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Influence of Molecular Weight on The Phase Behavior of Poly( $\omega$ -[(4-cyano-4'-  
biphenyl)oxy]alkyl Vinyl Ether]s with Ethyl, Propyl and Butyl Alkyl Groups

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

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V. Percec\* and M. Lee  
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 2-[4-cyano-4'-biphenyl]oxy]ethyl vinyl ether (6-2), 3-[4-cyano-4'-biphenyl]oxy]propyl vinyl ether (6-3) and 4-[4-cyano-4'-biphenyl]oxy]butyl vinyl ether (6-4) are described. The mesomorphic behavior of poly(6-2), poly(6-3), poly(6-4) with different degrees of polymerization and narrow molecular weight distribution was compared to that of 6-2, 6-3 and 6-4 and of 2-[(4-cyano-4'-biphenyl)oxy]ethyl ethyl ether (8-2), 3-[(4-cyano-4'-biphenyl)oxy]propyl ethyl ether (8-3) and 4-[4-cyano-4'-biphenyl]oxy]butyl ethyl ether (8-4) which are model compounds of the monomeric structural units of poly(6-2), poly(6-3) and poly(6-4). In the first heating scan, all three polymers exhibit an x (unidentified) mesophase which overlaps the glass transition temperature, and an enantiotropic nematic mesophase. In the second and subsequent heating and cooling scans, poly(6-3) and poly(6-4) display only the enantiotropic nematic mesophase. Both in the first and subsequent scans only poly(6-2) with degrees of polymerization lower than four exhibit an enantiotropic nematic mesophase.

### INTRODUCTION

Previous publications from this series and from other laboratories demonstrated that group transfer polymerization of mesogenic methacrylates<sup>1</sup> and cationic polymerization of mesogenic vinyl ethers<sup>2-8</sup> can be performed under living polymerization conditions. Our investigations on the polymerization of mesogenic vinyl ethers are performed with the initiating system  $\text{CF}_3\text{SO}_3\text{H}/(\text{CH}_3)_2\text{S}$  which induces a living polymerization at 0°C in methylene chloride<sup>9</sup>. Presently, we are performing experiments which provide a complete understanding of the influence of molecular weight on the phase behavior of poly( $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether)s with flexible spacers containing from two to eleven methylene units.

This paper will describe our results on the influence of molecular weight on the behavior of poly{2-[4-cyano-4'-biphenyl]oxy]ethyl vinyl ether} (6-2), poly{3-[4-cyano-4'-biphenyl]oxy]propyl vinyl ether} (6-3) and poly{4-[4-cyano-4'-biphenyl]oxy]butyl vinyl ether} (6-4). Their phase behavior will be compared to that of the model compounds of their monomeric structural units.

## EXPERIMENTAL

Scheme I outlines the synthesis of monomers and model compounds.

### Materials

3-Bromo-1-propanol (95%, Aldrich) and 4-chloro-1-butanol (94%, Lancaster Synthesis) were used as received. 2-[4-Cyano-4'-biphenyl]oxy]ethyl vinyl ether (6-2)<sup>5</sup>, 4-cyano-4'-hydroxybiphenyl<sup>3,10</sup> of purities higher than 99.5% and 1,10 phenanthroline palladium (II) diacetate<sup>10</sup> were synthesized as described previously. Methyl sulfide 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 H<sub>2</sub>SO<sub>4</sub>, 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.

### Techniques

<sup>1</sup>H-NMR (200MHz) 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 (T<sub>g</sub>) 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. In the present case both sets of data will be reported. 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 transitions and to analyze the anisotropic textures. 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<sup>4</sup> and 500 Å with CHCl<sub>3</sub> 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 4-cyano-4'-(2-hydroxyethan-1-yloxy)biphenyl (7-2)

2-[(4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (0.5 g, 1.885 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.038 g, 0.094 mmol) and methanol (15 ml). The mixture was refluxed for 12 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was recrystallized from a 1:9 mixture of acetone and n-hexane to yield 0.38 g of white crystals (84.2%) which were further purified by column chromatography (silica gel,  $\text{CHCl}_3$  eluent). mp, 128.7°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm), 4.02 (2 protons,  $-\text{CH}_2\text{OH}$ , t), 4.16 (2 protons,  $\text{PhOCH}_2-$ , t), 7.06 (2 aromatic protons, o to alkoxy, d), 7.53 (2 aromatic protons, m to alkoxy, d), 7.67 (4 aromatic protons, o and m to  $-\text{CN}$ , d of d).

Synthesis of 2-[(4-cyano-4'-biphenyl)oxy]ethyl ethyl ether (8-2)

4-Cyano-4'-(2-hydroxyethan-1-yloxy)biphenyl (0.35 g, 1.463 mmol) was added to a solution containing potassium t-butoxide (0.164 g, 1.463 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (7 ml). Diethyl sulfate (0.21 ml, 1.61 mmol) was added, and the reaction mixture was refluxed for 5 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 on a rotavapor. The resulting product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$  eluent) and then was recrystallized from methanol to yield 0.17 g (42.7%) of white crystals. Purity: 99% (HPLC). mp, 68.9°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 1.26 (3 protons,  $-\text{CH}_2\text{CH}_3$ , t), 3.65 (2 protons,  $-\text{CH}_2\text{CH}_3$ , q), 3.83 (2 protons,  $-\text{CH}_2\text{OCH}_2\text{CH}_3$ , t), 4.18 (2 protons,  $\text{PhOCH}_2-$ , t), 7.05 (2 aromatic protons, o to alkoxy, d), 7.52 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to  $-\text{CN}$ , d of d).

Synthesis of 4-cyano-4'-(3-hydroxypropan-1-yloxy)biphenyl (7-3)

4-Cyano-4'-hydroxybiphenyl (1.47 g, 7.53 mmol), sodium hydride (0.3 g, 7.59 mmol) and tetrabutylammonium hydrogensulfate (0.24 g, 0.71 mmol) were added to a mixture of toluene-DMSO (5:1) (22.1 ml). 3-Bromo-1-propanol (1.05 g, 7.55 mmol) was added to the resulting solution which was heated to 80°C for 28

hr. After cooling, the mixture was poured into water and then filtered. The obtained solid was dissolved in ethyl ether and then extracted with dilute aqueous NaOH, washed with water, dried over magnesium sulfate and then the solvent was removed in a rotavapor. The resulting product was recrystallized from methanol and then purified by column chromatography (silica gel, 1:1 ethyl acetate-hexane eluent) to yield 1.52 g (83%) of white crystals. mp, 114.6°C (DSC). Purity: 99.6% (HPLC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm); 2.09 (2 protons,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , m), 3.90 (2 protons,  $-\text{CH}_2\text{OH}$ , t), 4.19 (2 protons,  $\text{PhOCH}_2-$ , t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.54 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to  $-\text{CN}$ , d of d).

Synthesis of 3-[4-cyano-4'-biphenyl]oxypropyl vinyl ether (6-3)

4-Cyano-4'-(3-hydroxypropan-1-yloxy)biphenyl (2.0 g, 7.9 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.31 g, 0.79 mmol), *n*-butyl vinyl ether (43.1 ml) and dry chloroform (10.78 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,  $\text{CH}_2\text{Cl}_2$  eluent) and then was recrystallized from *n*-hexane to yield 1.83 g (83.0%) of white crystals. Purity: 99.9% (HPLC). mp, 78.7°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 2.18 (2 protons,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , m), 3.90 (2 protons,  $-\text{CH}_2\text{O}-$ , t), 4.01 and 4.05 (1 proton,  $-\text{OCH}=\text{CH}_2$  trans, d), 4.14 (2 protons,  $-\text{CH}_2\text{OPh}$ , t), 4.19 and 4.27 (1 proton,  $-\text{OCH}=\text{CH}_2$  cis, d), 6.50 (1 proton,  $-\text{OCH}=\text{CH}_2$ , q), 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  $-\text{CN}$ , d of d).

Synthesis of 3-[4-cyano-4'-biphenyl]oxypropyl ethyl ether (8-3)

4-Cyano-4'-(3-hydroxypropan-1-yloxy)biphenyl (0.5 g, 1.975 mmol) was added to a solution containing potassium *t*-butoxide (0.22 g, 1.975 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (10 ml). Diethyl sulfate (0.284 ml, 2.17 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,  $\text{CH}_2\text{Cl}_2$  eluent) and then was recrystallized from methanol to yield 0.34 g (58.0%) of white

crystals. Purity: 99.0% (HPLC). mp, 64.9°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.21 (2 protons, -OCH<sub>2</sub>CH<sub>3</sub>, t), 2.08 (2 protons, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, m), 3.50 (2 protons, -OCH<sub>2</sub>CH<sub>3</sub>, q), 3.62 (2 protons, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, t), 4.13 (2 protons, PhOCH<sub>2</sub>-, t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.52 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d).

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

4-Cyano-4'-hydroxybiphenyl (4.2 g, .0215 mol) and potassium carbonate (39 g, 0.3 mol) were added to a mixture of acetone-DMSO (10:1) (110 ml). 4-Chloro-1-butanol (11.67 g, 0.1075 mol) was added to the resulting reaction mixture which was heated to reflux for 3 days. After cooling, the mixture was poured into water and the separated solid was filtered. The obtained solid was recrystallized first from methanol and then from toluene to yield 2.82 g (49.1%) of white crystals. mp, 126.4 °C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.55-2.15 (4 protons, -(CH<sub>2</sub>)<sub>2</sub>-, m), 3.75 (2 protons, -CH<sub>2</sub>OH, t), 4.07 (2 protons, PhOCH<sub>2</sub>-, t), 7.02 (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 4-[4-Cyano-4'-biphenyl]oxy|butyl vinyl ether (6-4)

4-Cyano-4'-(4-hydroxybutan-1-yloxy)biphenyl (2.0 g, 7.48 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.29 g, 0.75 mmol), n-butyl vinyl ether (40.85 ml) and dry chloroform (10.2 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, the product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> eluent) and then was recrystallized first from ethanol and then from n-hexane to yield 1.82 g (82.9%) of white crystals. Purity: 99.8% (HPLC). mp, 73.3°C. T<sub>n-i</sub>, 77.1°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.91 (4 protons, -(CH<sub>2</sub>)<sub>2</sub>-, m), 3.78 (2 protons, -CH<sub>2</sub>OCH=CH<sub>2</sub>, t), 4.06 (3 protons, -OCH=CH<sub>2</sub> trans and PhOCH<sub>2</sub>-, m), 4.16 and 4.23 (1 proton, OCH=CH<sub>2</sub> cis, d), 6.50 (1 proton, OCH=CH<sub>2</sub>, q), 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 4-[4-cyano-4'-biphenyl]oxy|butyl ethyl ether (8-4)

4-Cyano-4'-(4-hydroxybutan-1-yloxy)biphenyl (0.5 g, 1.67 mmol) was added to a solution containing potassium t-butoxide (0.20 g, 1.67 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (10 ml). Diethyl sulfate (0.25 ml,

1.9 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<sub>2</sub>Cl<sub>2</sub> eluent) and then was recrystallized from methanol to yield 0.32 g (57.9%) of white crystals. Purity: 99% (HPLC). mp, 64.7°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.22 (3 protons, -OCH<sub>2</sub>CH<sub>3</sub>, t), 1.65-2.11 (4 protons, -(CH<sub>2</sub>)<sub>2</sub>-, m), 3.50 (4 protons, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, m), 4.05 (2 protons, PhOCH<sub>2</sub>-, t), 7.02 (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).

#### 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 ( $[M]_0/[I]_0$ ) 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

Polymerization results are reported in Tables I, II and III. All polymers have number average molecular weights which show a linear dependence of  $[M]_0/[I]_0$ , and narrow molecular weight distributions. Figure 1 presents a representative plot which demonstrates the living polymerization character for the case of monomer 6-3. The polymerization mechanism is outlined in Scheme II.<sup>9</sup> The thermal characterization of all intermediary alcohols, monomers and model compounds is

summarized in Table IV. The alcohol derivatives 7-2, 7-3 and 7-4 exhibit a monotropic nematic mesophase. 6-2 is crystalline, 6-3 exhibits a monotropic nematic mesophase, while 6-4 an enantiotropic nematic phase. The model compounds 8-2 and 8-3 are only crystalline. 8-4 displays a monotropic nematic mesophase.

Figure 2 presents the DSC traces of poly(6-2) with different molecular weights. The polymerization of 6-2 was investigated previously by Sagane and Lenz.<sup>8c</sup> Our present data do not agree completely with their results. In the first DSC heating scan, poly(6-2) presents an endothermic transition which overlaps the glass transition temperature. This transition does not appear on the second heating or on the cooling scans. Since we could not yet assign this phase, we will label it with x (Table I). Irrespective of thermal history of the sample, when the degree of polymerization of poly(6-2) is lower than 4.0, the polymer presents also an enantiotropic nematic mesophase. Poly(6-2) with higher degrees of polymerization do not present this nematic phase. The disappearance of this phase at higher polymer molecular weights is due to the steep increase of the dependence of the glass transition temperature versus polymer molecular weight with the increase of polymer molecular weight. At degrees of polymerization of about 7 and higher, the glass transition of poly(6-2) is very close to the nematic-isotropic transition temperature. Therefore, the mesophase becomes kinetically controlled, and due to its close proximity to glass transition, it can not be observed by DSC. Upon shearing the polymer sample on the optical polarized microscope just above its T<sub>g</sub>, we see the formation of the nematic phase. Figure 3 presents the dependence of glass transition, of the nematic-isotropic and of the x-nematic transition temperatures on molecular weight. This figure demonstrates that the slope of the T<sub>g</sub>-M<sub>n</sub> is higher than that of T<sub>n-i</sub>-M<sub>n</sub> and as a consequence, at higher polymer molecular weights, the nematic mesophase becomes kinetically controlled.

The second heating and the cooling DSC traces of poly(6-3) are presented in Figure 4a,b. This polymer presents an enantiotropic nematic mesophase. However, on the first heating scan, it also shows the x phase which overlaps the glass transition temperature (Table II). Figures 4 and 5 show the dependence of glass transition and nematic-isotropic transition temperatures on molecular weight. The slopes of both dependences are almost identical. In the case of poly(6-2) the slope of T<sub>g</sub>-M<sub>n</sub> was higher than that of T<sub>n-i</sub>-M<sub>n</sub>. At the same time in the case of polymers

with longer spacers, the slopes of the mesomorphic-isotropic phase transition temperatures versus  $M_n$  are higher than that of  $T_g$ - $M_n$ <sup>2,3</sup>.

In the first heating scan poly(6-4) with degrees of polymerization below five exhibits an enantiotropic nematic mesophase (Table III). Polymers with higher molecular weights exhibit the x phase followed by the enantiotropic nematic mesophase. The x phase can not be observed on the second heating and cooling scans (Figure 6a,b). The dependences of the phase transition temperatures of poly(6-4), collected from the first heating scans versus  $M_n$ , are plotted in Figure 7. Again we can observe similar slopes for the  $T_g$ - $M_n$  and  $T_{n-i}$ - $M_n$  dependences. It is very interesting to observe that the enthalpy changes associated with the nematic-isotropic transitions of poly(6-4) are very low.

In conclusion, mesomorphic poly(vinyl ether)s with long spacers exhibits smectic mesophases although their corresponding monomers and model compounds display nematic mesophases<sup>2,3</sup>. The corresponding polymers with short flexible spacers exhibit nematic mesophases. Their monomers and model compounds also exhibit nematic mesophases. In the case of polymers with short flexible spacers, the slopes of the  $T_g$ - $M_n$  and  $T_{n-i}$ - $M_n$  dependences are about equal, with the exception of poly(6-2) whose  $T_g$ - $M_n$  slope is steeper. In the case of polymers with long flexible spacers, the slope of  $T_{s-i}$ - $M_n$  is much steeper than that of  $T_g$ - $M_n$ . Last but not least, it is interesting to mention that the dimers and trimers of poly(6-2) as well as the low molecular weight oligomers of poly(6-3) have glass transition temperatures above room temperature and therefore, provide an interesting new approach to nematic glasses with fast dynamics. They may have the same potential applications as low molar mass glassy nematic liquid crystals<sup>11</sup>. The experiments described in this series of publication together with previous results on the same topic provided both by us<sup>12</sup> and by others<sup>13-17</sup> demonstrate the complexity of the influence of molecular weight on the phase transition of side chain liquid crystal polymers. The only case which was explained so far refers to systems in which the virtual or monotropic mesophase of the monomer or of the monomeric structural unit transforms into a monotropic or enantiotropic mesophase after polymerization<sup>18,19</sup>. The same explanation holds for situations when the monomeric structural unit exhibits an enantiotropic mesophase and the resulting polymer a broader range of temperature of its mesophase. However, the mechanism

which changes the nature of the mesophase upon increasing the degree of polymerization is not yet known.

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FIGURE AND SCHEME CAPTIONS

Scheme 1: Synthesis of 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2), 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3) and 4-[4-cyano-4'-biphenyl)oxy]butyl vinyl ether (6-4).

Scheme 2: Cationic polymerization of 6-2, 6-3 and 6-4.

Figure 1: The dependence of the number average molecular weight ( $M_n$ ) and of the polydispersity ( $M_w/M_n$ ) of poly(6-3) on the  $[M]_0/[I]_0$  ratio.

Figure 2: DSC traces displayed during the first heating (a), second heating scan (b) and first cooling scan (c) by poly(6-2) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 3: The dependence of phase transition temperatures on the degree of polymerization of poly(6-2). Data from first heating scan (fh) and second heating scan (sh):  $\Delta$ -T<sub>n-i</sub>(fh);  $\square$ -T<sub>x-n</sub>(fh); O-T<sub>g</sub>(fh);  $\blacktriangle$ -T<sub>n-i</sub>(sh);  $\bullet$ -T<sub>g</sub>(sh).

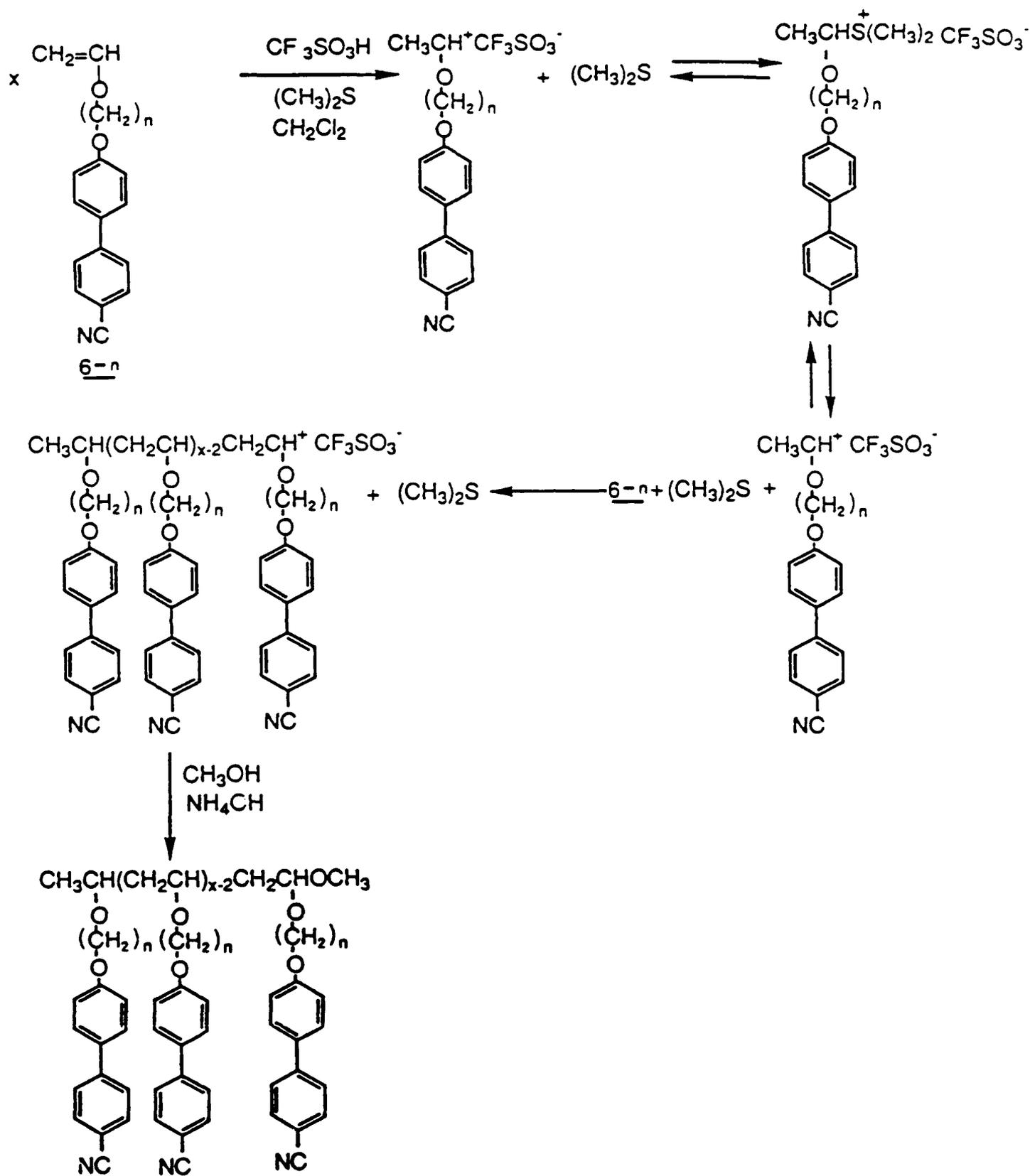
Figure 4: DSC traces displayed during the second heating scan (a) and first cooling scan (b) by poly(6-3) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 5: The dependence of phase transition temperatures on the degree of polymerization of poly(6-3). Data from first cooling scan:  $\Delta$ -T<sub>n-i</sub>; O-T<sub>g</sub>.

Figure 6: DSC traces displayed during the second heating scan (a) and first cooling scan (b) by poly(6-4) with different degrees of polymerization (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(6-4). Data from first heating scan:  $\Delta$ -T<sub>n-i</sub>;  $\square$ -T<sub>x-n</sub>; O-T<sub>g</sub>.





Scheme II

Table I. Cationic Polymerization of 2-[4-Cyano-4'-biphenyl)oxy]ethyl Vinyl Ether (6-2) (polymerization temperature, 0°C; polymerization solvent, methylene chloride;  $[M]_0=0.387$ ;  $[(CH_3)_2S]_0/[I]_0=10$ ; 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.	$[M]_0/[I]_0$	Polymer yield(%)	G P C		phase transitions(°C) and corresponding enthalpy changes (kcal/mru)		
			$M_{nx}10^{-3}$	Mw/Mn	D P	heating	cooling
1	2.0	34.7	0.54	1.22	2.1	g 34.5 X 37.5 (0.21) n 79.2 (0.061) i g 33.5 n 79.8 (0.061) i	i 76.3 (0.072) n 29.5 g
2	3.0	57.3	0.74	1.11	2.8	g 53.7 X 56.7 (0.29) n 81.1 (0.034) i g 51.0 n 80.2 (0.037) i	i 77.1 (0.040) n 43.5 g
3	4.0	54.7	0.86	1.21	3.4	g 60.1 X 66.7 (0.37) n 81.4 (0.008) i g 55.6 n 71.8 (0.027) i	i 70.8 (0.033) n 49.7 g
4	6.0	73.3	1.78	1.08	6.7	g 68.6 X 71.6 (0.34) i g 61.9 i	i 54.7 g
5	10.0	73.1	2.87	1.10	10.8	g 78.5 X 86.0 (0.18) i g 72.8 i	i 63.8 g
6	20.0	64.8	4.56	1.18	17.2	g 81.0 X 85.7 (0.25) i g 78.3 i	i 70.5 g

Table II. Cationic Polymerization of 3-[4-Cyano-4'-biphenyl]oxypropyl Vinyl Ether (6-3) (polymerization temperature, 0°C; polymerization solvent, methylene chloride;  $[M]_0=0.358$ ;  $[(CH_3)_2S]_0/[I]_0=10$ ; 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.	$[M]_0/[I]_0$	Polymer yield(%)	G P C			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
			$M_n \times 10^{-3}$	Mw/Mn	D P	heating	
1	6	80.0	1.57	1.06	5.6	g 38.2 X 41.3 (0.17) n 79.6 (0.10) i g 36.3 n 77.3 (0.11) i	i 72.3 (0.083) n 30.8 g
2	10	88.0	2.55	1.14	9.1	g 41.3 X 46.6 (0.18) n 84.9 (0.067) i g 40.1 n 83.5 (0.065) i	i 79.1 (0.071) n 38.5 g
3	13	87.3	3.29	1.20	11.8	g 45.1 X 49.6 (0.19) n 88.8 (0.078) i g 45.0 n 87.0 (0.095) i	i 82.5 (0.083) n 42.7 g
4	18	83.3	5.08	1.18	18.2	g 59.5 X 64.5 (0.26) n 97.8 (0.094) i g 56.4 n 95.9 (0.070) i	i 90.8 (0.078) n 50.3 g
5	23	82.0	6.04	1.11	21.6	g 61.7 X 66.4 (0.23) n 102.7 (0.078) i g 59.4 n 102.3 (0.086) i	i 97.6 (0.078) n 52.1 g
6	30	79.3	8.09	1.21	28.9	g 64.4 X 68.4 (0.21) n 104.5 (0.070) i g 63.0 n 104.3 (0.081) i	i 100.3 (0.075) n 54.1 g

Table III. Cationic Polymerization of 3-[4-Cyano-4'-biphenyloxy]propyl Vinyl Ether (6-3) (polymerization temperature, 0°C; polymerization solvent, methylene chloride;  $[M]_0=0.358$ ;  $[(CH_3)_2S]_0/[I]_0=10$ ; 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.	$[M]_0/[I]_0$	Polymer yield(%)	G P C			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
			Mnx 10 <sup>-3</sup>	Mw/Mn	D P	heating	cooling
1	6	80.0	1.16	1.20	3.9	g 15.4 n 77.1 (0.056) i g 15.2 n 76.7 (0.067) i	i 72.3 (0.047) n 10.3 g
2	10	88.0	1.52	1.10	5.2	g 24.5 n 75.2 (0.032) i g 24.0 n 74.8 (0.026) i	i 67.8 (0.026) n 16.9 g
3	13	87.3	2.93	1.20	10.0	g 30.2 X 45.4 (0.29) n 83.3 (0.019) i g 28.4 n 77.2 (0.029) i	i 69.5 (0.035) n 23.9 g
4	18	83.3	3.73	1.16	12.7	g 34.8 X 48.8 (0.49) n 85.5 (0.0029) i g 33.1 n 74.5 (0.003) i	i 67.3 (0.009) n 23.2 g
5	23	82.0	5.03	1.22	17.1	g 35.7 X 52.2 (0.30) n 84.7 (0.0079) i g 34.3 n 83.2 (0.003) i	i 69.5 (0.012) n 23.1 g
6	30	79.3	6.99	1.23	23.8	g 39.1 X 52.8 (0.39) n 87.4 (0.0058) i g 37.5 n 84.1 (0.012) i	i 70.1 (0.003) n 28.0 g

Table IV. Thermal Characterization of 4-Cyano-4'-( $\omega$ -hydroxyalkan-1-yloxy)biphenyls (7-2, 7-3 and 7-4),  $\omega$ -[(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ethers (6-2, 6-3 and 6-4) and  $\omega$ -[(4-Cyano-4'-biphenyl)oxy]alkyl Ethyl Ethers (8-2, 8-3 and 8-4)

Compound	phase transitions (0°C) and corresponding enthalpy changes (kcal/mol)	
	heating	cooling
<u>7-2</u>	k 128.7 (6.84) i [ n 126.5 (0.25) i]*	i 123.4 (0.31) n 105.4 (3.85) k
<u>6-2</u>	k 118.5 (8.21) i	i 83.4 (6.70) k
<u>8-2</u>	k 68.9 (5.46) i	i 13.3 (3.56) k
<u>7-3</u>	k 114.6 (7.45) i [ n 115.3 (0.26) i]	i 112.7 (0.30) n 67.5 (2.87) k
<u>6-3</u>	k 78.74 (9.02) i	i -10.4 (0.08) n -51.4 (2.30) k
<u>8-3</u>	k 64.9 (7.83) i	i -5.9 (4.13) k
<u>7-4</u>	k 126.4 (5.95) i [ n 124.8 (0.32) i]*	i 121.7 (0.31) n 99.3 (5.24) k
<u>6-4</u>	k 73.3 (7.82) n 77.1 (0.22) i	i 73.4 (0.29) n 48.4 (6.37) k
<u>8-4</u>	k 64.7 (7.87) i [ n 50.5 (0.062)] i	i 47.4 (0.094) n 33.1 (5.38) k

[ ]\* virtual data

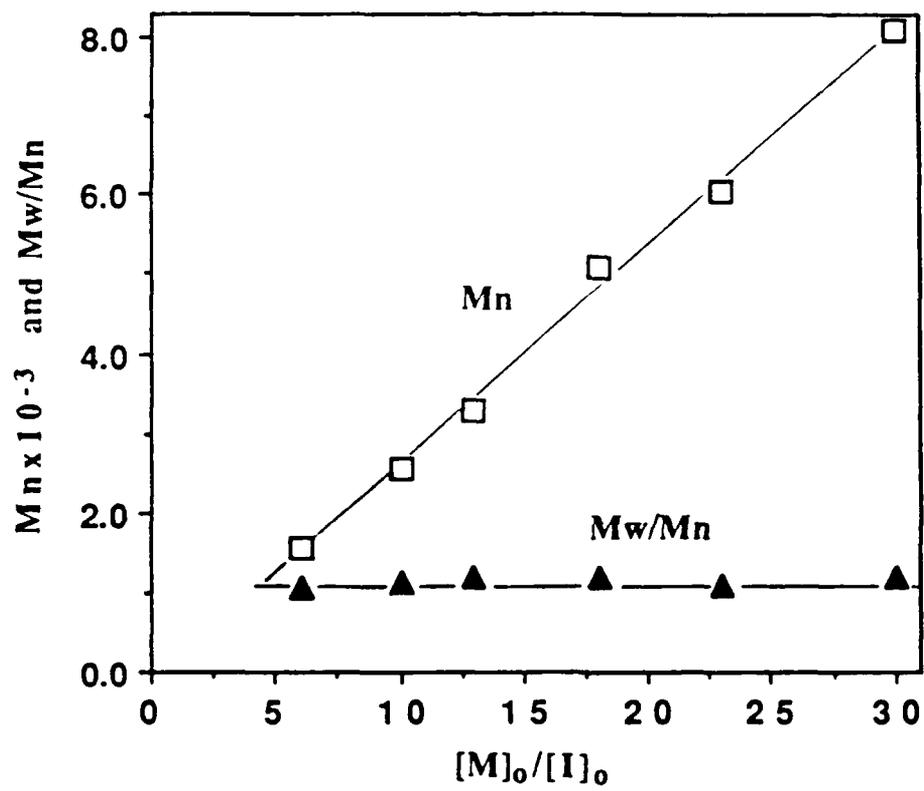


Figure 1

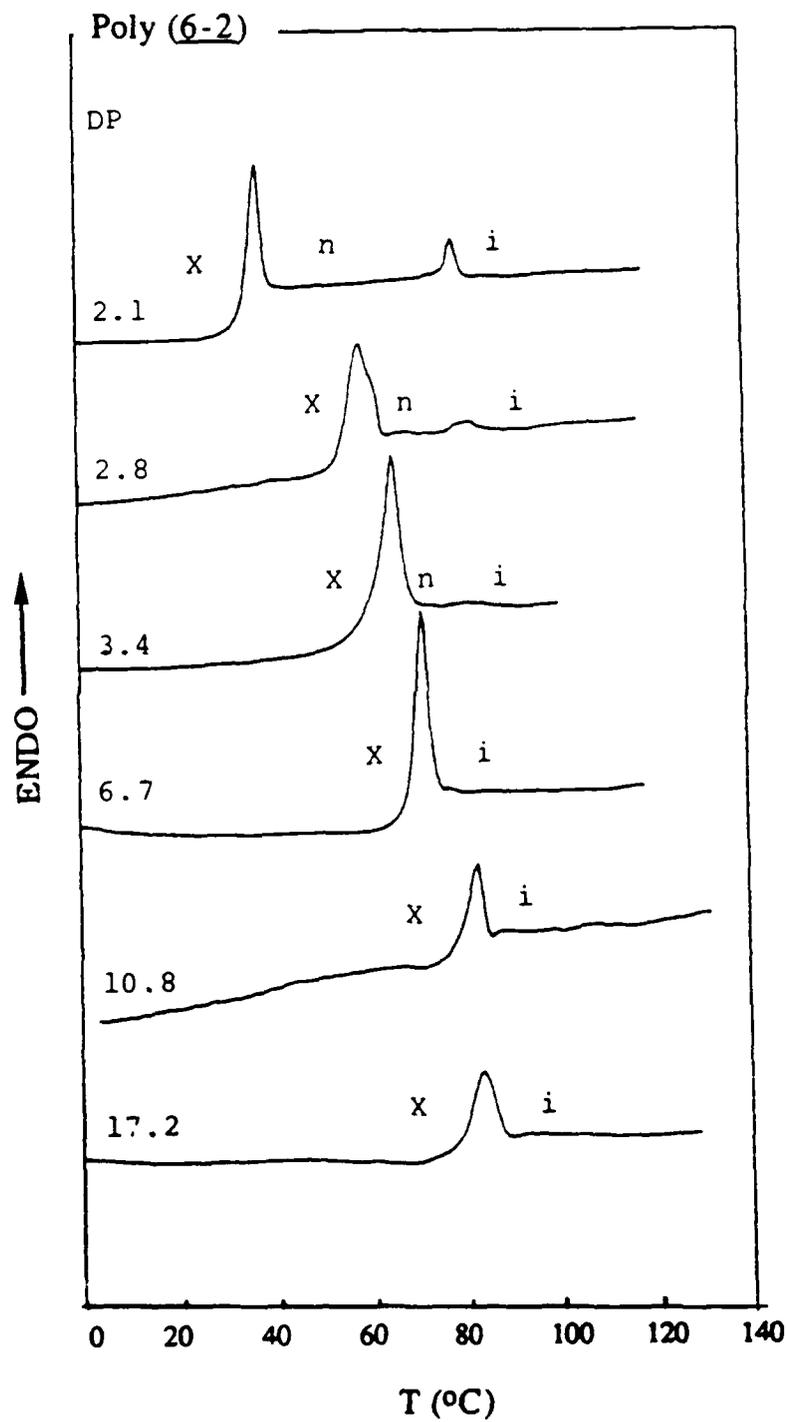


Figure 2a

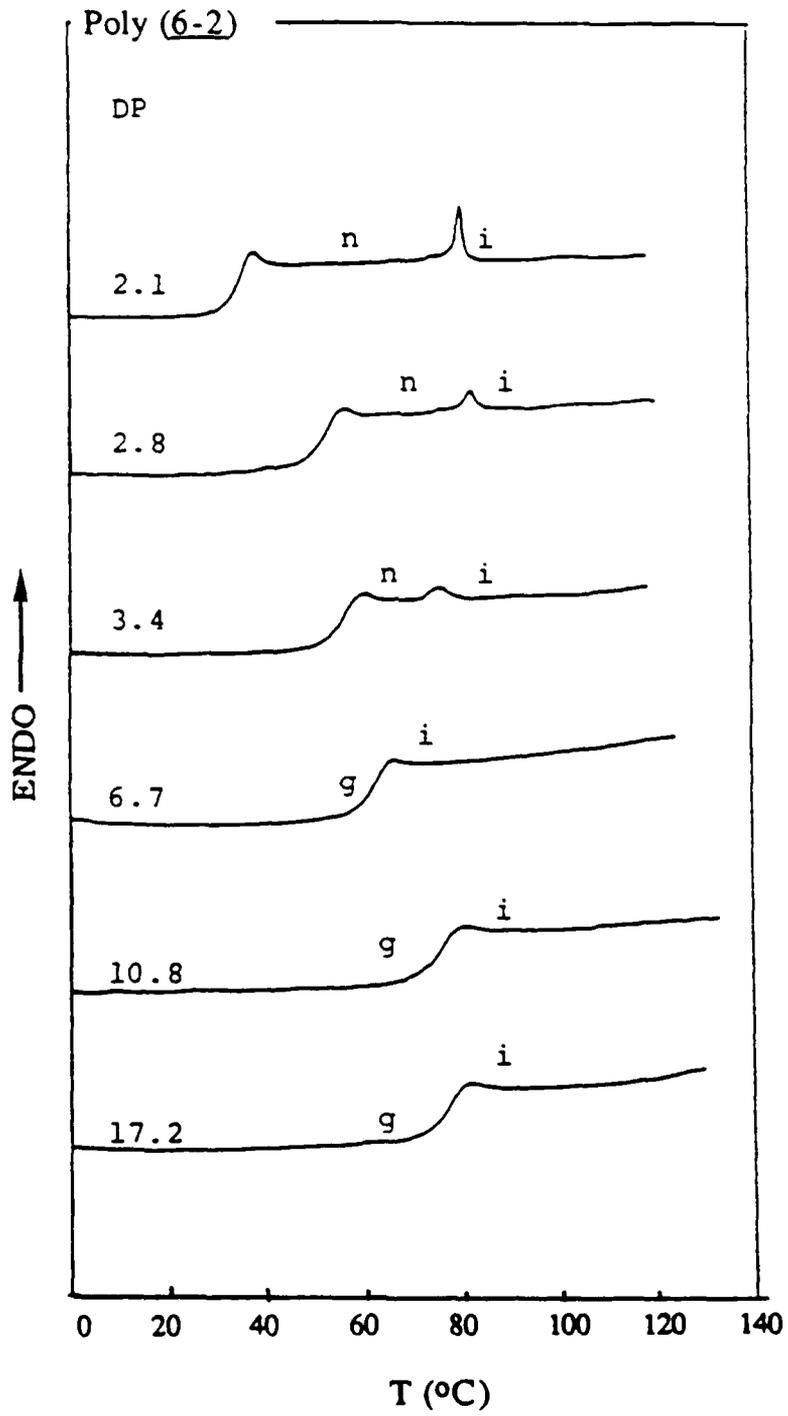


Figure 2b

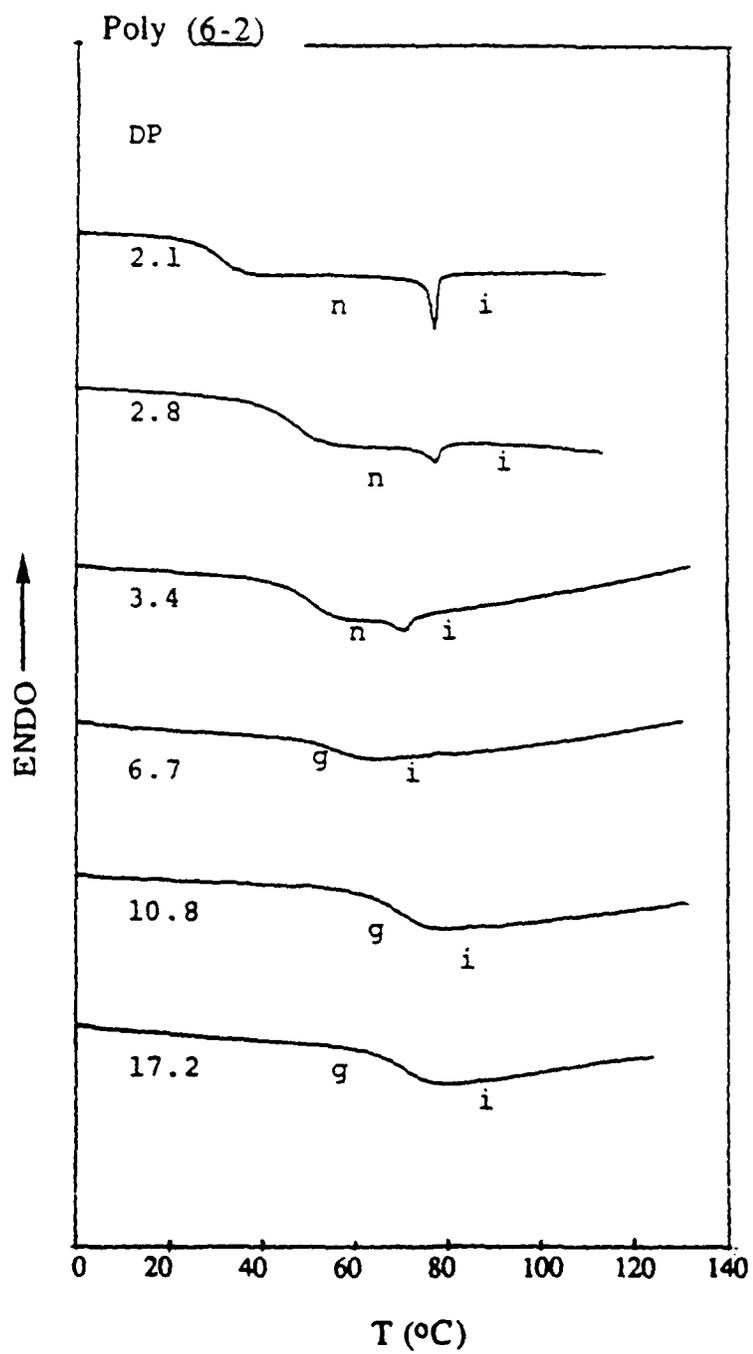


Figure 2c

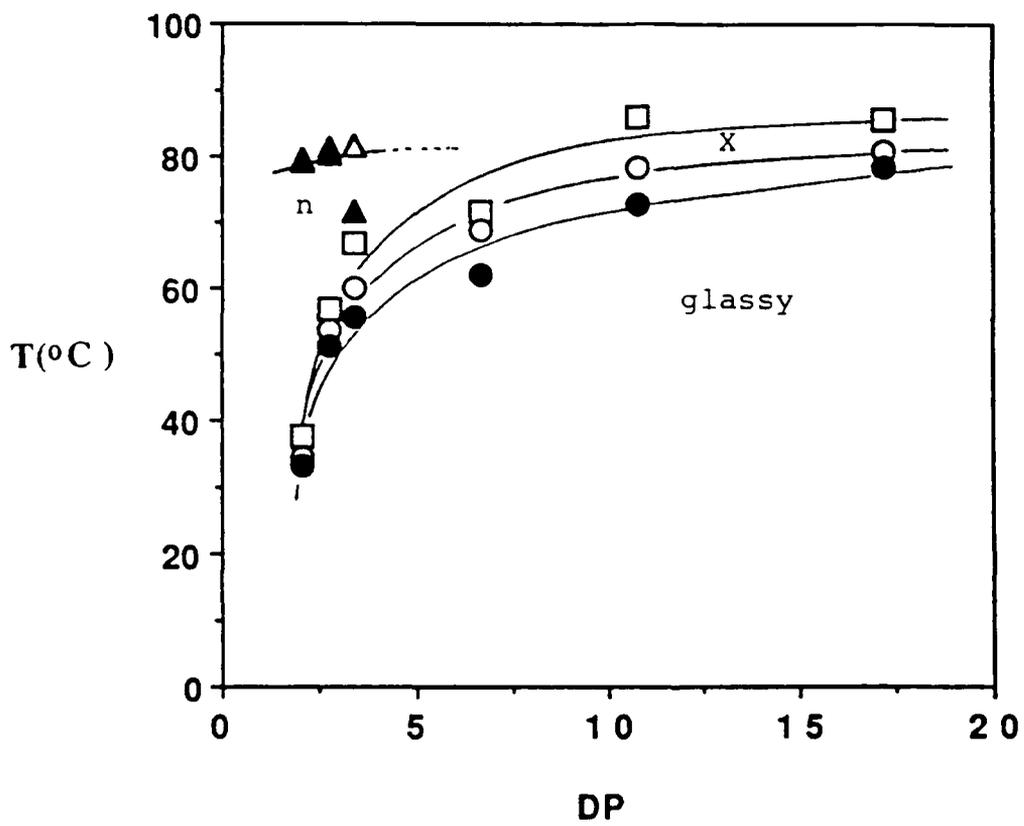


Figure 3

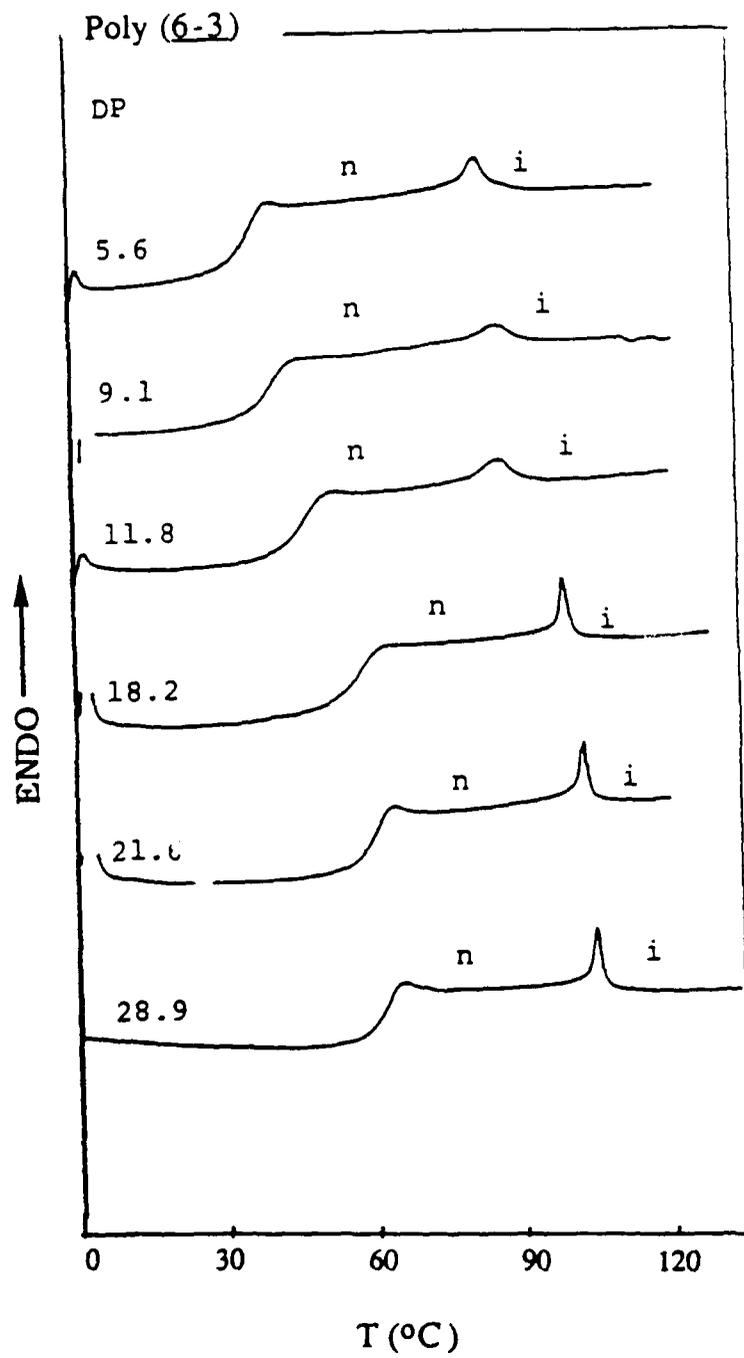


Figure 4a

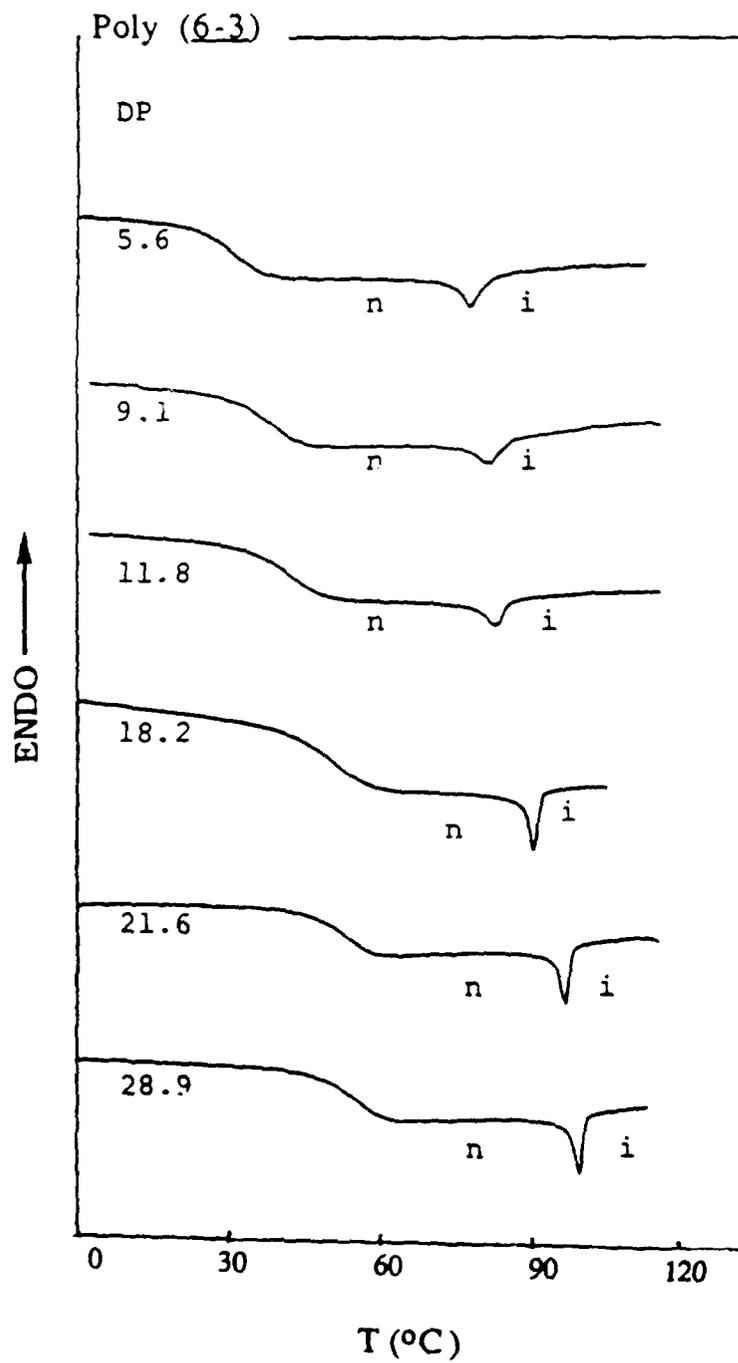


Figure 4b

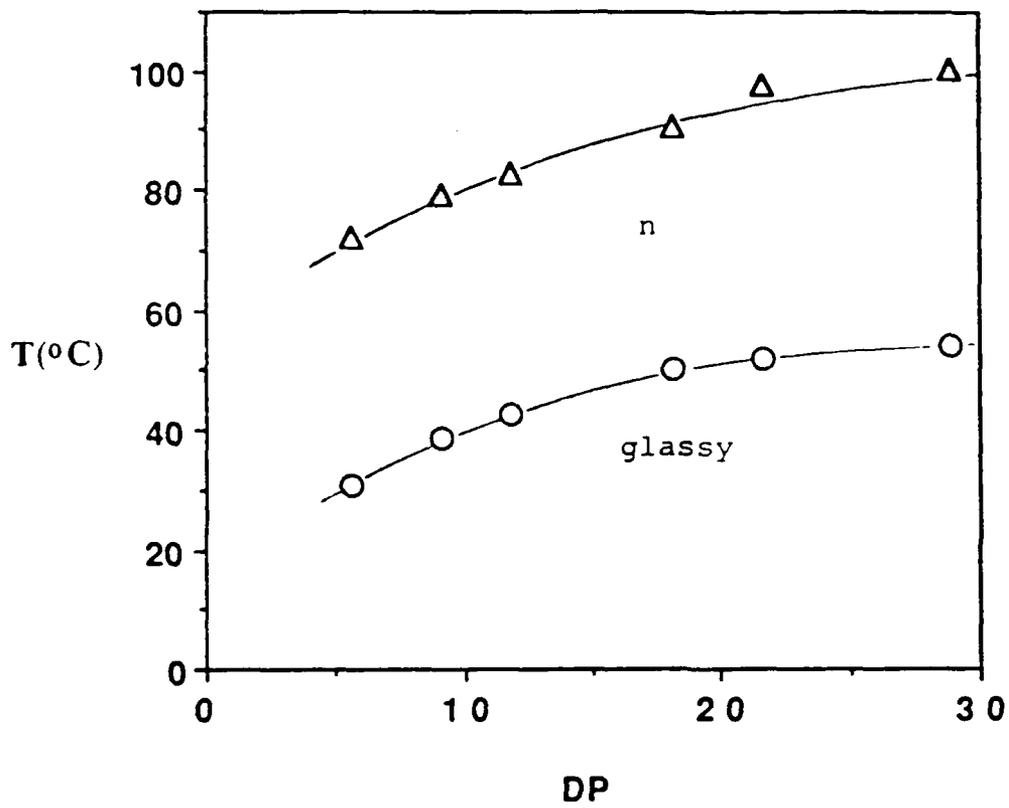


Figure 5

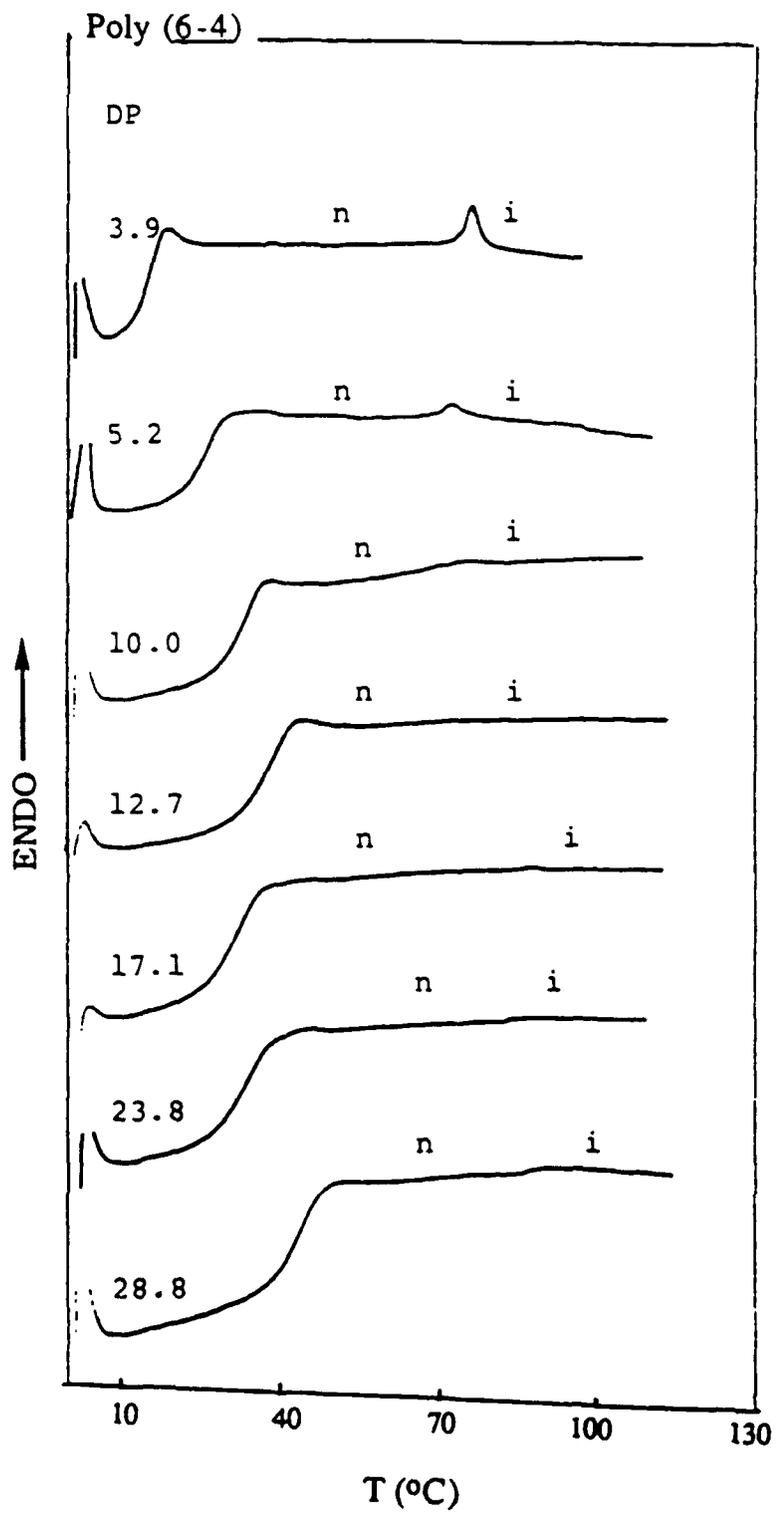


Figure 6a

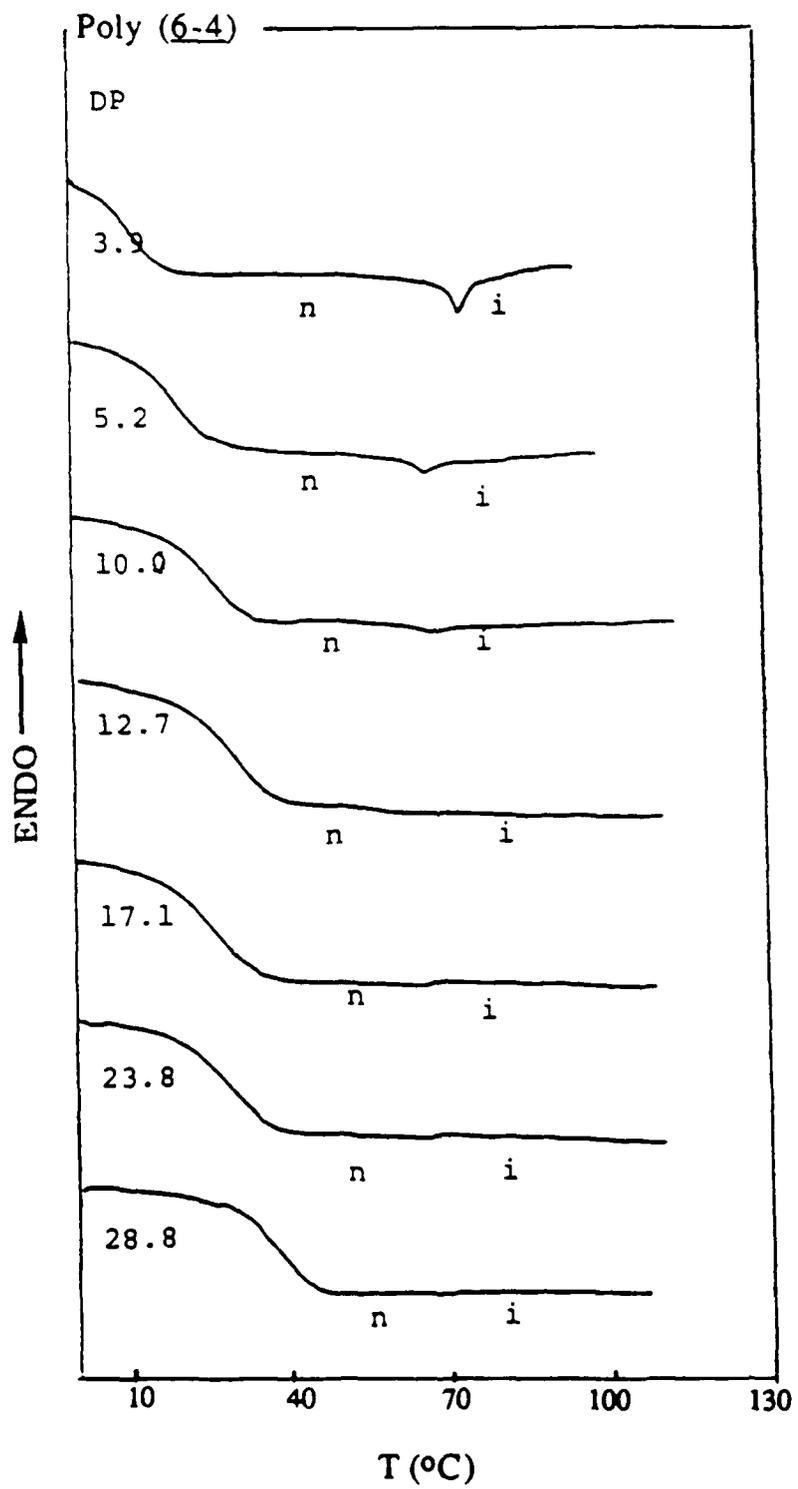


Figure 6b

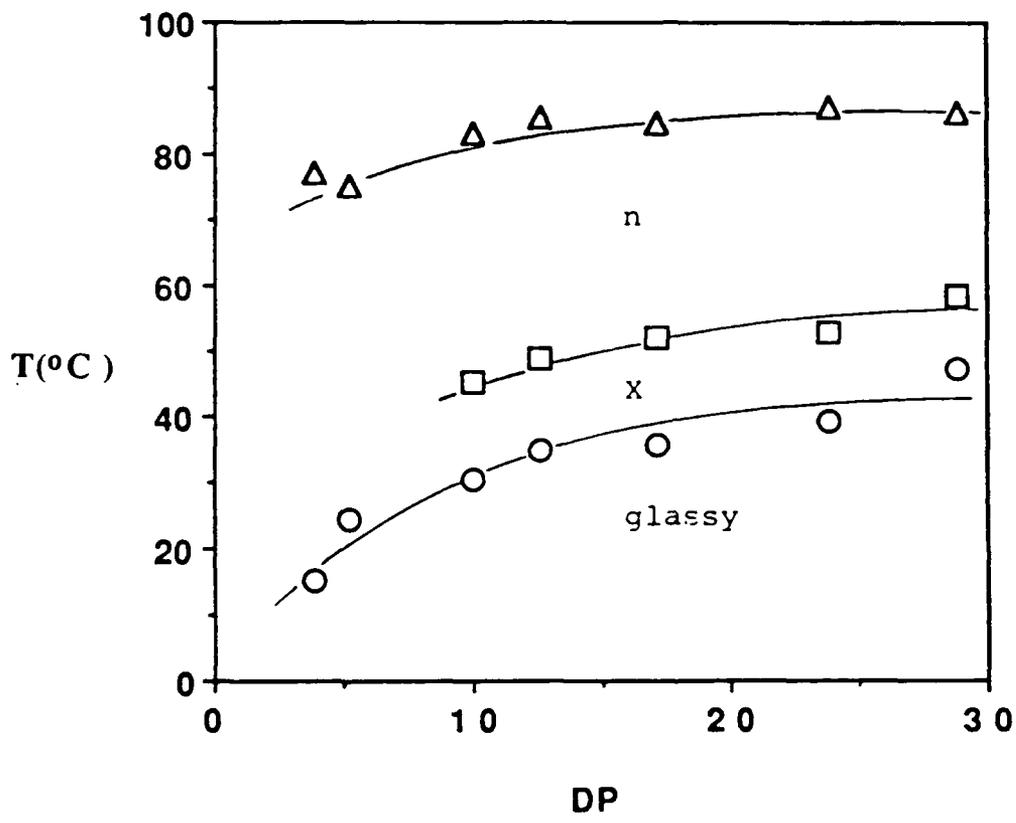


Figure 7