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12 PERSONAL AUTHOR(S) V. Percec*, M. Lee and C. Ackerman

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22a NAME OF RESPONSIBLE INDIVIDUAL: Virgil Percec

22b TELEPHONE (Include Area Code): (216) 368-4242

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V. Percec, M. Lee and C. Ackermann
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

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V. Percec*, M. Lee and C. Ackerman
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

* To whom all correspondence should be addressed.

ABSTRACT

The synthesis and living cationic polymerization of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7) are presented. The influence of molecular weight on the mesomorphic behavior of poly(6-5) and poly(6-7) is discussed and compared to that of 5-[(4-cyano-4'-biphenyl)oxy]pentyl ethyl ether (8-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl ethyl ether (8-7) which are models of the monomeric structural units of poly(6-5) and poly(6-7). Both (8-5) and (8-7) exhibit a monotropic nematic mesophase. Poly(6-5) with degrees of polymerization equal and lower than six exhibit an enantiotropic nematic mesophase. Poly(6-5)s with higher degrees of polymerization display both smectic A and nematic enantiotropic mesophases. Poly(6-7) exhibits an enantiotropic smectic A mesophase over the entire range of molecular weights.

INTRODUCTION

There are several reports on the influence of molecular weight on the phase transitions of side chain liquid crystalline polymers.[1-10] However, to our knowledge the present series of publications is the first one which attempts to provide a comprehensive study on the influence of molecular weight on the mesomorphic transitions of a series of polymers with spacer lengths varying from two to eleven methylenic units, and narrow molecular weight distribution. The polymers investigated by us are obtained through the living cationic polymerization of ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers. In all cases, their phase behavior was compared to that of the model compound of their monomeric structural unit, i.e., ω-[(4-cyano-4'-biphenyl)oxy]alkyl ethyl ether. So far, we have investigated the poly (vinyl ether)s based on the following alkyl spacers: ethyl, propyl and butyl[11], hexyl and octyl[12], and undecanyl[13]. The trend observed on studying the influence of the molecular weight on the mesomorphic behavior was strongly dependent on the spacer length.

These living polymerization experiments also allowed us to investigate the influence of copolymer composition on the phase behavior, at a constant molecular weight of the copolymer[14,15]. The trend which was most frequently encountered and which is generally accepted consists of the enlargement of the temperature range of the mesophase with the increase of the polymer molecular weight.[1-13] This dependence was recently explained based on thermodynamic principles assuming that the phase behavior of the polymer is dictated by that of the monomeric structural unit[16,17]. When the mesophases exhibited by the monomeric structural unit and by the polymers with various molecular weights are identical, the overall dependence of phase transitions on molecular weight could be easily explained.[15,16] However, there are situations when the mesophases of the polymer are different at different molecular weights and are also different from those of the monomeric structural unit.[4,7,9,10,12,13] This last trend could not be yet explained. A collection of experimental data which can provide a complete understanding of the dependence of the mesomorphic behavior as a function of both spacer length and polymer molecular weight is thus required.

This paper will describe the synthesis, the living cationic polymerization, and the phase behavior of the resulting polymers of the penultimate two monomers from the series of ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers, i.e, 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7).

EXPERIMENTAL

Materials

4-Cyano-4'-hydroxybiphenyl of higher purity than 99.9% and 1,10-phenanthroline palladium (II) diacetate were synthesized as described previously.[13,18] Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum. 7-Bromoheptanol (95%, Aldrich), 5-bromovaleric acid (97%, Aldrich) and the other reagents were used as received.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. 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 or exothermic peaks respectively. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. First heating scans sometimes differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. Although in the present case both sets of data are identical, they will be reported. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Metter FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures [19,20]. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of monomers

Scheme I outlines the general methods used in the synthesis of monomers and model compounds.

Synthesis of 4-cyano-4'-(7-hydroxyheptan-1-yloxy)biphenyl (7-7)

4-Cyano-4'-hydroxybiphenyl (5.0 g, 0.0256 mol) and potassium carbonate (10.61 g, 0.0768 mol) were added to a mixture of acetone-DMSO (10:1) (110 ml). 7-Bromoheptan-1-ol (5 g, 0.0256 mol) was added to the resulting solution which was heated to reflux for 24 hr. After cooling, the mixture was poured into water and then filtered. The obtained solid was recrystallized from methanol and then benzene, to yield 5.5 g (69.4%) of white crystals. mp, 76.9°C, T_{n-i}, 103.2°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.10-1.95 (10 protons, $-(C\underline{H}_2)_5-$, m), 3.67 (2 protons, $-C\underline{H}_2OH$, t), 4.00 (2 protons, $PhOC\underline{H}_2-$, t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.52 (2 aromatic protons, m to alkoxy, d), 7.67 (4 aromatic protons, o and m to-CN, d of d).

Synthesis of 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7)

4-Cyano-4'-(7-hydroxyheptan-1-yloxy)biphenyl (3.0 g, 9.7 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.39 g, 0.97 mmol), n-butyl vinyl ether (52.9 ml) and dry chloroform (14 ml). The mixture was heated to 60°C for 6 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then recrystallized from n-hexane to yield 2.8 g (86.2%) of white crystals. Purity: 99.5% (HPLC). mp, 58.7°C (DSC). ^1H-NMR ($CDCl_3$, TMS, δ, ppm): 1.10-1.95 (10 protons, $-(C\underline{H}_2)_5-$, m), 3.69 (2 protons, $-C\underline{H}_2O-$, t), 4.01 (3 protons, $-OCH=C\underline{H}_2$ trans and $PhOC\underline{H}_2-$, m), 4.14 and 4.21 (1 proton, $-OCH=C\underline{H}_2$ cis, d), 6.53 (1 proton, $OC\underline{H}=CH_2$, q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to-CN, d of d).

Synthesis of 7-[(4-cyano-4'-biphenyl)oxy]heptyl ethyl ether (8-7)

4-Cyano-4'-(7-hydroxyheptan-1-yloxy)biphenyl (1.0 g, 3.23mmol) was added to a solution containing potassium t-butoxide (0.36 g, 3.23 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (20 ml). Diethyl sulfate (0.44 ml, 3.35 mmol) was added and the reaction mixture was refluxed for 4 hr under argon. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous KOH, washed with water, dried over magnesium sulfate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.62 g (52.8%) of white crystals. Purity: 99% (HPLC). mp, 56.0°C (DSC). ^1H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (3 protons, $-OCH_2C\underline{H}_3$, t), 1.26-1.90 (10 protons, $-(C\underline{H}_2)_5-$, m), 3.48 (4 protons, $C\underline{H}_2OC\underline{H}_2CH_3$, m), 4.02 (2 protons, $PhOC\underline{H}_2$, t), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.67 (4 aromatic protons, o and m to -CN, d of d).

Synthesis of 5-bromopentan-1-ol

A solution of 1-bromovaleric acid (14.5 g, 0.08 mol) in dry tetrahydrofuran (185 ml) was added dropwise into an ice cooled solution of borane/THF complex (1M) (150 ml). The reaction mixture was stirred at 0°C for 4 hr and at room temperature for other 12 hr, and the mixture was again cooled with ice. Water was added dropwise to the ice cooled reaction mixture. Afterwards, a saturated aqueous

K_2CO_3 solution was added to the reaction mixture which separates into two layers. The aqueous layer was extracted two times with tetrahydrofuran, the organic layers were combined, dried over anhydrous magnesium sulfate and the solvent was removed on a rotavapor to yield 12.5 g (95%) of liquid. Purity: 100% (IR and NMR). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.56 (4 protons, $BrCH_2C\underline{H}_2C\underline{H}_2$-, m), 1.90 (2 protons, -$C\underline{H}_2CH_2OH$, t), 3.43 (2 protons, $BrC\underline{H}_2$-, t), 3.66 (2 protons, -$C\underline{H}_2OH$, t).

<u>4-Cyano-4'-(5-hydroxypentan-1-yloxy)biphenyl</u> (7-5)

Sodium metal (1.220g, 0.05334 mol) was dissolved in 305 ml of absolute ethanol, then 4-cyano-4'-hydroxybiphenyl (10.43 g, 0.053 mol) was added, and the mixture was stirred for 45 minutes at room temperature. The ethanol was removed in a rotavapor to leave the salt. Dried N-methyl-pyrrolidinone (75 ml) and 5-bromo-1-pentanol (8.93g, 0.0535 mol) were added, and the mixture was heated at 110 ^{o}C for 30 hours. After cooling, the reaction mixture was poured into water and the precipitate was washed with dilute NaOH and water. It was purified by column chromatography (silica gel, ethyl acetate/hexanes 6/4 eluent), and then it was recrystallized from chloroform to yield 7.53g (50.1%) of white crystals. Purity: 99.9% (HPLC). mp, 95.4^{o}C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.64-1.86 (6 protons, -$(C\underline{H}_2)_3$-, m), 3.71 (2 protons, -$C\underline{H}_2OH$, t), 4.03 (2 protons, $PhOC\underline{H}_2$-, t), 6.99 (2 aromatic protons, o to alkoxy, d), 7.54 (2 aromatic protons, m to alkoxy, d), 7.66 (4 protons, o and m to -CN, d of d).

<u>5-[(4-Cyano-4'-biphenyl)oxy]pentyl vinyl ether</u> (6-5)

4-Cyano-4'-(4-hydroxypentan-1-yloxy)biphenyl (2.80g, 9.95 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.193g, 4.77 mmol), n-butyl vinyl ether (45 ml, 0.348 mol), and dry chloroform (15 ml). The mixture was heated to 60^{o}C for 18 hours. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, CH_2Cl_2 and then petroleum ether/ethyl ether=6/4 eluent) to yield 2.80g (91%) of white crystals. Purity: 99% (HPLC). mp, 52.4^{o}C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.57-1.93 (6 protons, -$(C\underline{H}_2)_3$-, m), 3.73 (2 protons, -$C\underline{H}_2OCH{=}CH_2$, t), 4.03 (3 protons, -$OCH{=}C\underline{H}_2$ trans and $PhOC\underline{H}_2$-, m), 4.15 and 4.22 (1 proton, $OC\underline{H}{=}CH_2$ cis, d), 6.49 (1 proton, $OC\underline{H}{=}CH_2$, q), 6.99 (2 aromatic protons, o to alkoxy, d), 7.53 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, m and o to -CN, d of d).

5-[(4-Cyano-4'-biphenyl)oxy]pentyl ethyl ether (8-5)

4-Cyano-4'-(5-hydroxypentan-1-yloxy)biphenyl (0.4974g, 1.77 mmol), potassium t-butoxide (0.2105g, 1.782 mmol), and a few crystals of 18-crown-6 were refluxed in dry THF (20 ml) for 75 minutes. Diethyl sulfate (0.3017 g, 1.918 mmol) (98%, Aldrich) was added, and the reaction mixture was refluxed for 4 hours. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aquous KOH, washed with water, dried over magnesium sulfate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.26g (48%) white crystals. Purity: 99.85% (HPLC). mp, 53.5°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.21 (3 protons, $0CH_2C\underline{H}_3$, t), 1.60-1.92 (6 protons, $-(CH_2)_3-$, m), 3.48 (4 protons, $C\underline{H}_2OC\underline{H}_2CH_3$, m), 4.02 (2 protons, $PhOC\underline{H}_2$, t), 6.99 (2 aromatic protons, o to alkoxy, d), 7.53 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d).

Cationic Polymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°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 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 solutions into methanol until GPC traces showed no traces of monomer. Tables I and II summarize the polymerization results. Although the polymer yields are lower than expected due to losses during the purification process, the conversions were almost quantitative in all cases.

RESULTS AND DISCUSSION

Figure 1a and b plots the dependences of Mn and Mw/Mn versus $[M]_o/[I]_o$ ratio for poly(6-5) and poly(6-7). Both sets of data demonstrate that within this range of molecular weights the polymerizations of 6-5 and 6-7 follow a living mechanism. The mechanism of this polymerization reaction is outlined in scheme II.

Figure 2 presents the heating and cooling DSC traces of 7-5, 7-7, 6-5, 6-7, 8-5 and 8-7. As we can observe from this figure, only the alcohol derivatives 7-7 and 7-5 display an enantiotropic nematic mesophase. Both the monomers (6-5 and 6-7) and the monomeric model compounds (8-5 and 8-7) exhibit a monotropic nematic mesophase. The phase transition temperatures and the corresponding thermodynamic parameters of these monomers and models are summarized in Table III.

The DSC traces obtained during the first and subsequent heating scans are identical both for the case of poly(6-5) and poly(6-7). The experimental data collected from both scans are reported in Tables I and II. However, only second heating and first cooling DSC scans will be presented in more detail. Figure 3 presents the DSC traces of poly (6-5). Poly(6-5)s with degrees of polymerization below 10 exhibit an enantiotropic nematic mesophase while 7-5, which represents the "polymer" with a degree of polymerization equal to one, displays only a monotropic nematic mesophase. Poly(6-5) with degrees of polymerization from 10 to 30 exhibit enantiotropic nematic and s_A mesophases.

The dependence of glass transition and of mesomorphic transition temperatures of poly(6-5) are plotted in Figure 4 as a function of the degree of polymerization. We can observe that the slope of the s_A-nematic versus molecular weight dependence is steeper than that of the nematic-isotropic versus molecular weight dependence. This trend provides a narrowing of the nematic range of poly(6-5) by increasing the degree of polymerization. Based on this trend, we can speculate that poly(6-5) with high molecular weights would have to exhibit only the s_A mesophase. So far, we do not have yet a polymer which does this.

The DSC traces collected from the second heating scan and first cooling scans of poly(6-7) are presented in Figure 5. The DSC traces of the first, second and subsequent heating scans are identical over the entire range of molecular weights. Poly(6-7) exhibits only an enantiotropic s_A mesophase. The monomeric model compound 7-7 exhibits a monotropic nematic mesophase. Therefore, we can speculate that the change from nematic to s_A occurs at a degree of polymerization between one and 3.3. The dependences of Tg, Ts_A-i and Ti-s_A versus molecular weight obtained from the first and second heating, and first cooling scans are summarized in Table II. The corresponding plots for the data obtained from the second heating and first cooling scans are presented in Figure 6. The plots from Figures 4 and 6 demonstrate the strong influence of the spacer length on the overal dependence of polymer phase transitions on molecular weight. This effect is particularly interesting for the case of poly(6-5) and poly(6-7) since these two polymers are based on odd spacers which have very similar lengths.

The conclusion derived from these two experiments is that so far there is no general trend which is followed when studying the influence of molecular weight on the phase transitions of side chain liquid crystalline polymers. The observed trend is most probably determined both by the overal entropic change of the system as discussed previously[16,17] and by the anisotropy of the polymer backbone within its various mesophases [1, 21-27].

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FIGURE AND SCHEME CAPTIONS

Scheme 1: Synthesis of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7).

Scheme 2: Cationic polymerization of 6-5 and 6-7.

Figure 1: The dependence of the number average molecular weight (Mn) and of the polydispersity (Mw/Mn) of poly(6-5) (a) and poly(6-7) (b) on the $[M]_o/[I]_o$ ratio.

Figuer 2a: Heating and cooling DSC scans of 7-5 (a, b), 6-5 (c, d) and 8-5 (e, f).

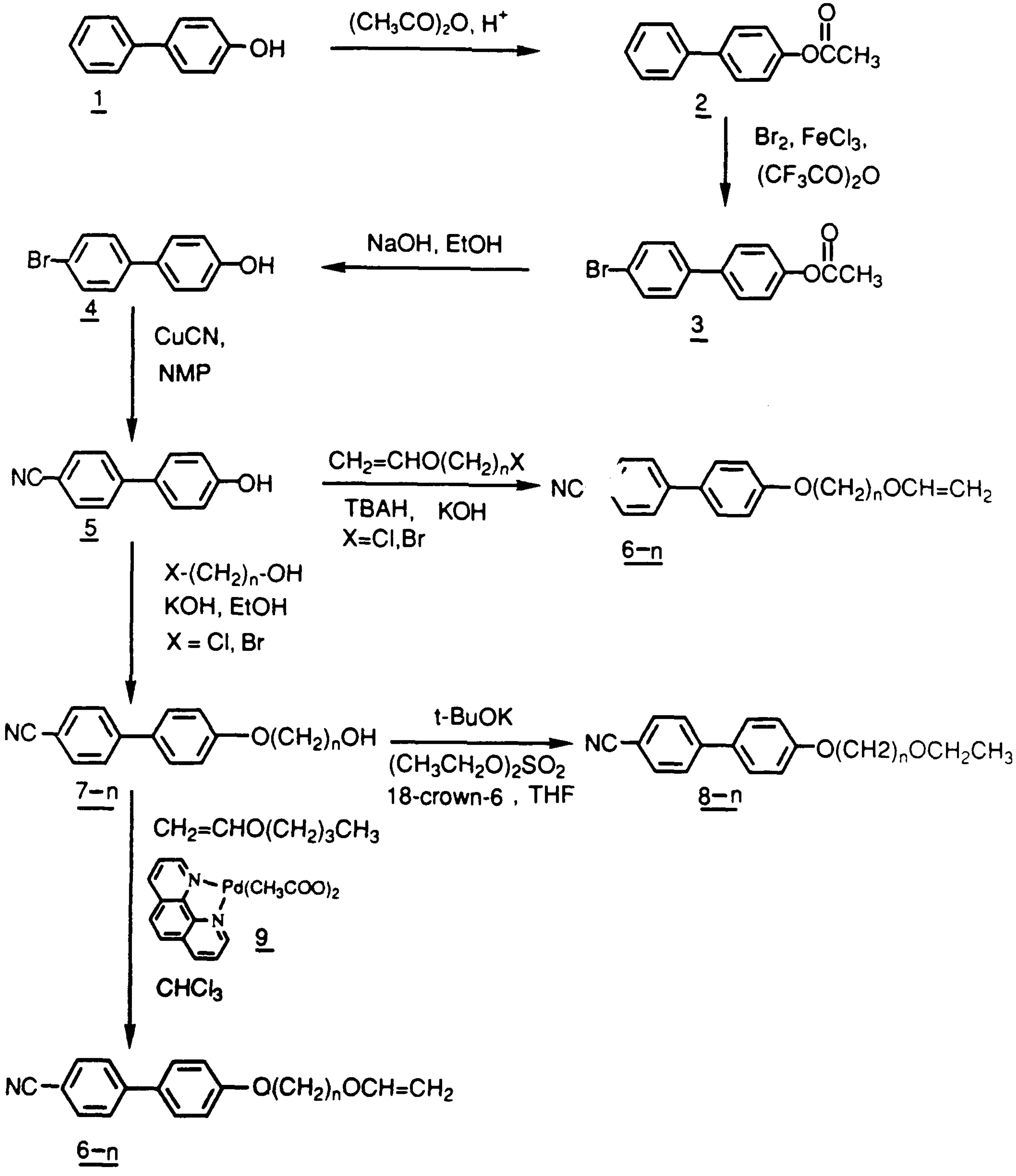
Figuer 2b: Heating and cooling DSC scans of 7-7 (a, b), 6-7 (c, d) and 8-7 (e, f).

Figure 3a: DSC traces displayed during the second heating scan (a) and first cooling scan (b) by poly(6-5) with different degrees of polymerization (DP). DP is *printed on the top of each DSC scan.*

Figure 4: The dependence of phase transition temperatures on the degree of polymerization of poly(6-5). a) data from second heating scan: O-Tg; □-Ts$_A$-n; Δ-Tn-i; b) data from first cooling scan: ●-Tg; ■-Tn-s$_A$; ▲-Ti-n.

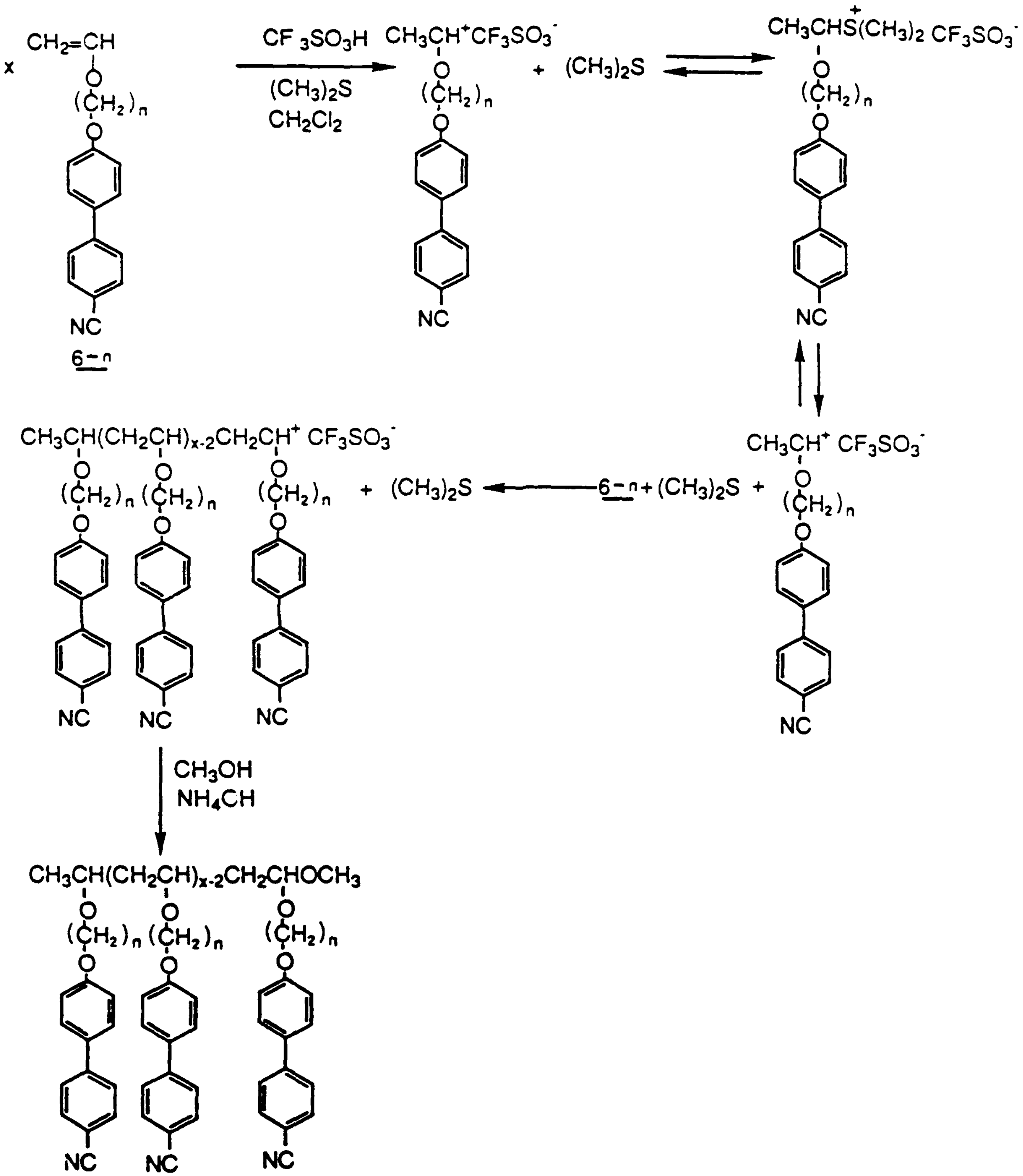
Figure 5: DSC traces displayed during the second heating scan (a) and first cooling scan (b) by poly(6-7) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 6: The dependence of phase transition temperatures on the degree of polymerization of poly(6-7). a) data from second heating scan: O-Tg; □-Ts$_A$-i; b) data from first cooling scan: ● -Tg; ■-Ti-s$_A$.



OH
1
$(CH_3CO)_2O$, H^+
$OCCH_3$
O
2
Br_2, $FeCl_3$,
$(CF_3CO)_2O$
Br
3
NaOH, EtOH
4
CuCN,
NMP
NC
5
$CH_2{=}CHO(CH_2)_nX$
TBAH, KOH
X=Cl,Br
$O(CH_2)_nOCH{=}CH_2$
6-n
$X\text{-}(CH_2)_n\text{-}OH$
KOH, EtOH
X = Cl, Br
$O(CH_2)_nOH$
7-n
t-BuOK
$(CH_3CH_2O)_2SO_2$
18-crown-6 , THF
$O(CH2)_nOCH_2CH_3$
8-n
$CH_2{=}CHO(CH_2)_3CH_3$
N
$Pd(CH_3COO)_2$
9
$CHCl_3$
6-n

Scheme I



x
CH2=CH
O
(CH2)n
O
NC
6-n
CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+CF3SO3-
O
(CH2)n
O
NC
+ (CH3)2S
CH3CHS+(CH3)2 CF3SO3-
O
(CH2)n
O
NC
CH3CH(CH2CH)x-2CH2CH+ CF3SO3-
O
(CH2)n
O
NC
+ (CH3)2S
6-n + (CH3)2S +
CH3CH+ CF3SO3-
O
(CH2)n
O
NC
CH3OH
NH4CH
CH3CH(CH2CH)x-2CH2CHOCH3
O
(CH2)n
O
NC

Scheme II

Table I. Cationic Polymerization of 5-[4-Cyano-4'-biphenyl)oxy]pentyl Vinyl Ether (6-5) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o$=0.325; $[(CH_3)_2S]_o/[I]_o$=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.	$[M]_o/[I]_o$	Polymer yield(%)	GPC			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
			Mnx10^{-3}	Mw/Mn	D P	heating	cooling
1	4	75.8	1.38	1.10	4.5	g 19.2 n 95.2 (0.11) i g 18.7 n 94.3 (0.15) i	i 91.1 (0.13) n 13.2 g
2	6	79.2	1.85	1.11	6.0	g 24.7 n 98.3 (0.14) i g 22.2 n 97.7 (0.14) i	i 93.2 (0.15) n 16.5 g
3	9	82.3	3.05	1.21	9.9	g 29.8 s_A 80.1 n 100.8 (0.11)* i g 27.5 s_A 78.2 n 100.8 (0.12)* i	i 96.5 (0.14)* n 76.0 s_A 21.4 g
4	13	87.1	3.94	1.13	12.8	g 33.8 s_A 90.1 n 104.4 (0.14)* i g 33.2 s_A 89.1 n 103.2 (0.13)* i	i 101.4 (0.14)* n 84.2 s_A 28.2 g
5	18	82.3	5.19	1.15	16.9	g 35.4 s_A 95.0 n 112.3 (0.12)* i g 33.8 s_A 95.6 n 112.0 (0.13)* i	i 107.1 (0.10)* n 93.3 s_A 30.4 g
6	23	85.0	7.50	1.21	24.4	g 38.2 s_A 99.1 n 113.6 (0.14)* i g 36.8 s_A 102.7 n 113.8 (0.14)* i	i 109.6 (0.11)* n 96.3 s_A 35.0 g
7	30	88.0	9.49	1.12	30.9	g 39.3 s_A 104.9 n 115.4 (0.12)* i g 37.5 s_A 104.4 n 115.5 (0.10)* i	i 111.7 (0.11)* n 101.8 s_A 34.2 g

* overlapped peaks

Table II. Cationic Polymerization of 7-[4-Cyano-4'-biphenyl)oxy]heptyl Vinyl Ether (6-7) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o=0.298$; $[(CH_3)_2S]_o/[I]_o=10$; 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	$[M]_o/[I]_o$	Polymer	G P C			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
No.		yield(%)	$Mn \times 10^{-3}$	Mw/Mn	D P	heating	cooling
1	2	44.2	1.10	1.12	3.3	g 5.3 s_A 89.5 (0.43) i g 5.1 s_A 89.7 (0.44) i	i 85.8 (0.43) s_A 0.1 g
2	4	31.0	1.69	1.18	5.1	g 10.8 s_A 108.0 (0.42) i g 10.8 s_A 108.8 (0.80) i	i 104.6 (0.40) s_A 7.1 g
3	6	55.9	2.32	1.14	6.9	g 13.2 s_A 116.0 (0.39) i g 13.0 s_A 116.0 (0.40) i	i 111.3 (0.39) s_A 8.6 g
4	8	61.6	2.43	1.09	7.3	g 14.3 s_A 120.1(0.39) i g 14.1 s_A 120.6 (0.39) i	i 115.6 (0.39) s_A 9.2 g
5	10	68.0	2.85	1.05	8.5	g 15.6 s_A 123.1 (0.36) i g 15.6 s_A 123.5 (0.74) i	i 117.7 (0.39) s_A 10.6 g
6	13	63.3	4.36	1.16	13.0	g 17.6 s_A 131.3 (0.36) i g 17.6 s_A 132.0 (0.37) i	i 127.7 (0.36) s_A 12.4 g
7	18	65.3	5.41	1.34	16.1	g 19.5 s_A 133.0 (0.38) i g 18.8 s_A 133.5 (0.71)	i 128.7 (0.36) s_A 14.7 g
8	23	69.3	7.90	1.20	23.6	g 20.4 s_A 137.3 (0.38) i g 20.1 s_A 137.6 (0.35) i	i 132.2 (0.36) s_A 14.9 g
9	30	74.3	8.84	1.15	26.4	g 21.2 s_A 140.3 (0.34) i g 20.8 s_A 140.8 (0.35) i	i 134.0 (0.34) s_A 15.0 g

Table III. Thermal Characterization of 4-Cyano-4'-(ω-hydroxyalkan-1-yloxy)biphenyls (7-5) and (7-7), ω-[(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ethers (6-5) and (6-7), and of ω-[(4-Cyano-4'-biphenyl)oxy]alkyl Ethyl Ethers (8-5) and (8-7).

Compound	phase transitions (0°C) and corresponding enthalpy changes (kcal/mol)	
	heating	cooling
7-5	k 95.5 (7.69) n 108.1 (0.18) i	i 104.4 (0.25) n 28.6 (3.68) k
6-5	k 52.4 (7.94) i	i 38.6 (0.086) n 9.8 (6.20) k
8-5	k 53.5 (6.96) i	i 34.5 (0.062) n 27.6 (5.79) k
7-7	k 95.5 (9.67) n 108.1 (0.18) i	i 100.2 (0.27) n 33.0 (3.96) k
6-7	k 58.7 (9.9) i [n 54.5 (0.21) i]*	i 50.6 (0.17) n 29.4 (7.67) k
8-7	k 56.0 (9.7) i [n 55.4 (0.21)]*	i 50.9 (0.15) n 1.6 (5.56) k

*[ ] virtual data

* overlapped peaks

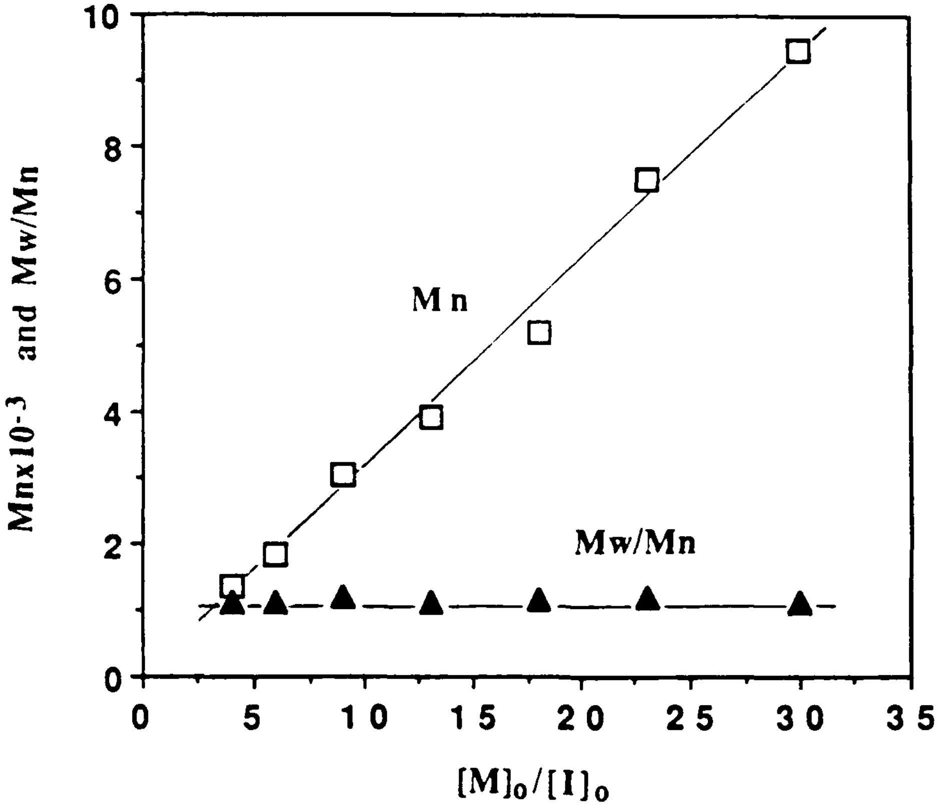


Figure 1a

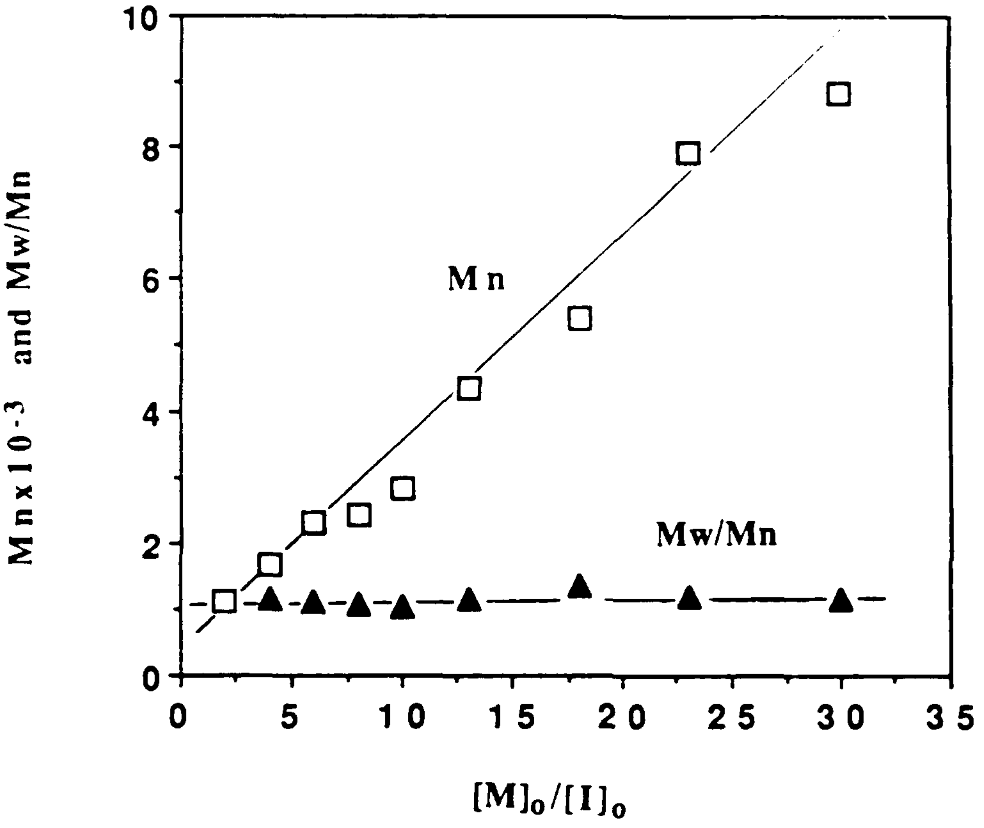


Figure 1b

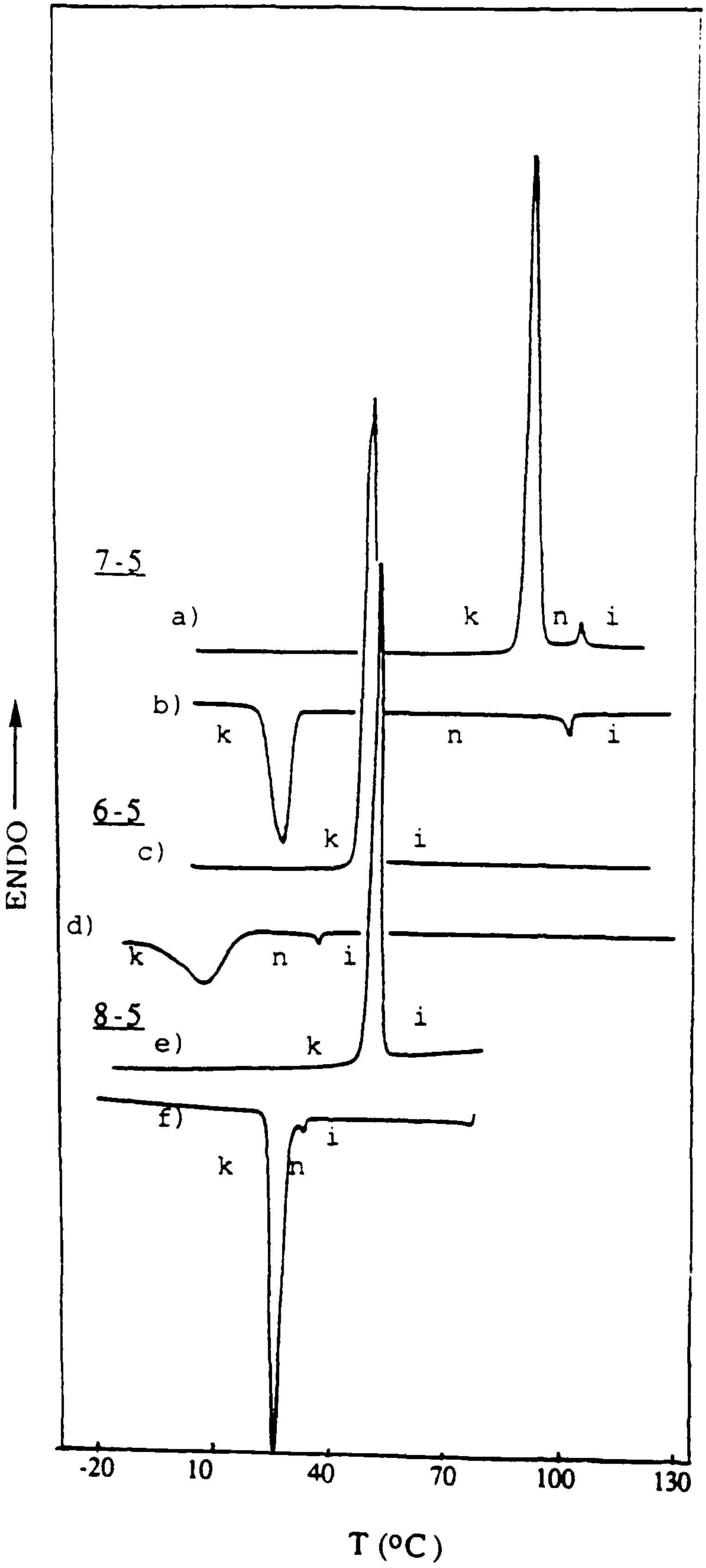


Figure 2a

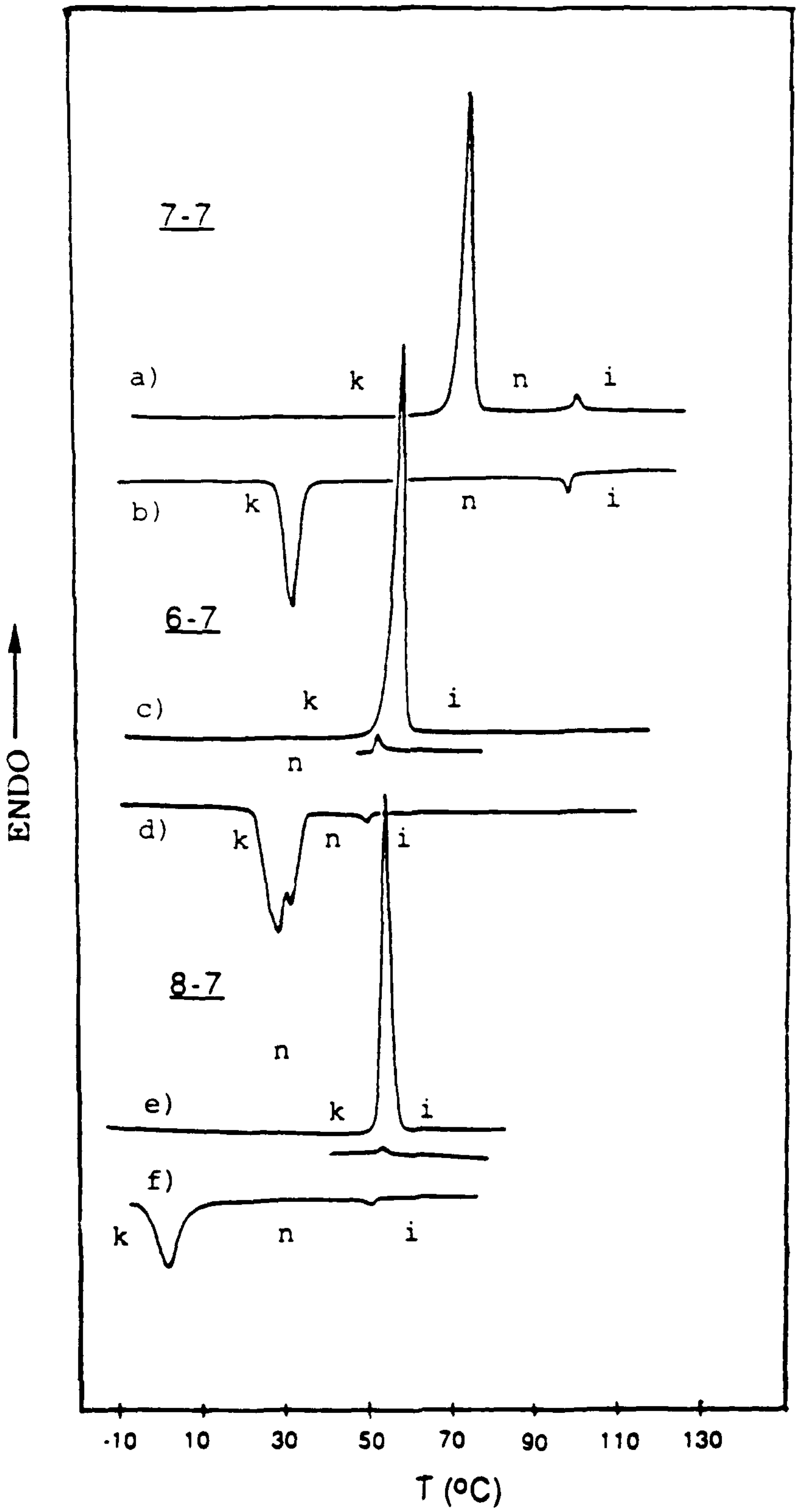

7-7
a)
k
n
i
b)
k
n
i
6-7
c)
k
i
n
d)
k
n
i
8-7
n
e)
k
i
f)
k
n
i
ENDO
-10
10
30
50
70
90
110
130
T (°C)

Figure 2b

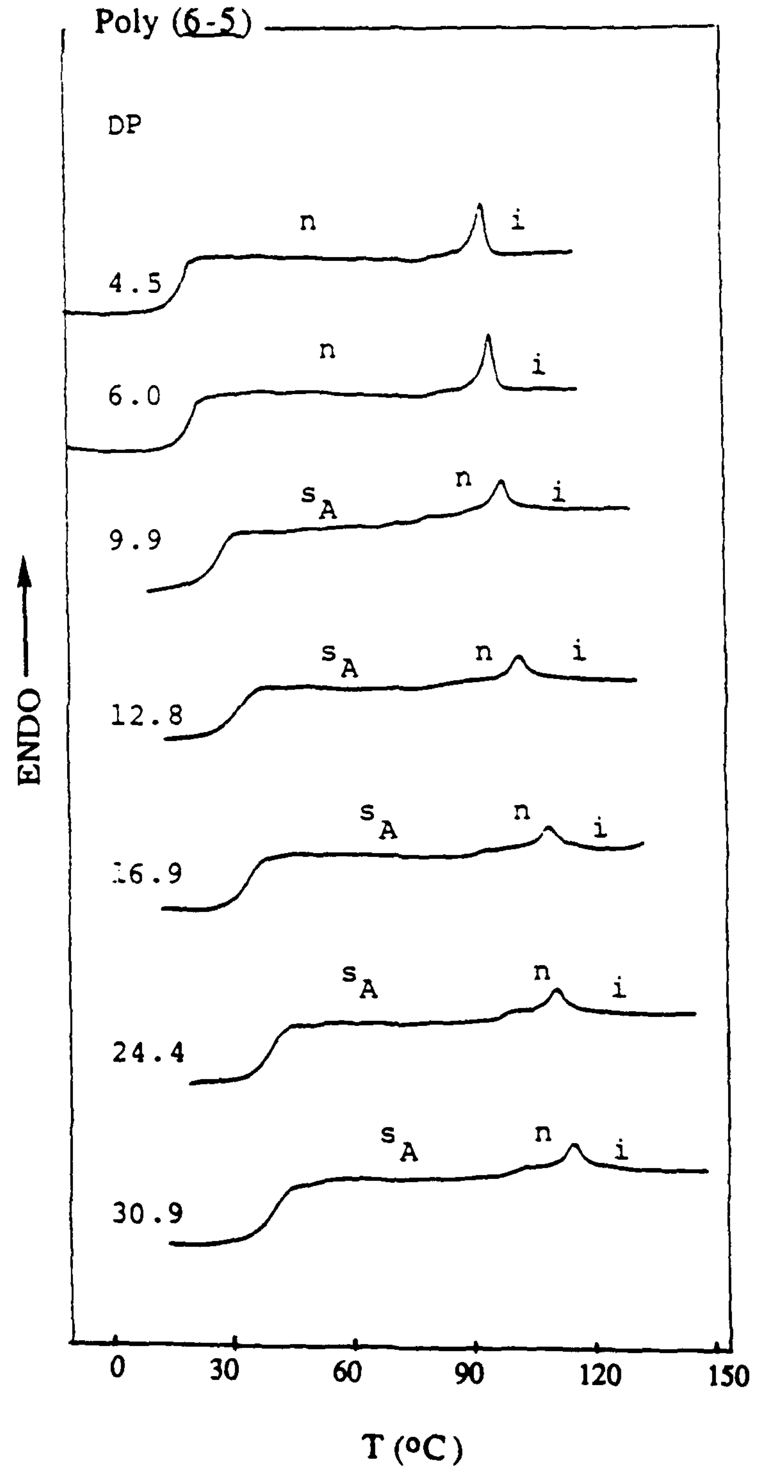


Figure 3a

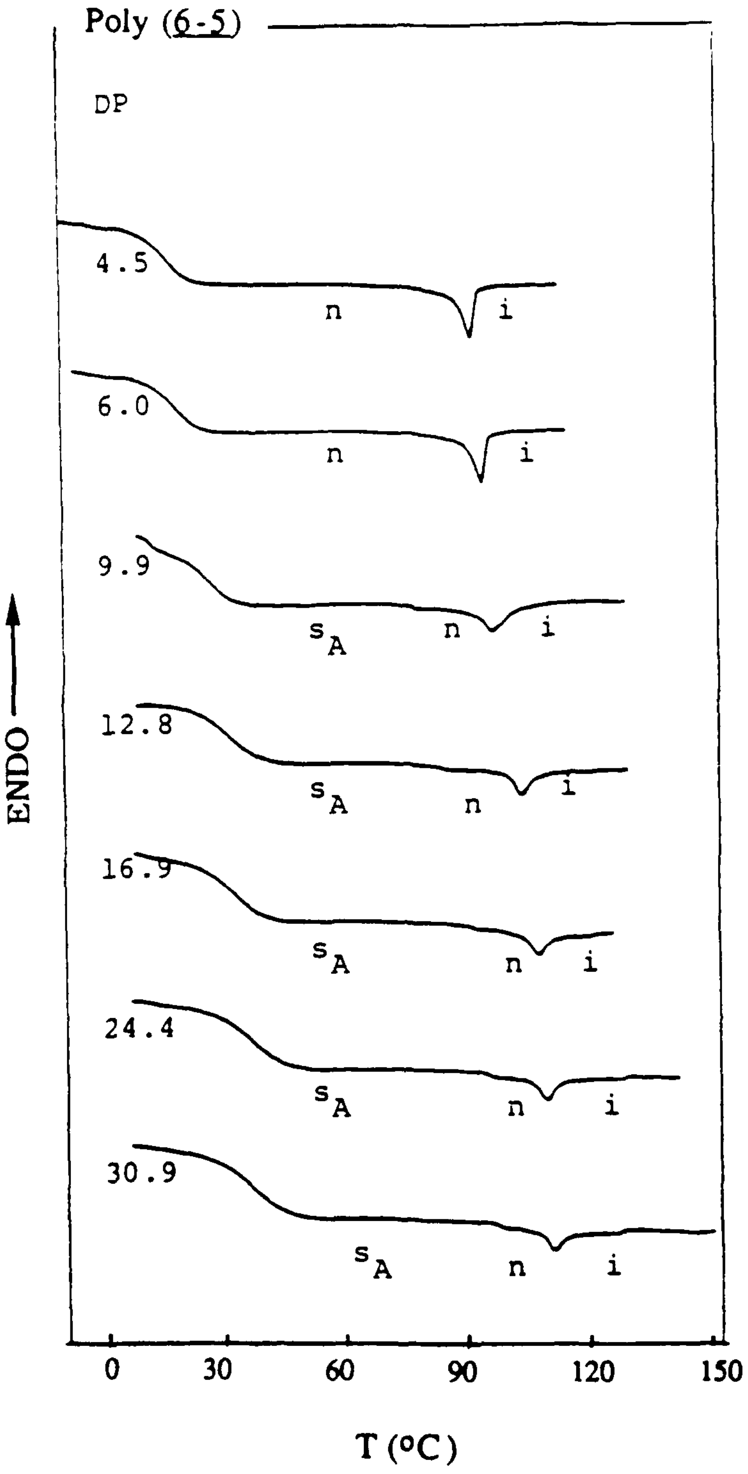

Poly (6-5)
DP
4.5
n
i
6.0
n
i
9.9
s_A
n
i
12.8
s_A
n
i
16.9
s_A
n
i
24.4
s_A
n
i
30.9
s_A
n
i
ENDO
0
30
60
90
120
150
T (°C)

Figure 3b

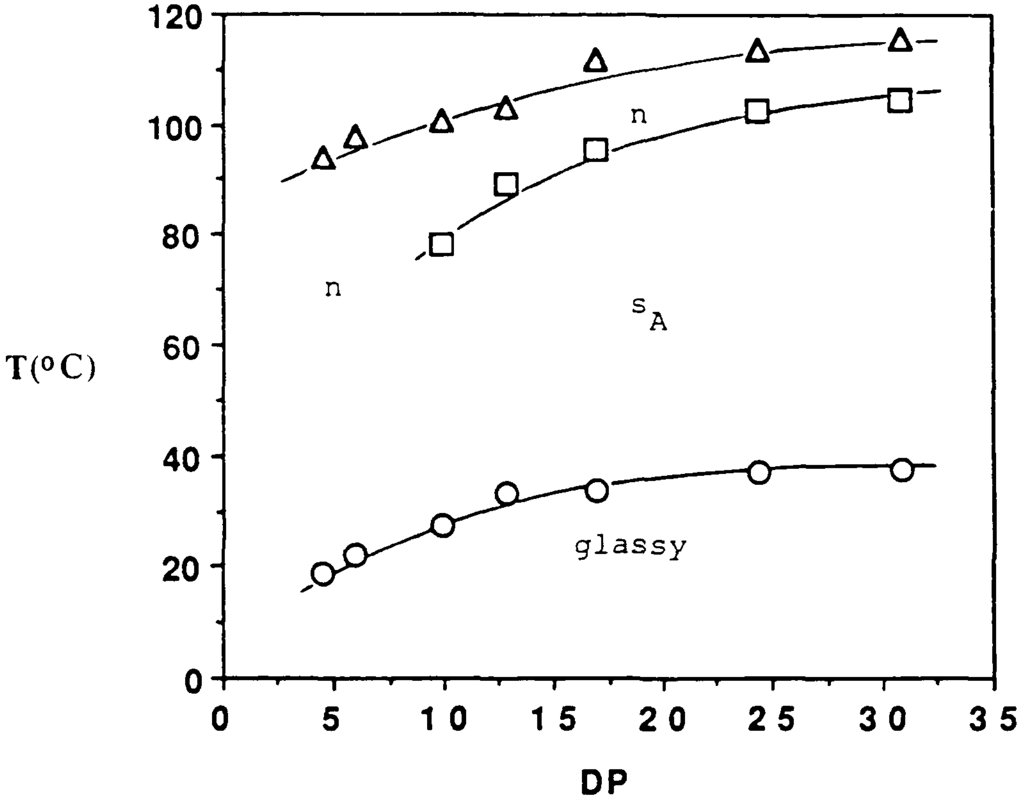


Figure 4a

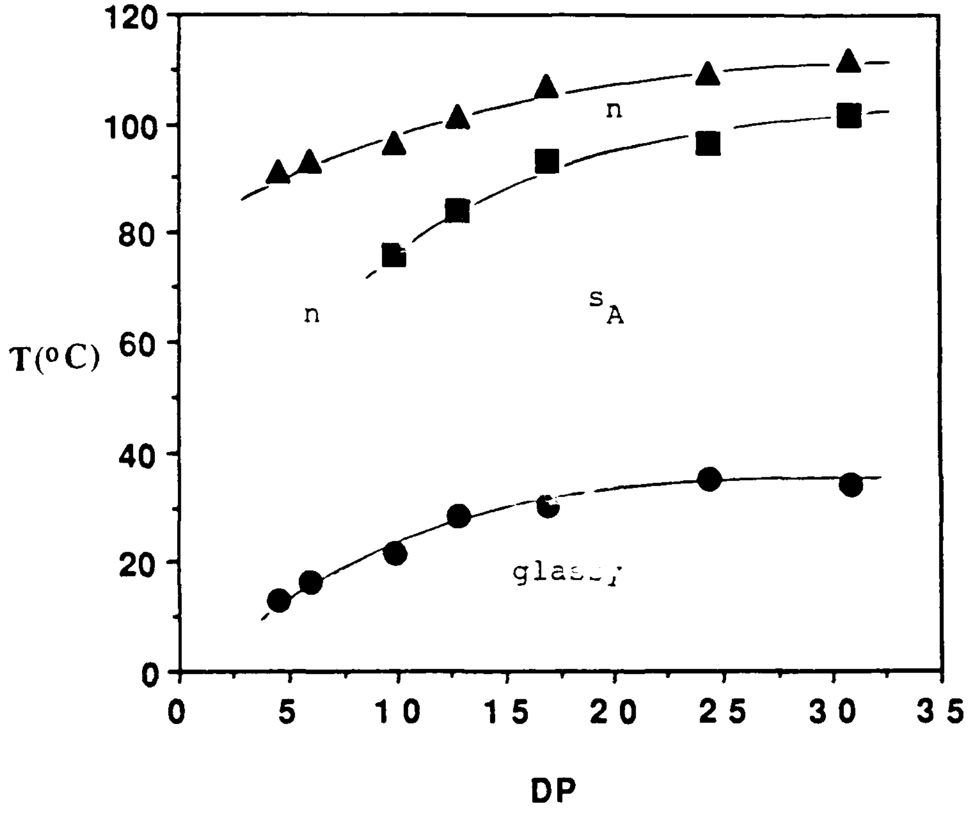
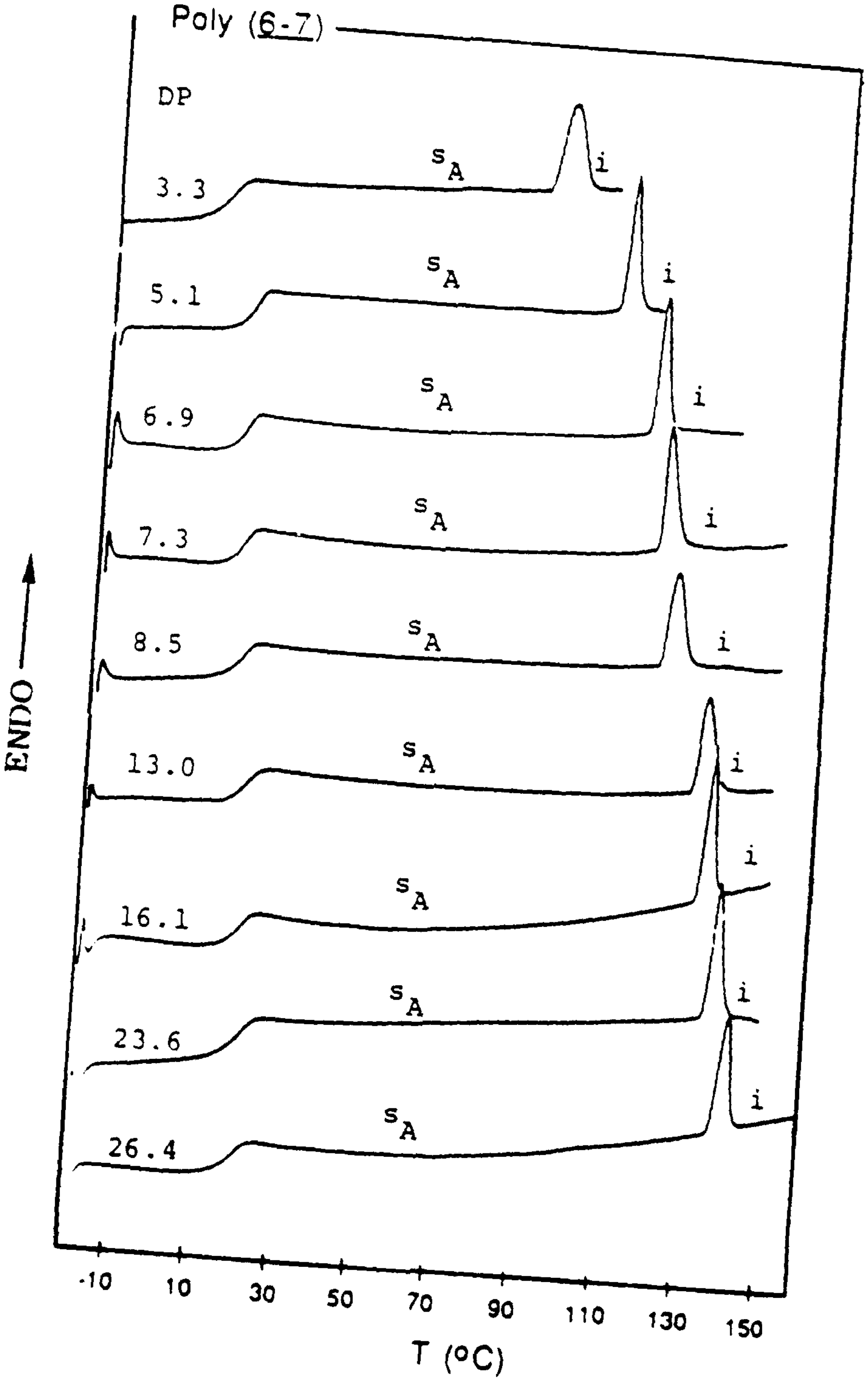


Figure 4b



Poly (6-7)
DP
3.3
5.1
6.9
7.3
8.5
13.0
16.1
23.6
26.4
s_A
i
ENDO
-10
10
30
50
70
90
110
130
150
T (°C)

Figure 5a

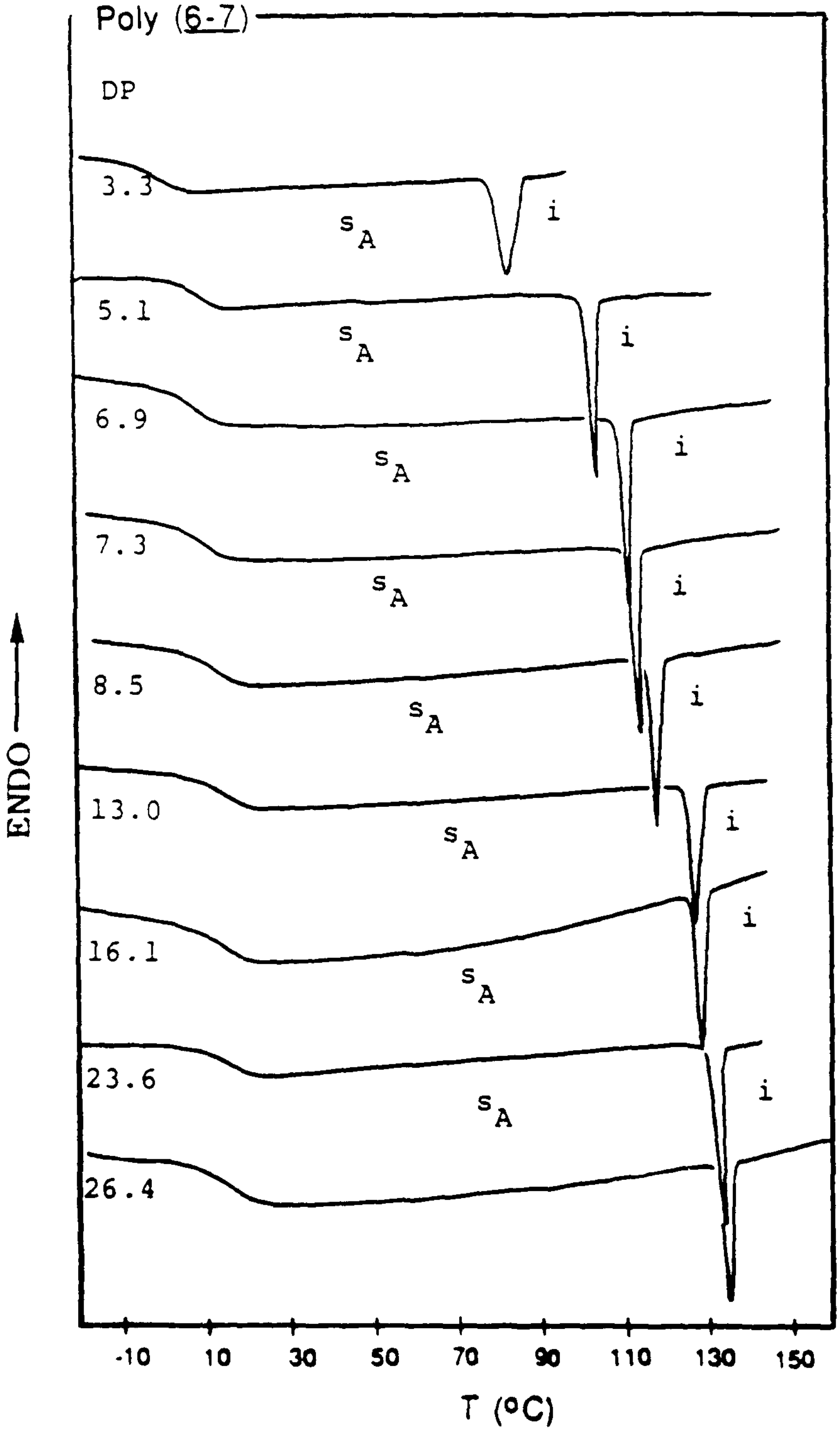

Poly (6-7)
DP
3.3
5.1
6.9
7.3
8.5
13.0
16.1
23.6
26.4
s_A
i
ENDO
-10
10
30
50
70
90
110
130
150
T (°C)

Figure 5b

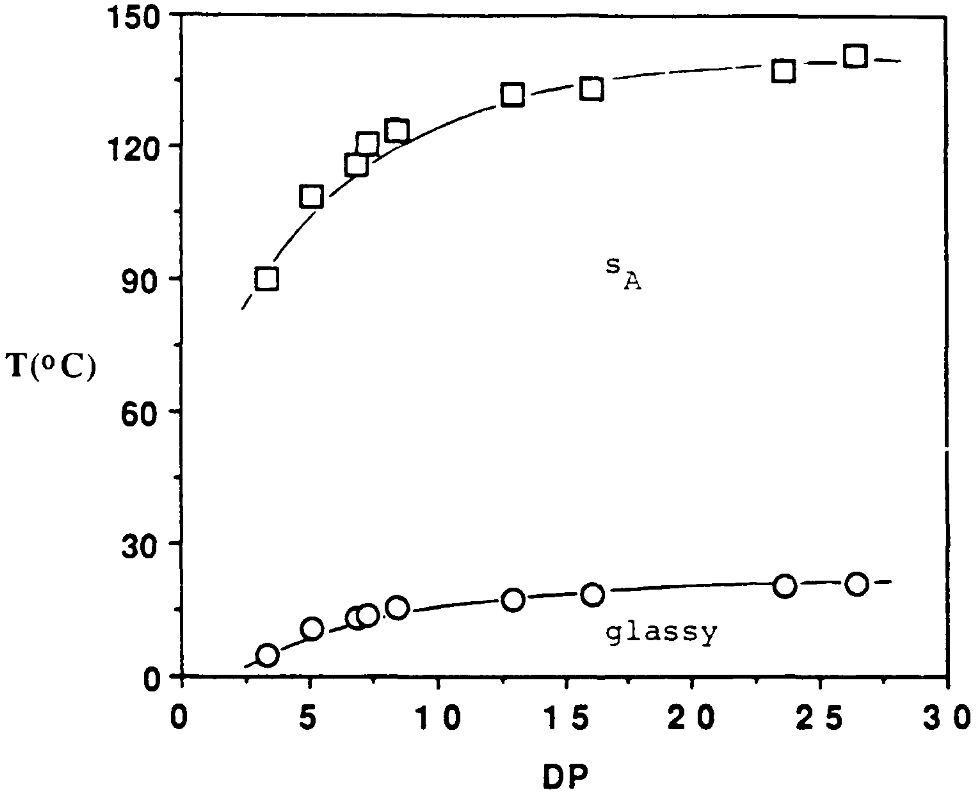


Figure 6a

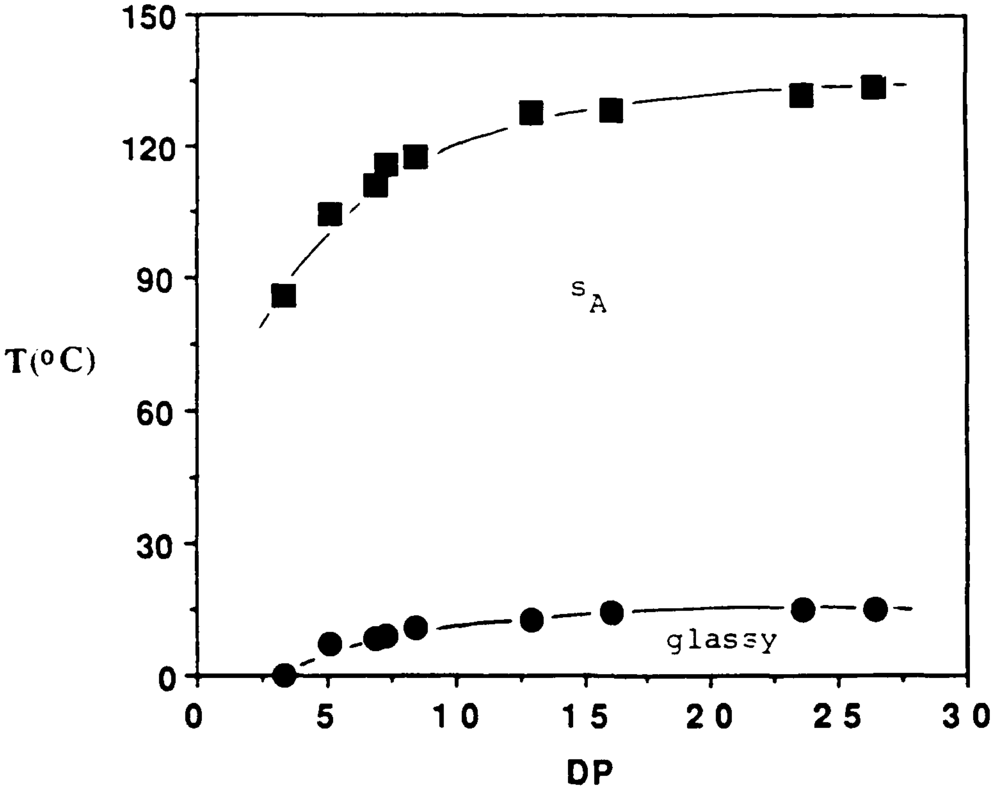


Figure 6b