s_X; ● -Tg:

Figure 6: DSC traces displayed during the first heating scan (a), the first cooling scan (b) and the second heating scan (c) by poly(14-8-co-14-11)X/Y.

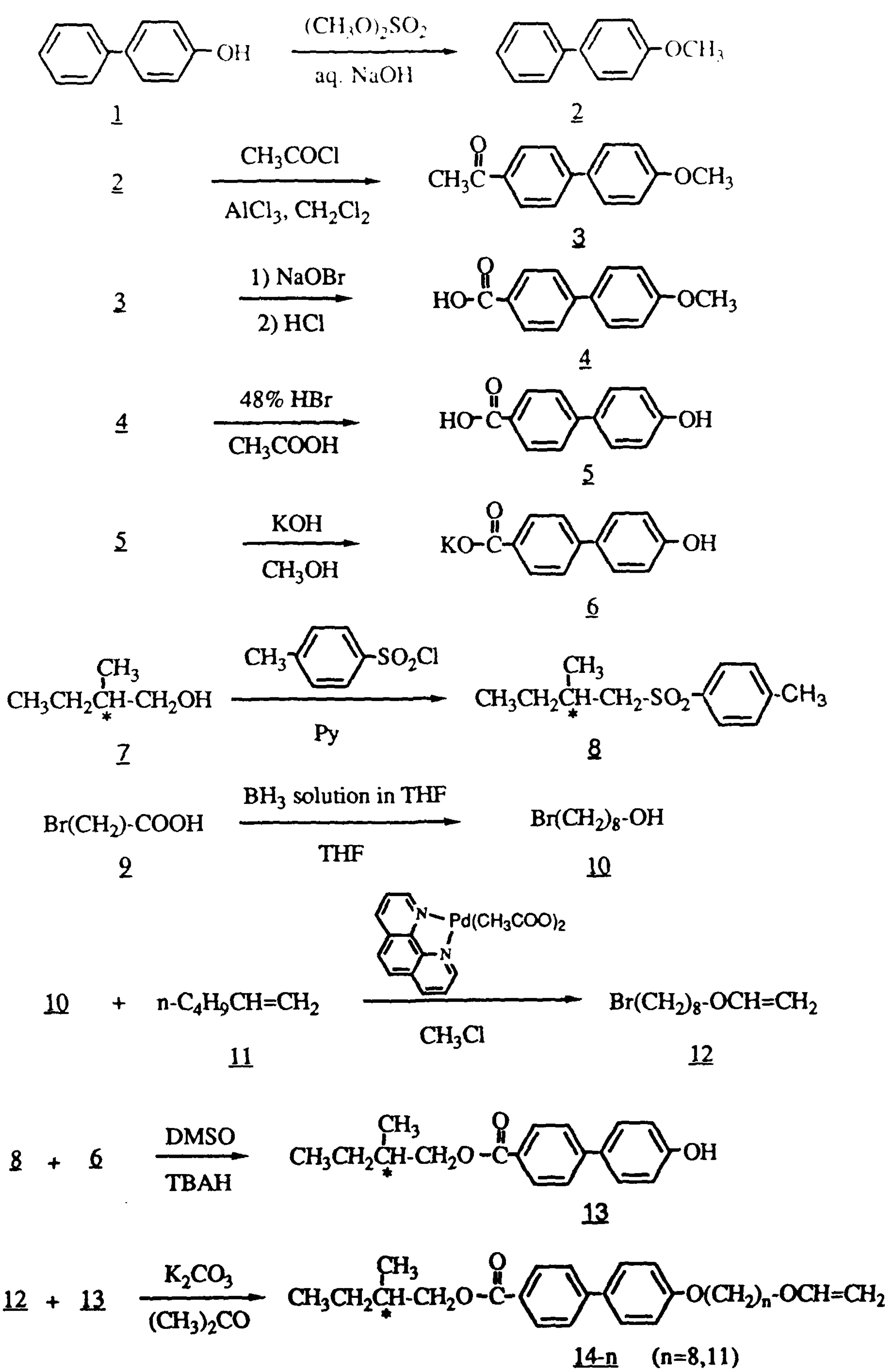
Figure 7: The dependence of phase transition temperatures on the degree of polymerization of poly(14-8-co-14-11)X/Y. a) data from the first heating: ○ -Tg; ◇ -Ts$_X$-s$_C$*; △-Ts$_C$*-s$_A$; □ -Ts$_A$-i; b) data from the second heating scan: ⊙ -Tg; ◈ -Ts$_X$-s$_C$*; ◬ -Ts$_C$*-s$_A$; ⊡ -Ts$_A$-i; c) data from the first cooling scan: ■ -Ti-s$_A$; ▲ -Ts$_A$-s$_C$*; ◆ -TsC*-s$_X$; ● -Tg.

Table II. Cationic Copolymerization of 14-11 with 14-8 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o=[14\text{-}11]+[14\text{-}8]=0.208\text{-}0.244M$; $[M]_o/[I]_o=15$; $[(CH_3)_2S]_o/[I]_o=10$; 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.	[14-11]/[14-8] (mol/mol)	Polymer yield(%)	$Mn \times 10^{-3}$	Mw/Mn	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
			GPC	GPC		heating	cooling
1	0/10	85	5.7	1.06	13	g 10.2 s_X 21.2 (0.42) s_{C^*} 92.9 (0.37) s_A 115.6 (4.62) i g 8.0 s_X 21.1 (0.48) s_{C^*} 92.8 (0.34) s_A 115.6 (4.62) i	i 108.9 (4.56) s_A 88.3 (0.44) s_{C^*} 13.5 (4.55) s_X 5.1 g
2	1/9	87	7.0	1.09	16	g 7.2 s_{C^*} 83.1 (0.44) s_A 116.5 (4.87) i g 5.2 s_{C^*} 83.3 (0.39) s_A 116.3 (4.72) i	i 109.9 (4.82) s_A 77.9 (0.30) s_{C^*} 1.7 g
3	2/8	84	5.9	1.09	13	g 9.0 s_{C^*} 76.6 (0.28) s_A 118.2 (4.64) i g 6.1 s_{C^*} 76.6 (0.34) s_A 118.5 (4.64) i	i 110.9 (4.49) s_A 71.3 (0.34) s_{C^*} 1.7 g
4	3/7	77	6.7	1.14	15	g 4.5 s_{C^*} 63.6 (0.23) s_A 113.4 (4.66) i g 4.2 s_{C^*} 63.9 (0.17) s_A 113.0 (4.72) i	i 108.2 (4.53) s_A 60.2 (0.25) s_{C^*} -0.5 g
5	4/6	82	6.4	1.08	14	g 4.7 s_{C^*} 52.8 (0.21) s_A 115.3 (4.88) i g 3.3 s_{C^*} 53.0 (0.17) s_A 115.3 (4.94) i	i 109.4 (4.86) s_A 48.7 (0.17) s_{C^*} -0.2 g
6	5/5	83	6.4	1.15	15	g 5.2 s_{C^*} 43.4 (0.10) s_A 115.2 (4.75) i g 2.5 s_{C^*} 45.5 (0.10) s_A 116.8 (5.00) i	i 111.6 (4.98) s_A 41.8 (0.17) s_{C^*} -0.2 g
7	6/4	85	6.3	1.07	14	g 5.2 s_{C^*} 40.1 (0.10) s_A 115.2 (5.01) i g 3.2 s_{C^*} 40.0 (0.10) s_A 115.3 (5.22) i	i 109.4 (5.16) s_A 35.7 (0.08) s_{C^*} 0.7 g
8	7/3	79	7.0	1.13	15	g 5.2 s_X 14.4 (0.25) s_{C^*} 41.3 (0.04) s_A 117.0 (5.29) i g 3.7 s_X 14.1 (0.40) s_{C^*} 41.3 (0.02) s_A 117.2 (5.19) i	i 110.9 (5.25) s_A 36.9 (0.18) s_{C^*} 8.8 (0.14) sX 1.6 g
9	8/2	81	6.8	1.15	15	g 6.6 s_X 16.5 (0.63) s_{C^*} 40.6 (0.02) s_A 116.7 (5.22) i g 3.3 s_X 16.2 (0.28) s_{C^*} 41.2 (0.06) s_A 117.1 (5.32) i	i 111.4 (5.24) s_A 37.1 (0.08) s_{C^*} 10.1 (0.73) s_X 1.6 g
10	9/1	80	7.1	1.12	15	g 9.0 k 50.3 (9.71) s_A 120.1 (5.60) i g 6.6 s_X 21.1 (1.48) s_{C^*} 44.3 (0.08) s_A 119.8 (5.44) i	i 113.0 (5.30) s_A 39.6 (0.14) s_{C^*} 12.9 (1.32) s_X 3.5 g
11	10/0	93	8.2	1.12	17	g 10.1 k 57.1 (12.90) s_A 118.1 (5.69) i g 8.2 s_X 24.9 (2.10) s_{C^*} 52.2 (0.17) s_A 118.1 (5.56) i	i 112.3 (5.35) s_A 48.4 (0.17) s_{C^*} 15.6 (2.05) s_X 7.9 g

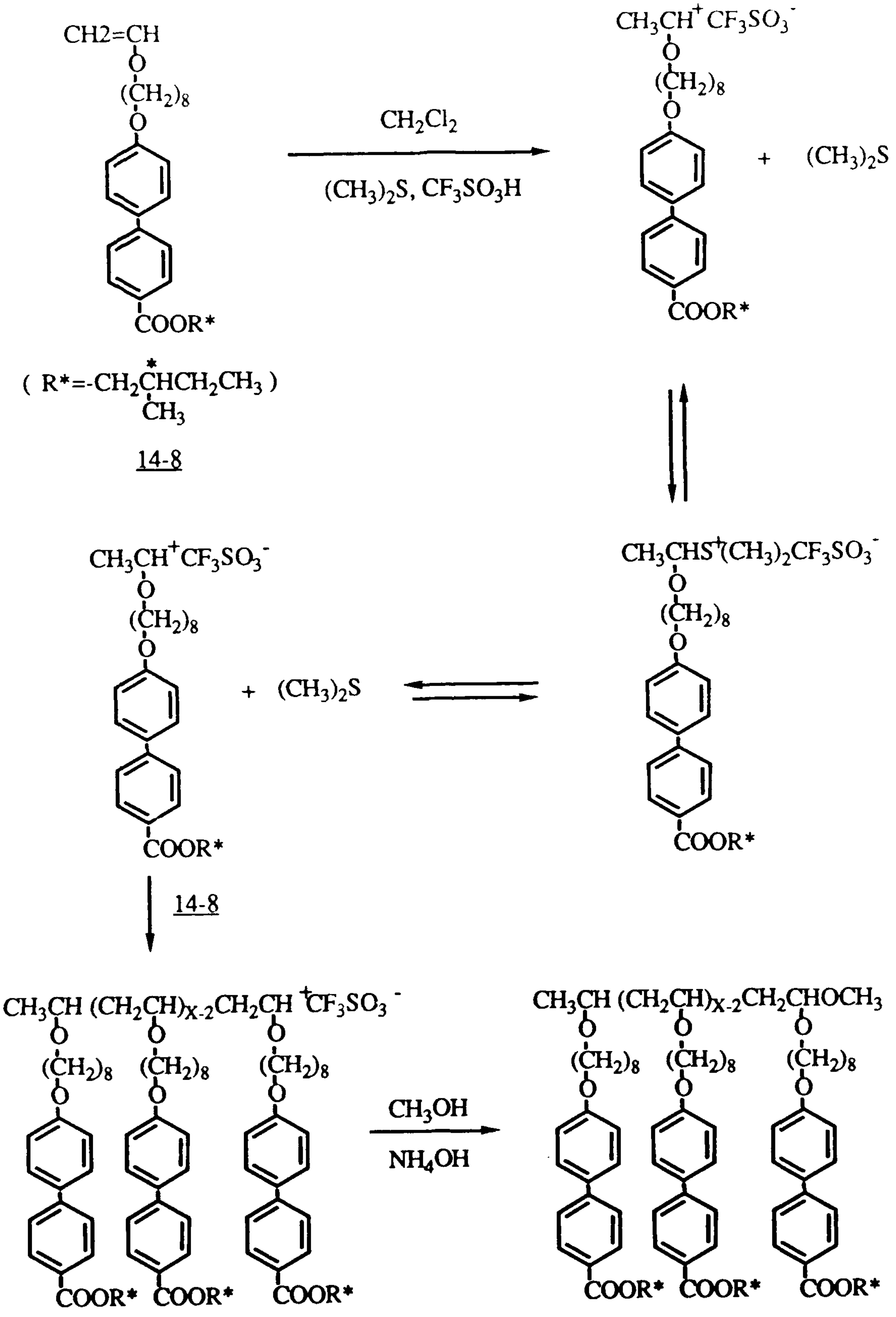
Table I. Cationic Polymerization of 4-{[S(-)-2-Methyl-1-Butyl]oxycarbonyl}-4'-(8-Oxyoctyl Vinyl Ether)Biphenyl (<u>14-8</u>) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o=0.244$; $[(CH_3)_2S]_o/[I]_o=20$; polymerization time, 1hr) and Characterization of the Resulting 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(%)	$M_n \times 10^{-3}$	Mw/Mn	DP		phase transitions (°C) and corresponding enthalpy changes (kJ/mru)	
			GPC	GPC	GPC	NMR	heating	cooling
1	5	77	2.72	1.09	6	7	g -7.1 s_{C^*} 80.3 (0.29) s_A 97.2 (4.99) i	i 90.4 (4.75) s_A 75.1 (0.27) s_{C^*} -12.1 g
							g -8.0 s_{C^*} 80.0 (0.27) s_A 97.1 (4.99) i	
2	7	85	3.29	1.10	8	10	g 1.0 s_{C^*} 83.4 (0.26) s_A 101.9 (5.08) i	i 95.9 (4.84) s_A 78.0 (0.33) s_{C^*} -7.2 g
							g -3.9 s_{C^*} 82.8 (0.24) s_A 102.1 (4.95) i	
3	10	73	4.86	1.08	11	14	g 5.1 s_{C^*} 89.6 (0.24) s_A 111.1 (4.47) i	i 104.9 (4.42) s_A 84.9 (0.33) s_{C^*} 0.2 g
							g 2.7 s_{C^*} 89.3 (0.38) s_A 111.5 (4.56) i	
4	13	83	5.71	1.06	13	19	g 10.2 s_X 21.2 (0.42) s_{C^*} 92.9 (0.37) s_A 115.6 (4.71) i	i 108.9 (4.56) s_A 88.3 (0.44) s_{C^*} 13.5 (0.55) s_X 5.1 g
							g 8.0 s_X 21.1 (0.48) s_{C^*} 92.8 (0.34) s_A 115.6 (4.62) i	
5	17	80	7.29	1.08	17	23	g 25.7 s_X 37.0 (1.70) s_{C^*} 96.1 (0.29) s_A 119.1 (4.42) i	i 112.8 (4.51) s_A 91.9 (0.44) s_{C^*} 22.1 (1.08) s_X 19.0 g
							g 22.5 s_X 31.8 (0.59) s_{C^*} 96.1 (0.38) s_A 119.2 (4.40) i	
6	25	88	10.2	1.10	23	38	g 34.5 s_X 47.2 (2.75) s_{C^*} 99.8 (0.37) s_A 123.6 (4.40) i	i 116.4 (4.34) s_A 94.7 (0.29) s_{C^*} 32.9 (1.65) s_X 22.5 g
							g 27.6 s_X 44.5 (1.36) s_{C^*} 99.8 (0.49) s_A 123.5 (4.34) i	

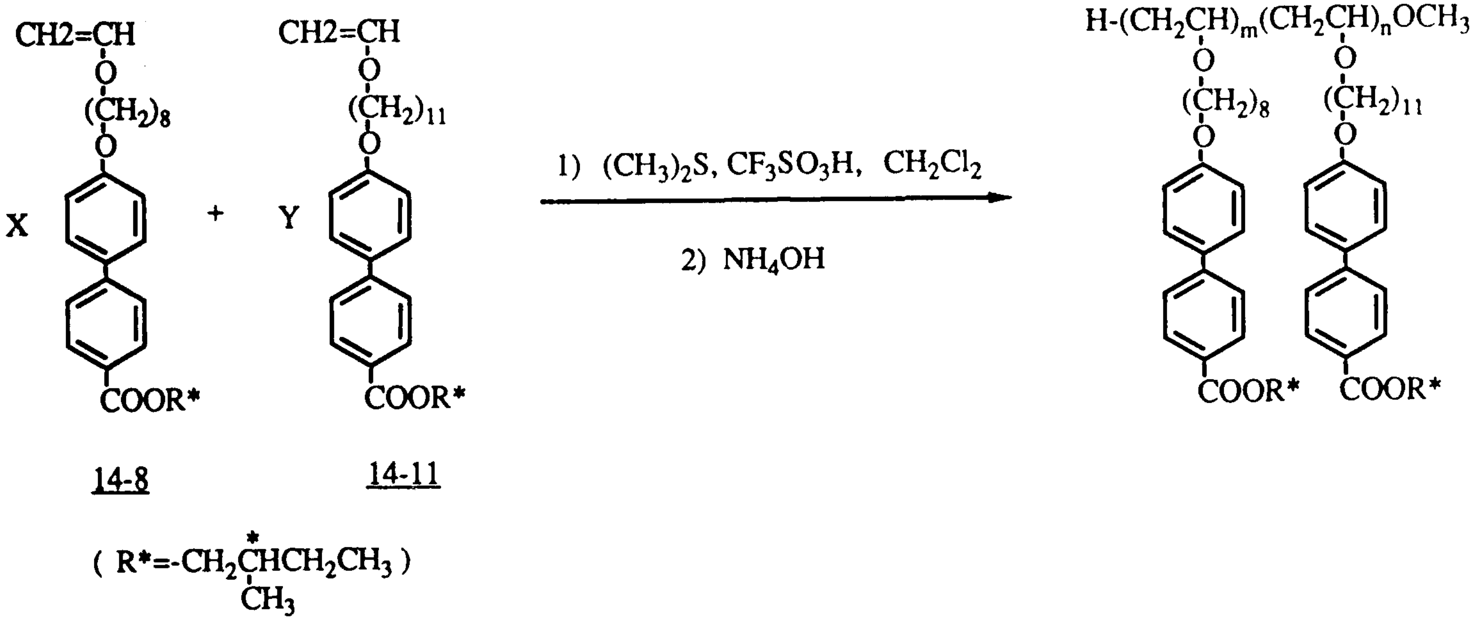


Scheme I

a


CH2=CH
CH₂Cl₂
(CH₃)₂S, CF₃SO₃H
CH₃CH⁺ CF₃SO₃⁻
(CH₃)₂S
(R*=-CH₂C*HCH₂CH₃)
CH₃
14-8
CH₃CHS⁺(CH₃)₂CF₃SO₃⁻
COOR*
14-8
CH₃CH (CH₂CH)X-2CH₂CH ⁺CF₃SO₃⁻
CH₃OH
NH₄OH
CH₃CH (CH₂CH)X-2CH₂CHOCH₃

Scheme II



X
Y
+
CH2=CH
O
$(CH_2)_8$
O
COOR*
CH2=CH
O
$(CH_2)_{11}$
O
COOR*
1) $(CH_3)_2S$, CF_3SO_3H, CH_2Cl_2
2) NH_4OH
$H\text{-}(CH_2CH)_m(CH_2CH)_nOCH_3$
$(CH_2)_8$
$(CH_2)_{11}$
COOR*
COOR*
14-8
14-11
(R*=-$CH_2\overset{*}{C}HCH_2CH_3$)
CH_3

Scheme III

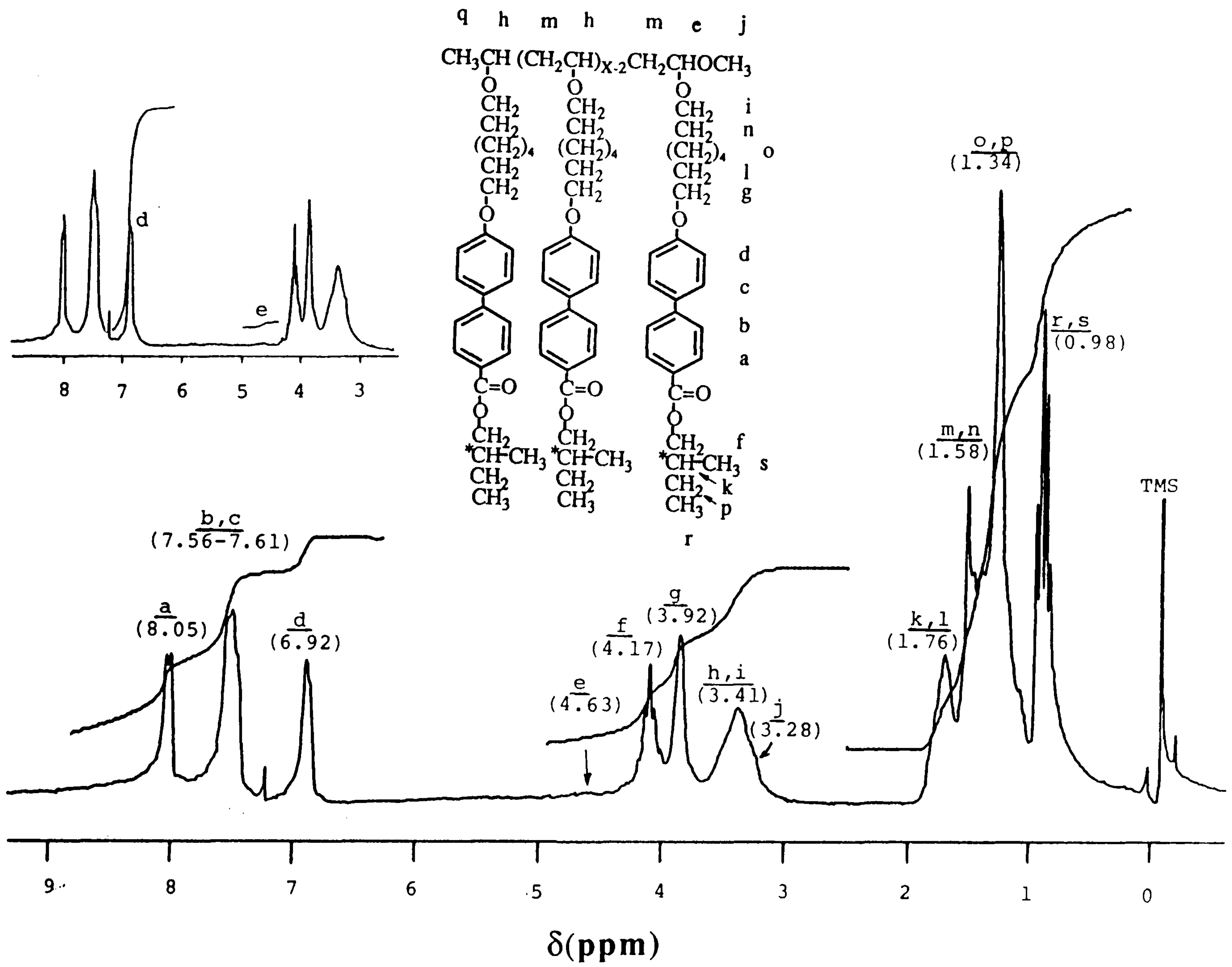
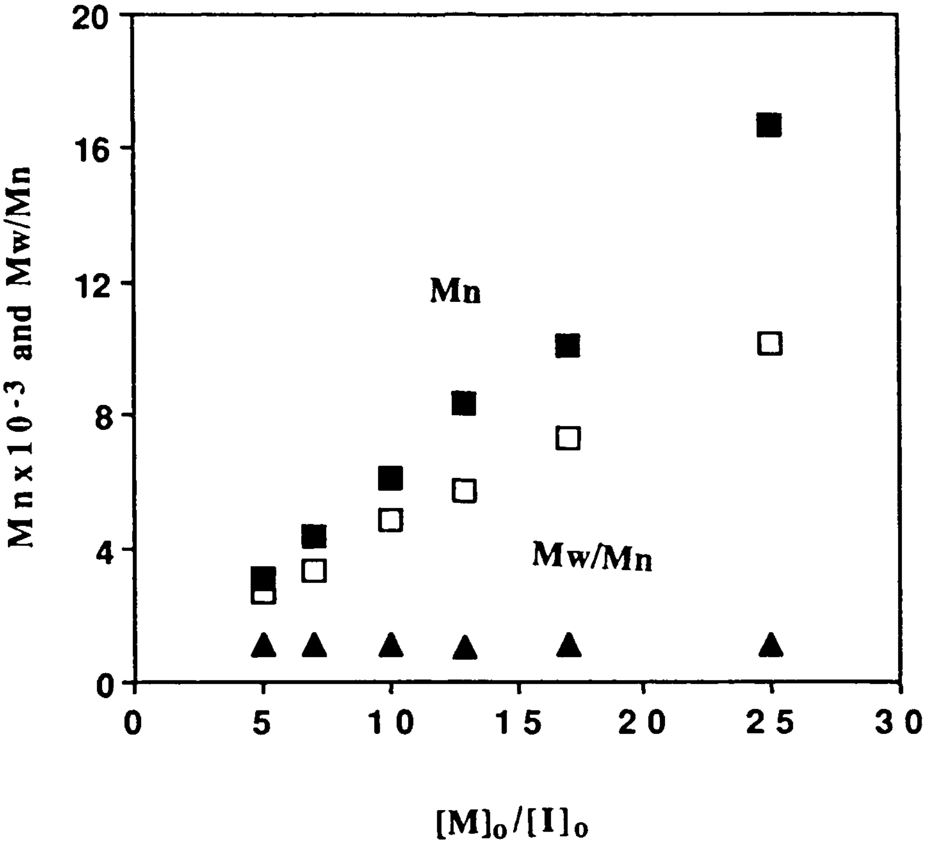

q h m h m e j
CH3CH (CH2CH)X-2CH2CHOCH3
i
n
o
l
g
d
c
b
a
C=O
f
*CH-CH3
s
k
p
r
d
e
8 7 6 5 4 3
b,c (7.56-7.61)
a (8.05)
d (6.92)
e (4.63)
f (4.17)
g (3.92)
h,i (3.41)
j (3.28)
k,l (1.76)
m,n (1.58)
o,p (1.34)
r,s (0.98)
TMS
9 8 7 6 5 4 3 2 1 0
δ(ppm)

Figure 1.



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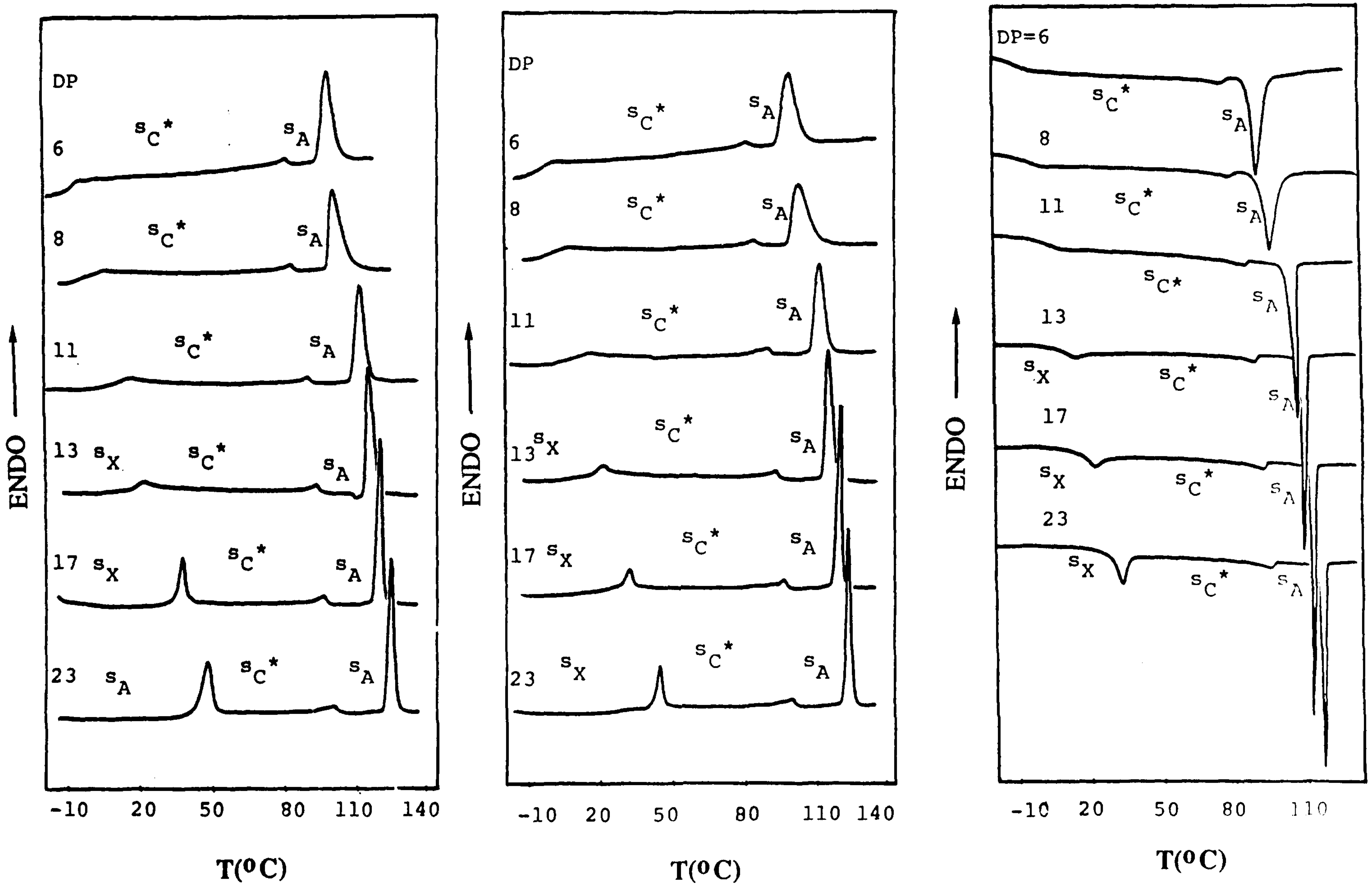


Figure 3. a) b)

Figure 4a)

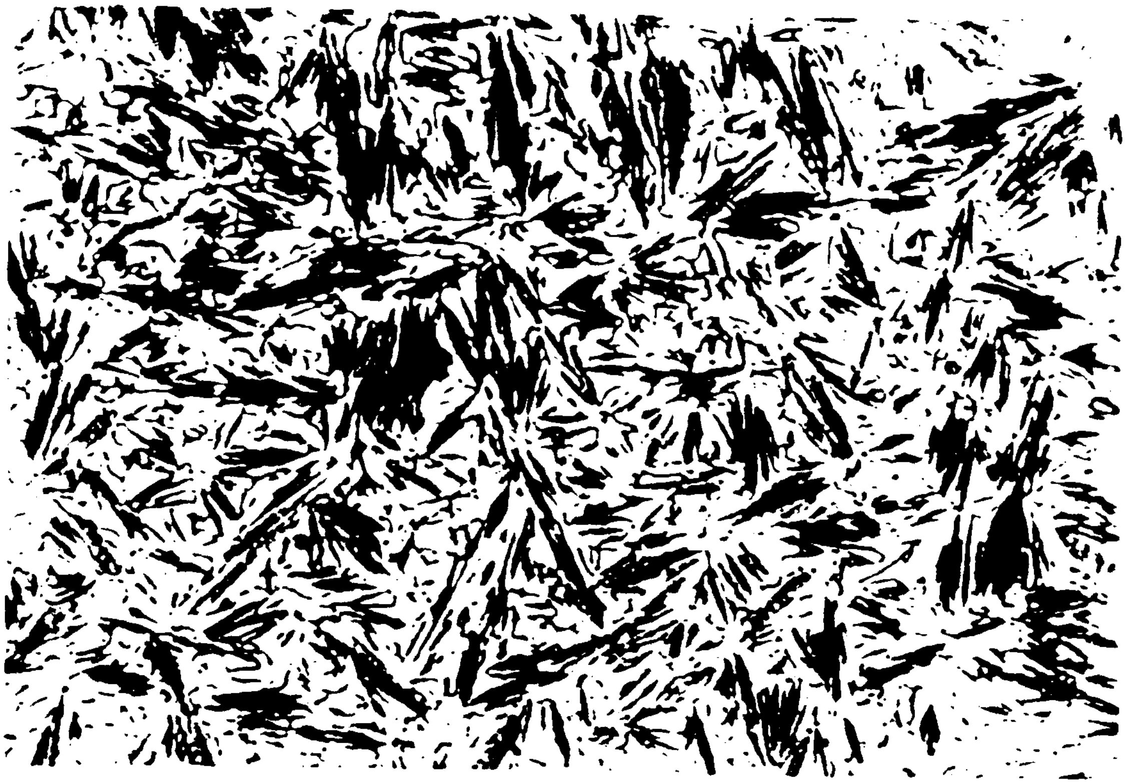


Figure 4b)

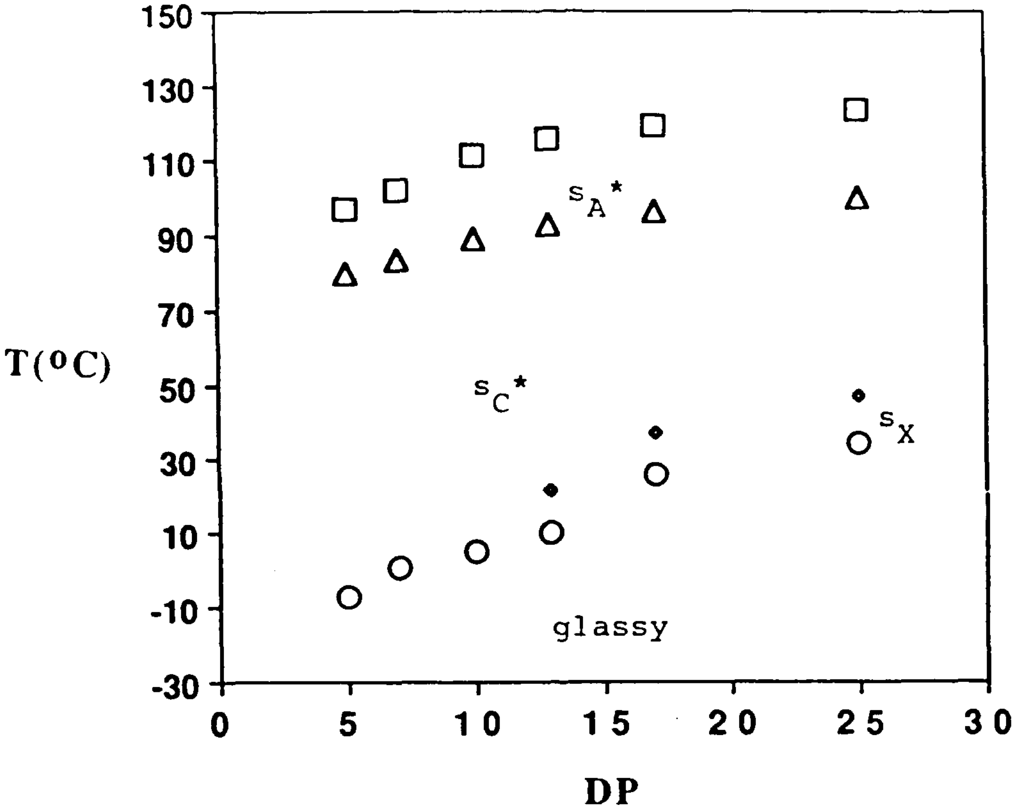


Figure 5a)

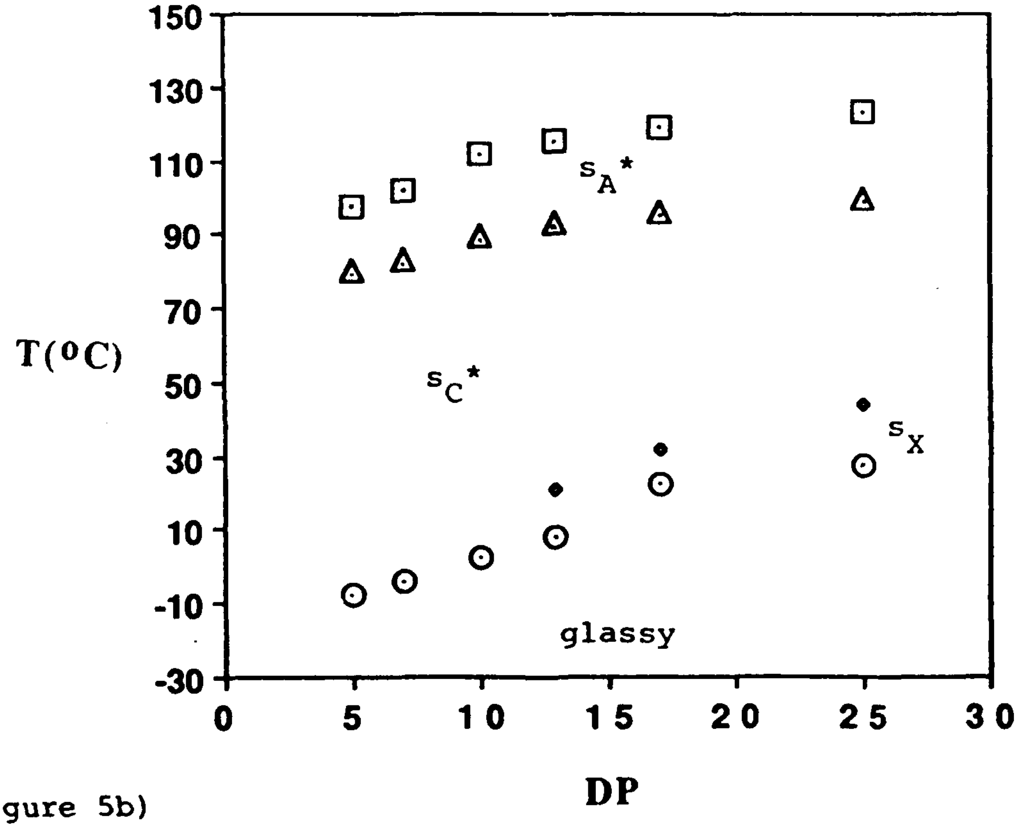


Figure 5b)

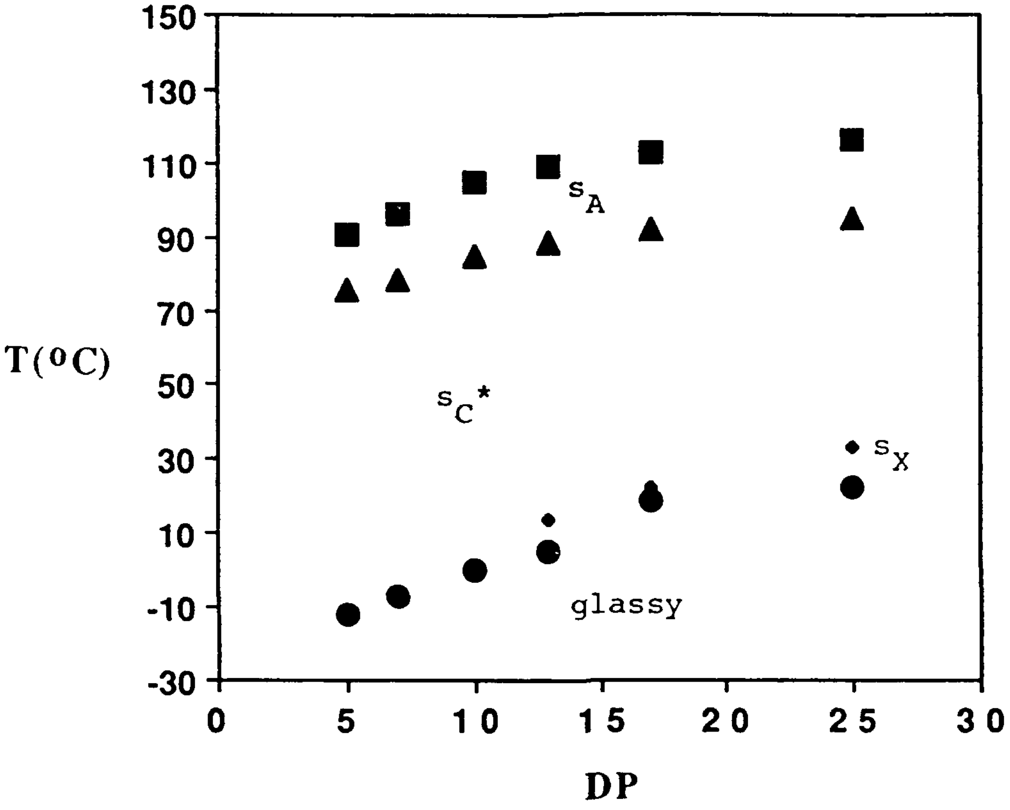

150
130
110
90
70
50
30
10
-10
-30
T(°C)
0
5
10
15
20
25
30
DP
S_A
$S_C{}^*$
S_X
glassy

Figure 5c)

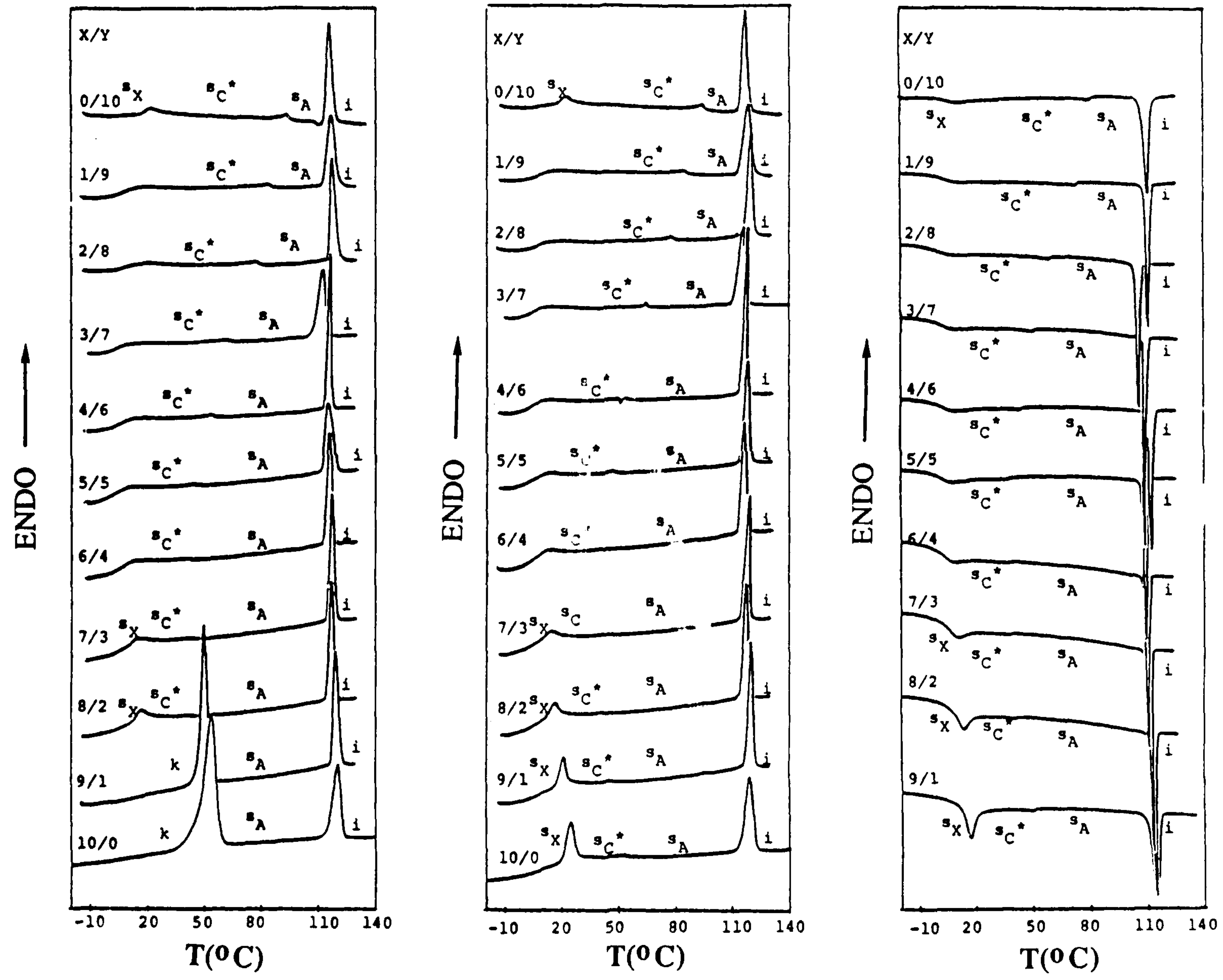

X/Y
0/10
1/9
2/8
3/7
4/6
5/5
6/4
7/3
8/2
9/1
10/0
ENDO
s_X
s_C^*
s_A
i
k
-10
20
50
80
110
140
T(°C)

Figure 6. a) b) c)

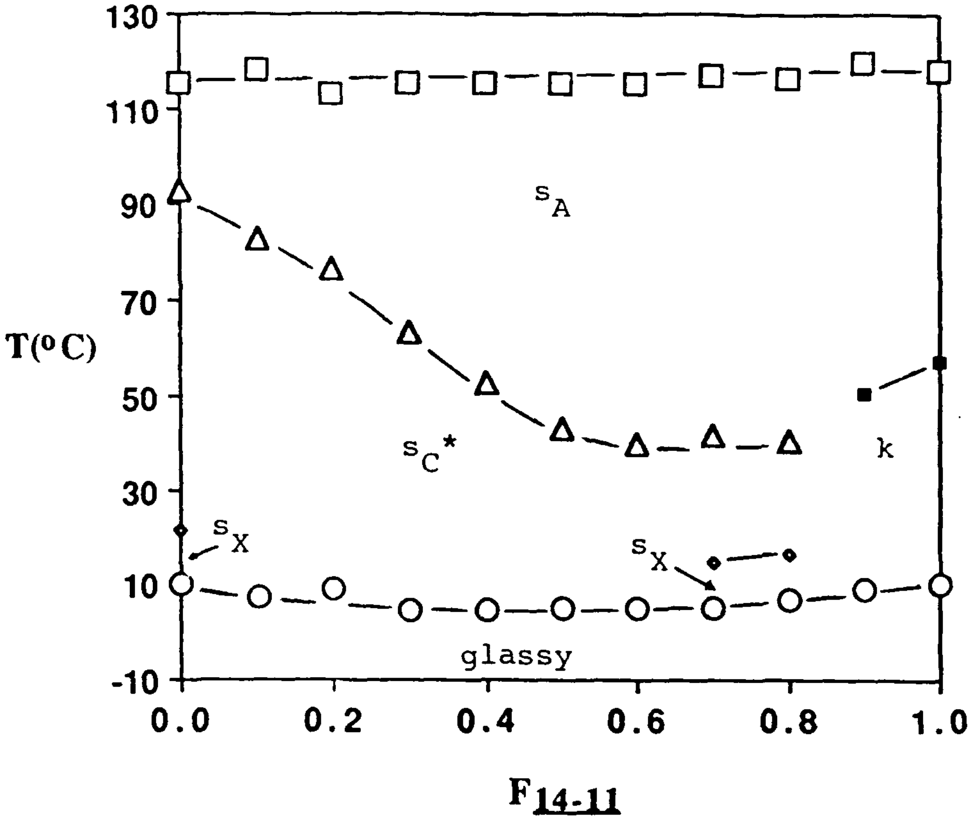


Figure 7a.

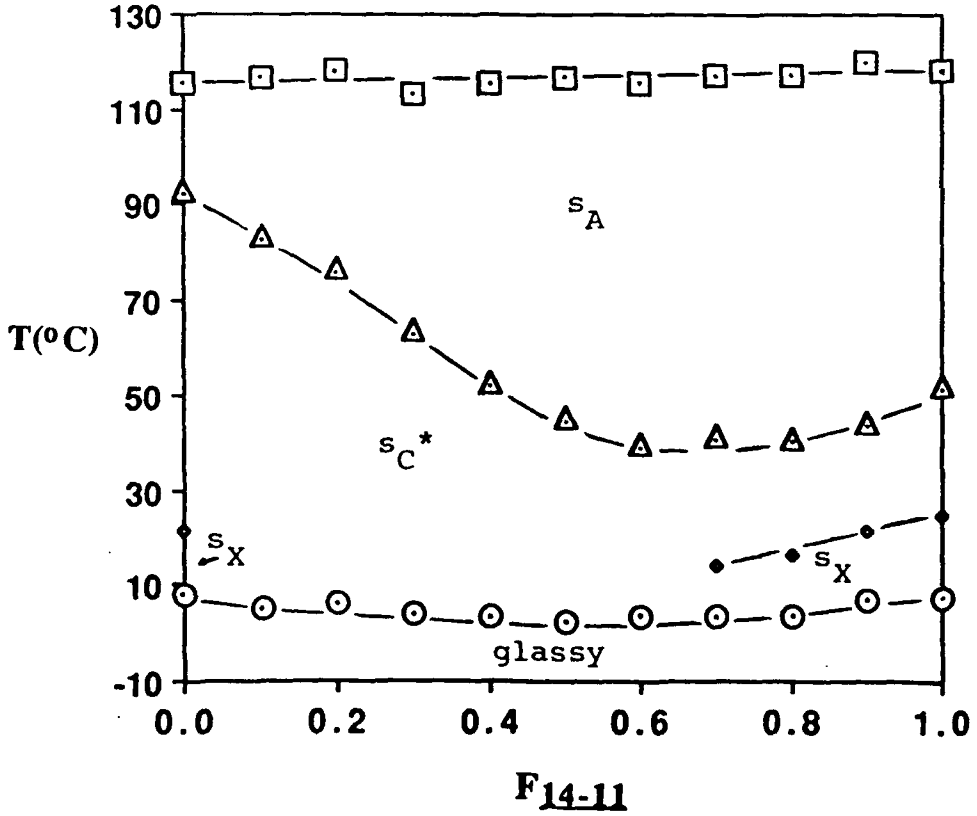
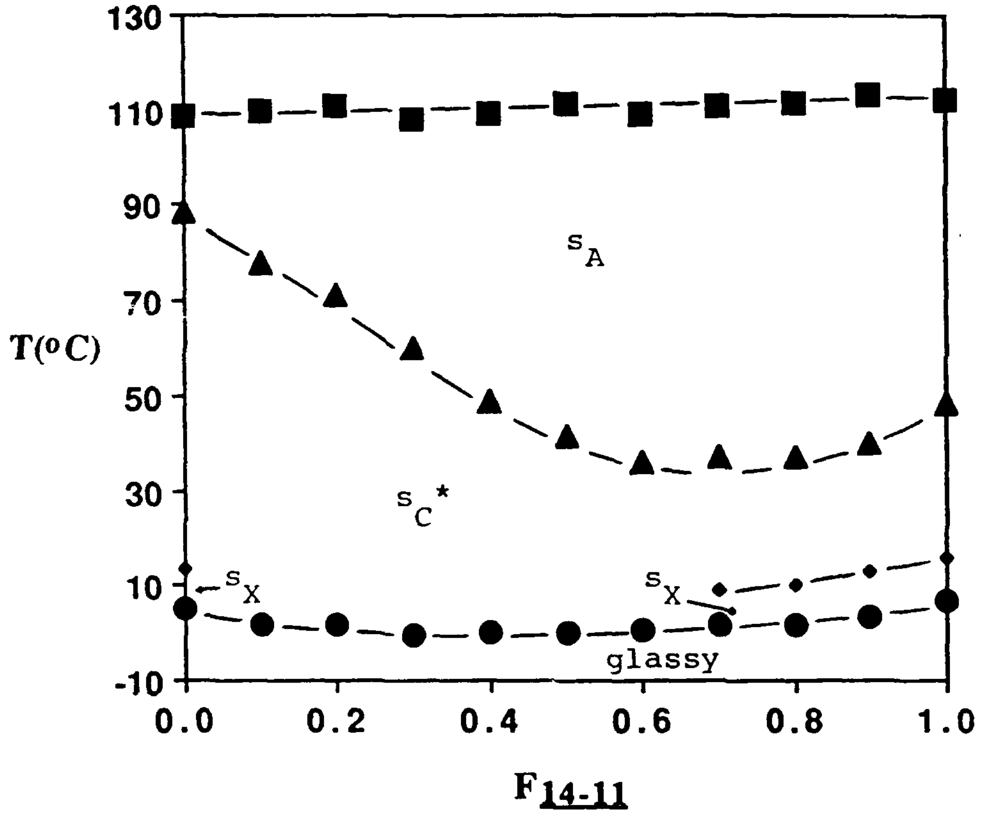


Figure 7b.

m



130
110
90
70
50
30
10
-10
T(°C)
S_A
S_C*
S_X
S_X
glassy
0.0
0.2
0.4
0.6
0.8
1.0
F14-11

Figure 7c.