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Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization. 19. Synthesis and Characterization of Poly[2-(4-Biphenyloxy)ethyl Vinyl Etherby

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization.19.[a] Synthesis and Characterization of Poly[2-(4-Biphenyloxy)ethyl Vinyl Ether].

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ABSTRACT

The synthesis and living cationic polymerization of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE) are described. Poymers with degrees of polymerization from 3.8 to 22.1 and narrow molecular weight distribution were synthesized and characterized by differential scanning calorometry (DSC) and thermal optical polarized microscopy. When determined from their first DSC heating scans poly(BEVE)s exhibit only a crystalline phase over the entire range of molecular weights. When determined from the second and first cooling scans, poly(BEVE) with a degree of polymerization of 3.8 exhibits an enantiotropic smectic mesophase and a crystallization process on the heating scan, while the polymers with degrees of polymerization from 4.7 to 8.1 exhibit only an enantiotropic smectic mesophase. The polymers with higher degrees of polymerization do not exhibit any mesophase. An explanation for this behavior is provided.

INTRODUCTION

The dependence of phase transitions on polymer molecular weight is an important factor which requires elucidation in order to provide a systematic approach to the molecular engineering of side chain liquid crystalline polymers. Up to now, it is generally accepted that the thermal stability of the mesophase increases with the increase of the polymer molecular weight.[1-4,6-10] This dependence was explained based on thermodynamic principles assuming that the phase behavior of the polymer is dictated by that of the monomeric structural unit.[11,12] 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 explained.

However, the number and type of mesophase exhibited by a certain polymer is also molecular weight dependent.[4,6,9] Elucidation of this phenomenon requires the synthesis of polymers with well defined molecular weights and narrow molecular weight distributions.

Recently, cationic polymerization of mesogenic vinyl ethers provided a very attractive technique to design side chain liquid crystalline polymers since it leads to polymers with controlled molecular weights and narrow molecular weight distributions.[5 10,13] Although most of the experiments performed in our laboratory were carried out with vinyl ethers based on 4-cyano-4'-hydroxybiphenyl,[9] we have also shown that vinyl ethers containing a large variety of functionalities such as crown ethers,[13a,b] acidic protons[13c], double bonds,[13d,13e] and ester groups[10] can be polymerized under living conditions, especially with the initiating system $CF_3SO_3H/S(CH_3)_2$.[14]

This paper will present the synthesis and living cationic polymerization of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE) and the mesomorphic behavior of the resulting polymers with different molecular weights.

EXPERIMENTAL

Materials

4-Hydroxy biphenyl (98%, Aldrich) and 2-chloro ethyl vinyl ether (Polysciences, bp 109-110 °C) were used as received. 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.

Techniques

^1H-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 differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures[15,16]. 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 2-(4-Biphenylyloxy)ethyl Vinyl Ether

This monomer was synthesized as described previously.[5] After the recrystallization from methanol, the monomer was further purified by column chromatography (silica gel, CH_2Cl_2 eluent) to achieve higher purity than 99%. mp; 83.8 °C (DSC), ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm); 3.92-4.30 (6H, -$(C\underline{H}_2)_2$- and -CH=$C\underline{H}_2$, m), 6.55 (1H, -$C\underline{H}=CH_2$, q), 7.02 (2 aromatic protons, o to oxy, m), 7.24-7.64 (7 aromatic protons, m to oxy and o,m,p to phenoxy, m).

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 summarizes 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

Scheme I outlines the polymerization mechanism which is discussed in more detail in the other publications.[14,17] The cationic polymerization was initiated with the system $CF_3SO_3H/S(CH_3)_2$ and was performed at 0°C in CH_2Cl_2. Polymerization results are summarized in Table I. Conversions are below 100% due to polymer loss during the purification process. However, after quenching the polymerization, GPC and NMR showed that monomer conversion was quantitative. As presented in Table I, the molecular weights by determined GPC demonstrate that the ratio of $[M]_o/[I]_o$ provides a very good control of the polymer molecular weight, although they are relative to polystyrene standards. In addition, all polymers exhibit narrow molecular weight distributions. Absolute number average molecular weights and degrees of polymerization were determined by 200 MHz ^{1}H-NMR spectroscopy.

A representative ^{1}H-NMR spectrum with its protonic assignments is presented in Figure 1. The resonances of the expected methoxy chain end which are formed by quenching the living chain end with ammoniacal methanol can be easily observed at 3.35 ppm. Degrees of polymerization were determined by measuring the ratio of the signal at 4.80 ppm to the signal at 6.93 ppm. The degrees of polymerization determined by NMR are summarized in Table 1. Figure 2 presents the plot of Mn determined by GPC and NMR and Mw/Mn versus $[M]_o/[I]_o$ obtained for the cationic polymerization of BEVE. As expected, the plot of relative and absolute Mn versus $[M]_o/[I]_o$ provide different slopes (Figure 2). This plot demonstrates that within this range of molecular weights BEVE can be polymerized by a living mechanism.

Figure 3 presents the DSC traces of poly(BEVE) with various degrees of polymerization. The polymerization of BEVE was investigated previously in our and in other laboratories.[5,6a] However, there is no available information on the polymers with degrees of polymerization below 20 which were investigated in this paper. As we can observe from Figure 3, the DSC curves of the first heating scan (Figure 3a) differ from those of the second heating scan (Figure 3b). However, second and subsequent heating scans exhibit identical DSC traces. First and subsequent cooling scans also exhibit identical traces (Figure 3c). On the first heating scan, all polymers exhibit a crystalline melting transition (Figure 3a, Table I).

On the second heating and cooling scans, the phase behavior of poly(BEVE) is strongly dependent on the molecular weight of the polymer (Figure 3b,c). Poly(BEVE) with DP=3.8 undergoes the transition from smectic to isotropic followed by crystallization through endothermic and exothermic peaks on the second heating scan. If poly(BEVE) with DP=3.8 is reheated in the DSC instrument from a temperature which is above the crystallization, the transition from this smectic phase to isotropic phase can be easily observed as shown in Figure 3b. Polymers with degrees of polymerization from 4.7 to 8.1 exhibit only an enantiotropic smectic phase. Due to their close proximity of the isotropization temperature to the glass transition temperature, DSC measurements can hardly detect this transition. However, optical polarized microscopy reveals clearly the formation of batonnets below the isotropization temperature. This texture is representative for a smectic mesophase (Figure 4).[15,16] However, if these polymers are annealed within their mesophase below the melting transition temperature determined during the first heating scan, they crystallize. This means that under equilibrium condition, poly(BEVE) exhibit a monotropic smectic mesophase. Poly(BEVE) with higher degrees of polymerization do not exhibit this smectic mesophase. The disappearance of this phase at higher molecular weights is due to the steep increase of the dependence of the glass transition temperature versus polymer molecular weight with the increase of degree of polymerization. At degrees of polymerization of about 10.8 and higher, the glass transition of poly(BEVE) is very close to the smectic-isotropic transition temperature. Therefore, the mesophase becomes kinetically controlled, and due to its close proximity to glass transition, it can not be observed. Additional examples of this behavior are available in the literatures.[6c,9b]

Thermal transition temperatures collected from Figure 3 are summarized in Table I and plotted in Figure 5a (data from the first heating scan) and Figure 5b (data from second heating and first cooling scans). Figure 5b demonstrates that the slope of the Tg-Mn is steeper than that of T_{s-i}-Mn. Consequently, at a certain degree of polymerization the Tg-Mn dependence will intercept the T_{s-i}-Mn dependence and therefore, above this molecular weight the smectic phase becomes virtual.

In conclusion, the results described in this paper have demonstrated that the phase behavior of poly(BEVE) is strongly dependent on molecular weight and therefore, the nature of the highest temperature phase changes as the degree of polymerization increases. Poly(BEVE) presents the second example of side chain polymer based on 4-hydroxy biphenyl which exhibits liquid crystallinity. The other is poly(4-biphenylyl acrylate) which exhibits a smectic mesophase.[1,18]

ACKNOWLEDGMENTS

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FIGURES AND SCHEME CAPTIONS

Scheme I: Cationic polymerization of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE)

Figure 1: 200 MHz ^{1}H-NMR spectrum of poly(BEVE) with theoretical DP=7.

Figure 2: The dependence of the number average molecular weight (Mn) determined by GPC; ❑ and by NMR; O and of the polydispersity (Mw/Mn); ▲ of poly(BEVE) by GPC on the $[M]_0/[I]_0$ 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(BEVE) with different degrees of polymerization (DP) determined by GPC. DP is printed on the top of each DSC traces.

Figure 4: Representative optical polarized micrographs (100x) of the smectic mesophase displayed by poly(BEVE) with DP=5.5 obtained at 60 °C on the cooling scan.

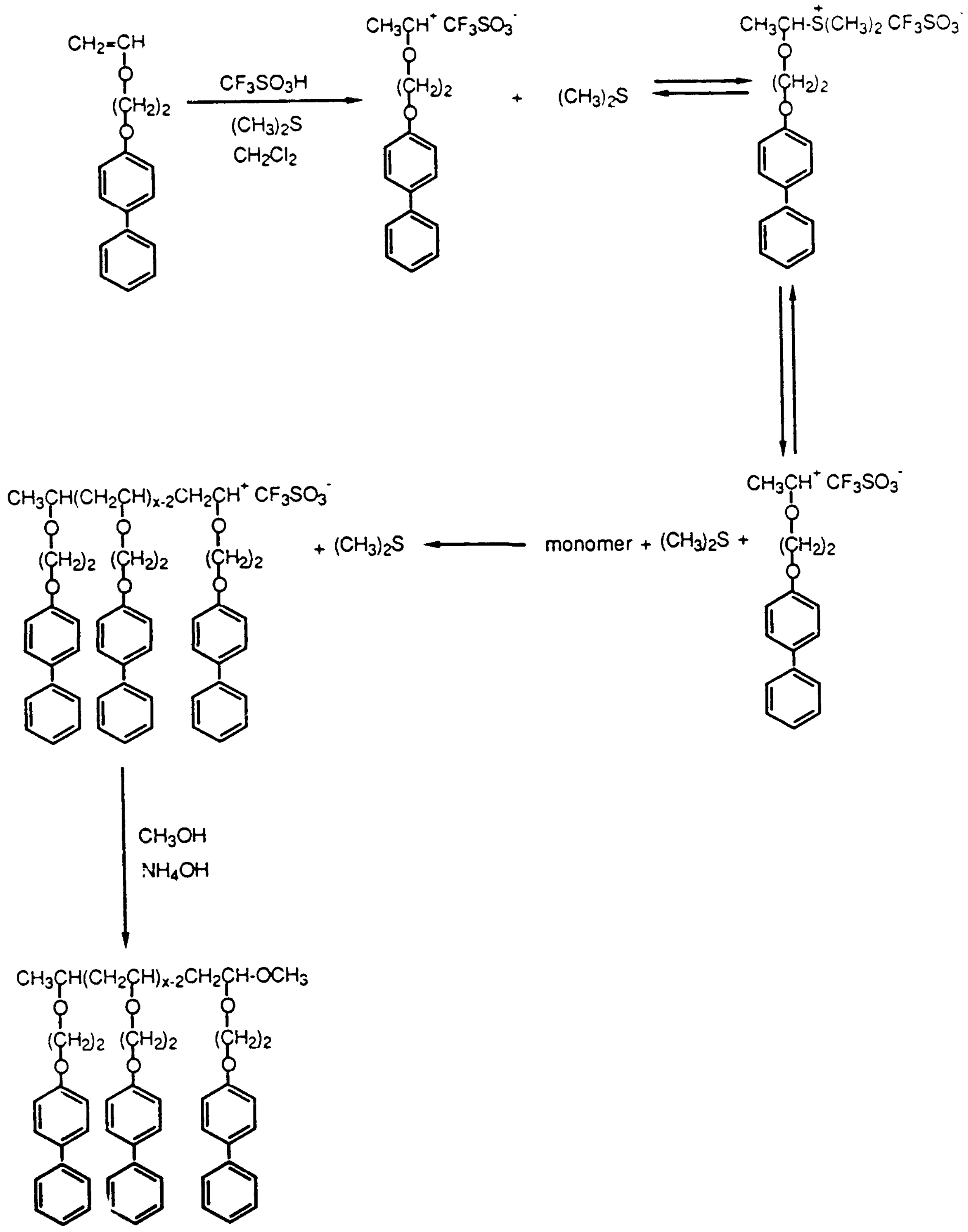
Figure 6: The dependence of phase transition temperatures on the degree of polymerization of poly(BEVE) (determined by GPC). a) data from first heating: ■-T_{k-i}; O-Tg; b) data from the second heating (h) and the first cooling scan: ❑-T_{s-i} (h); Δ-T_{k-s} (h); O-Tg (h); ■-Ti-s (c); O-Tg(c).

Table I. Cationic Polymerization of 2-(4-Biphenyloxy)ethyl Vinyl Ether (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0$=0.42; $[(CH_3)_2S]_0/[I]_0$=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(%)	$Mn\times10^{-3}$	Mw/Mn	D P	DP	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
			GPC			NMR	heating	cooling
1	2.0	48	0.9	1.07	3.8	2.5	k 60.5 (1.76) i g 25.6 k 37.7 (-0.29) k 55.3 (0.41)[a] s 58.3 i	i 43.0 (0.07) s 18.7 g
2	4.0	80	1.1	1.10	4.7	5.0	k 66.8 (1.56) i g 35.2 s 67.2 (-)[b] i	i 62.2 (-)[b] s 28.2 g
3	5.0	87	1.3	1.09	5.5	6.7	k 65.2 (1.42) i g 38.3 s 66.5 (-)[b] i	i 61.7 (-)[b] s 32.2 g
4	6.0	91	1.5	1.11	6.2	8.3	k 66.4 (1.28) i g 42.7 s 67.0 (-)[b] i	i 62.6 (-)[b] s 35.6 g
5	7.0	89	1.9	1.07	8.1	9.2	g 55.2 k 67.8 (1.05) i g 45.2 s 66.0 (-)[b] i	i 62.0 (-)[b] 38.2 g
6	10.0	82	2.6	1.07	10.8	13.8	g 56.3 k 70.5 (1.00) i g 50.2 i	i 43.1 g
7	12.0	80	2.9	1.09	11.9	14.6	g 58.9 k 70.1 (1.04) i g 52.1 i	i 45.7 g
8	20.0	87	5.3	1.08	22.1	27.0	g 61.0 k 71.0 (0.85) i g 55.8 i	i 49.8 g

[a] overlapped peaks

[b] data from optical microscopy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CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+ CF3SO3-
+ (CH3)2S
CH3CH-S+(CH3)2 CF3SO3-
(CH2)2
monomer + (CH3)2S +
+ (CH3)2S
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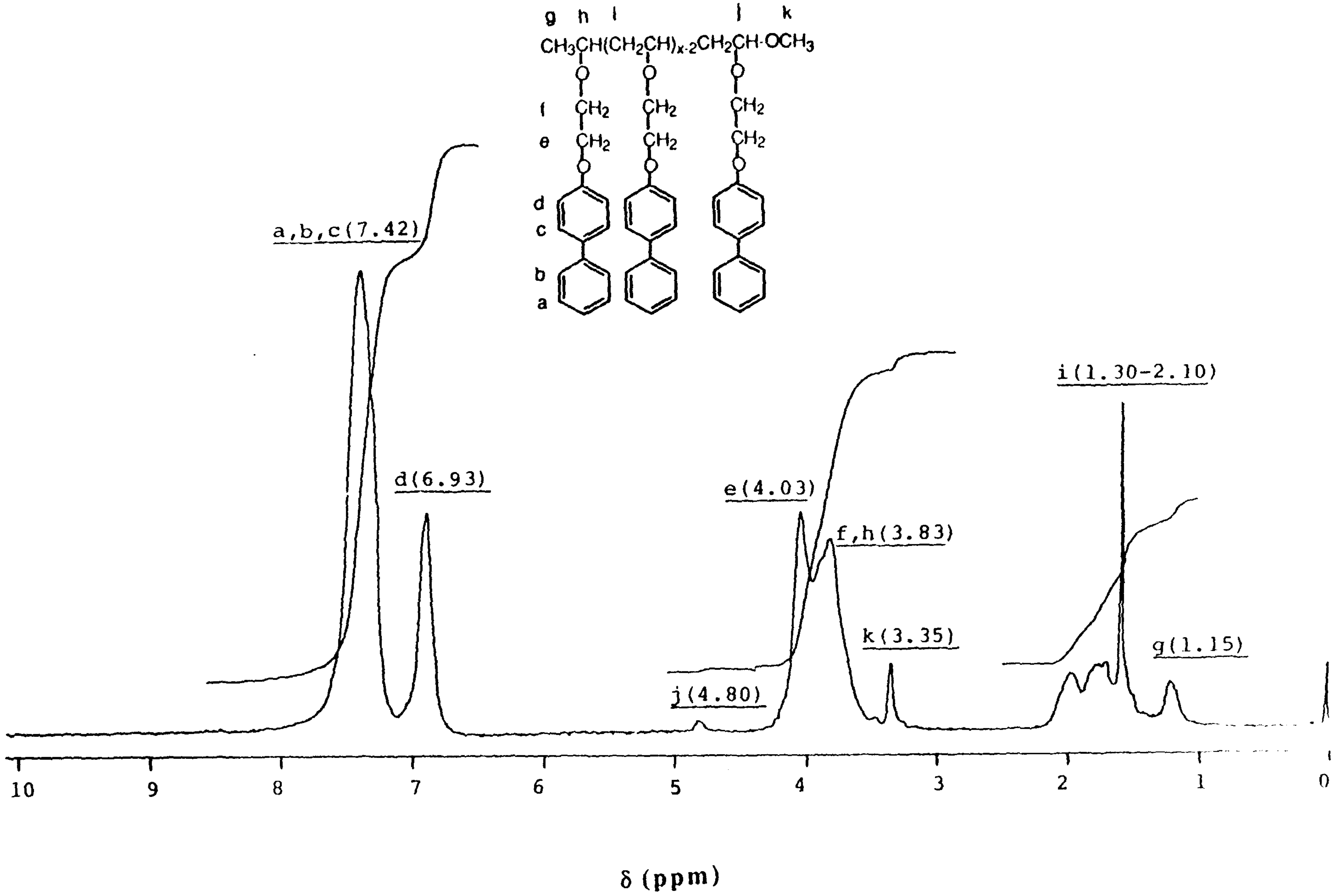
CH3OH
NH4OH
CH3CH(CH2CH)x-2CH2CH-OCH3

Scheme I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d
c
b
a
a,b,c(7.42)
d(6.93)
j(4.80)
e(4.03)
f,h(3.83)
k(3.35)
i(1.30-2.10)
g(1.15)
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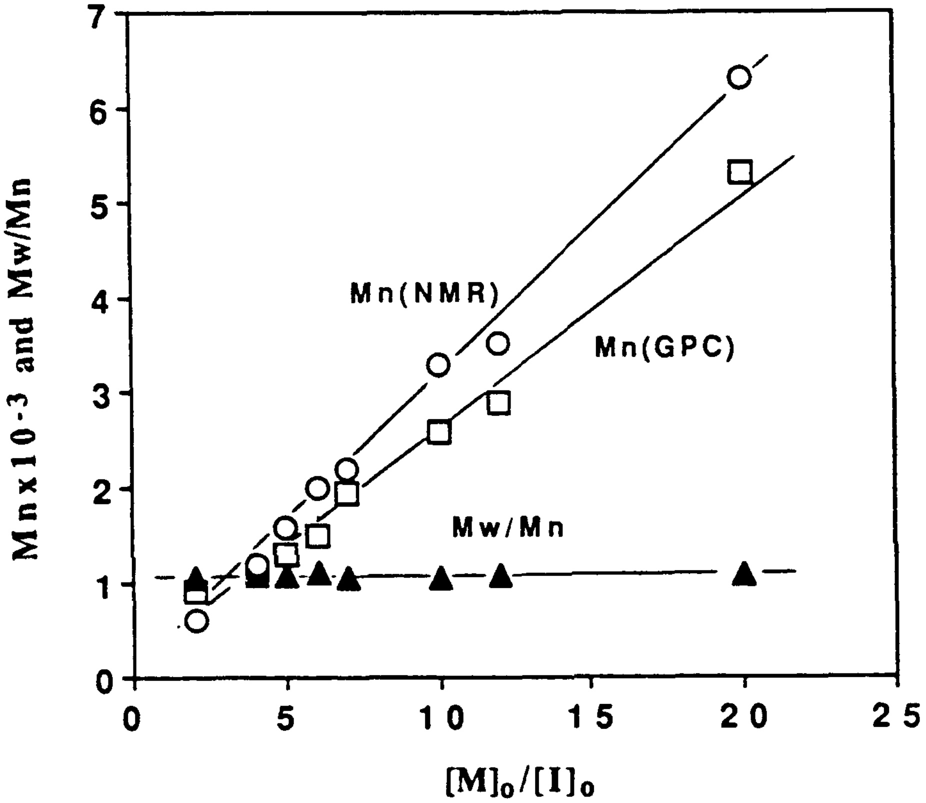
0
δ (ppm)

Figure 1



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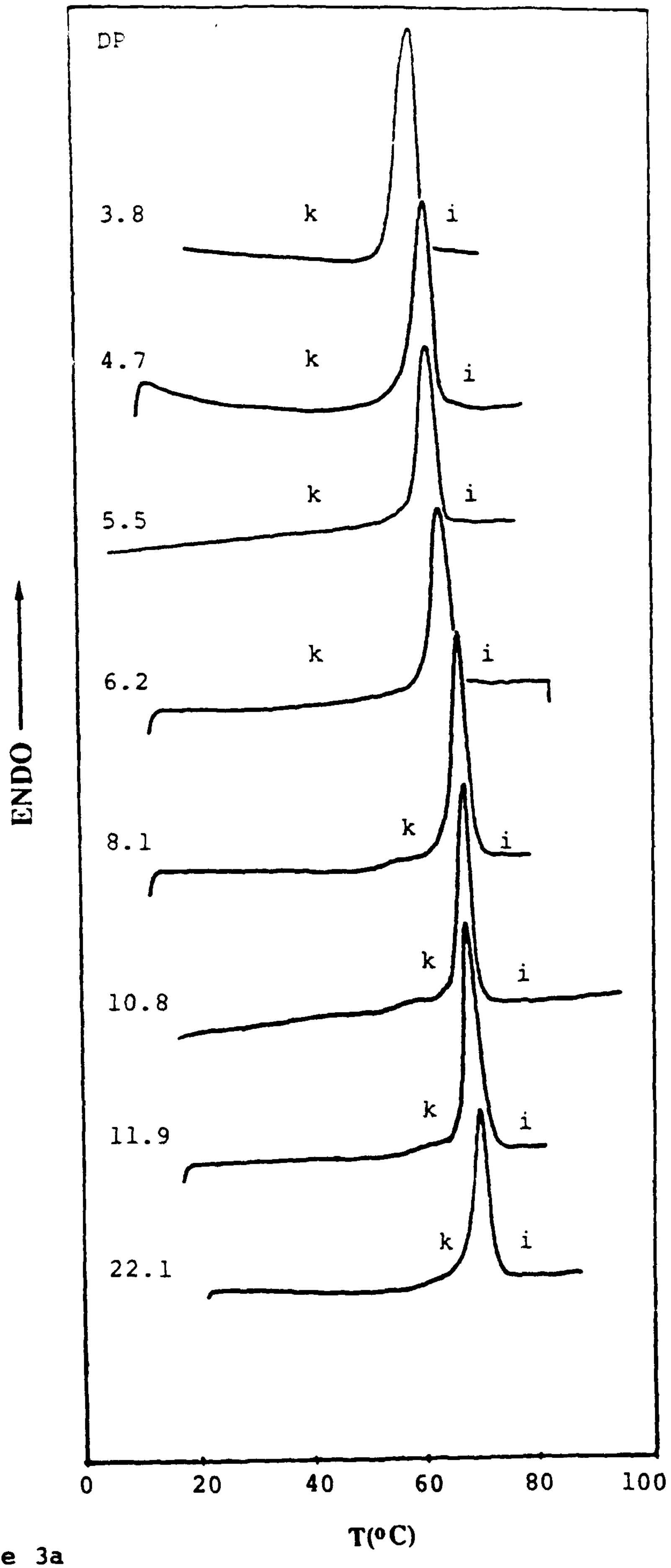
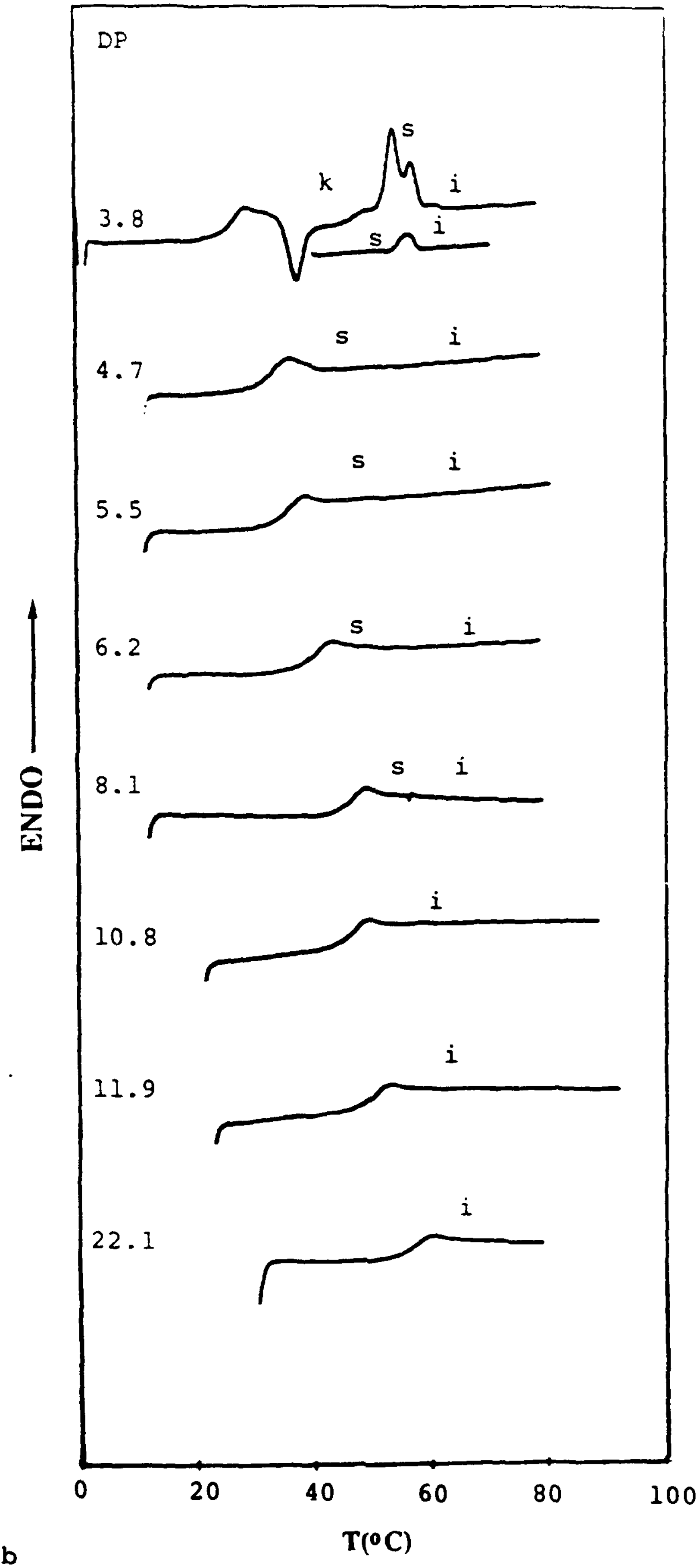


Figure 3a


DP
3.8
k
s
i
s
i
4.7
s
i
5.5
s
i
6.2
s
i
8.1
s
i
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ENDO
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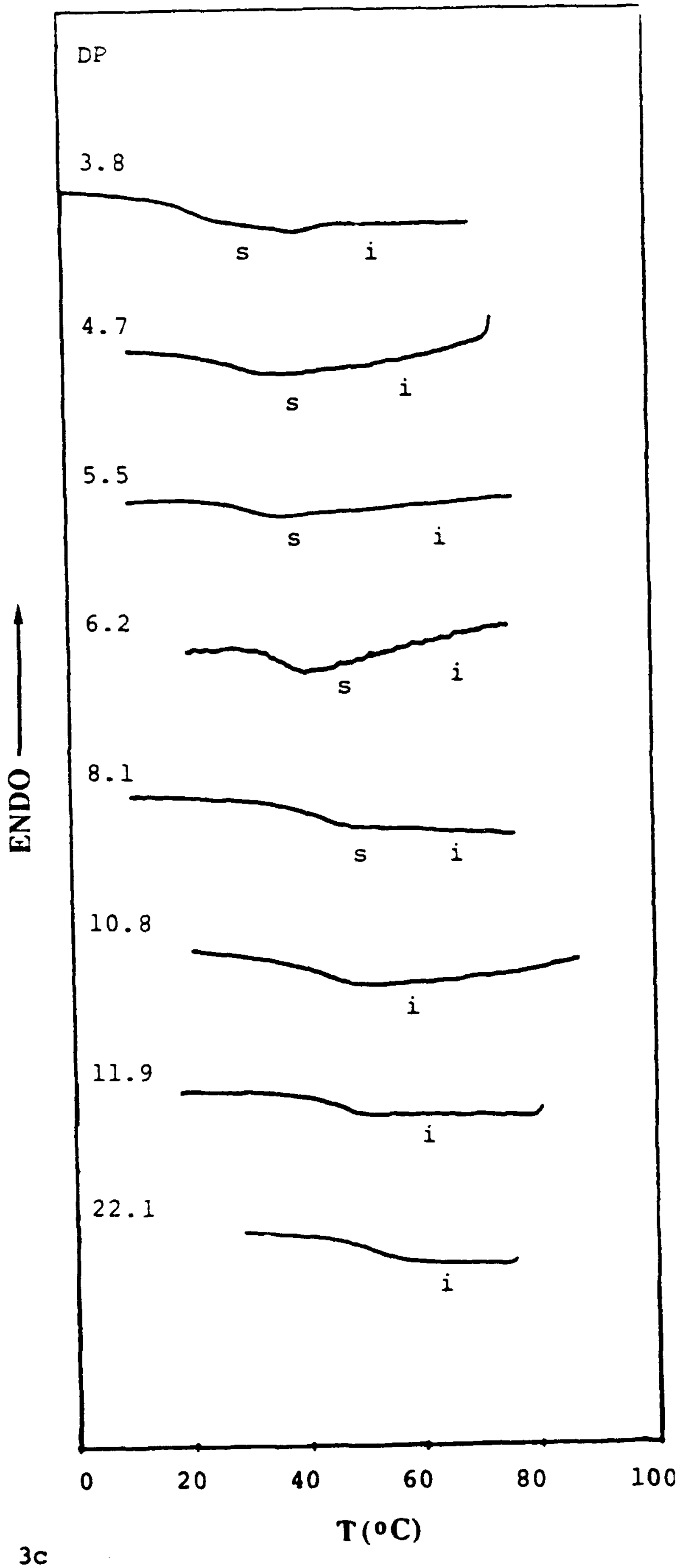
20
40
60
80
100
T(°C)

Figure 3b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s
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s
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i
ENDO
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20
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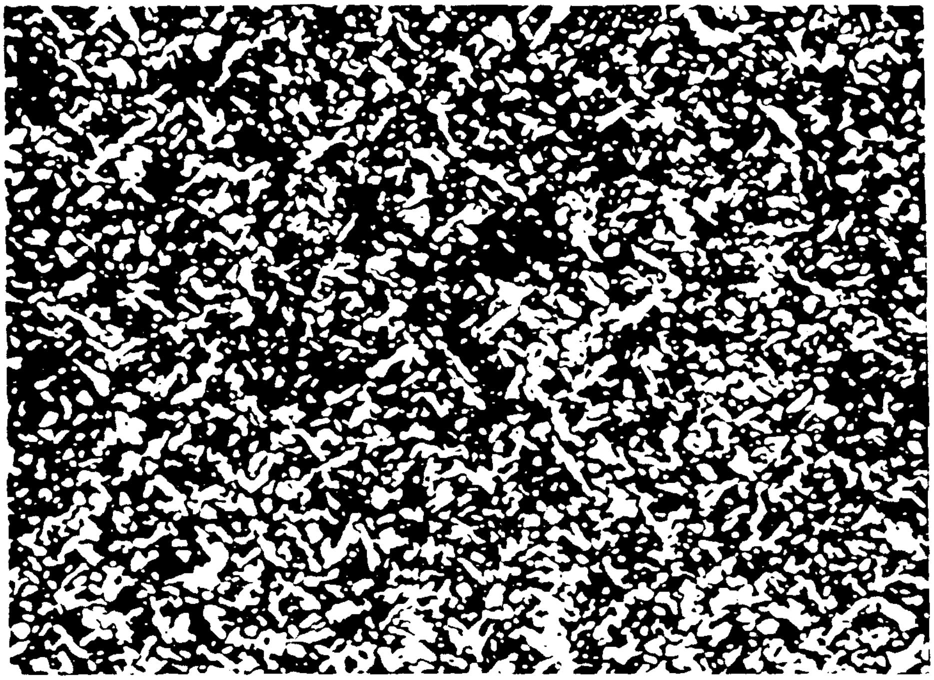
60
80
100
T(°C)

Figure 3c



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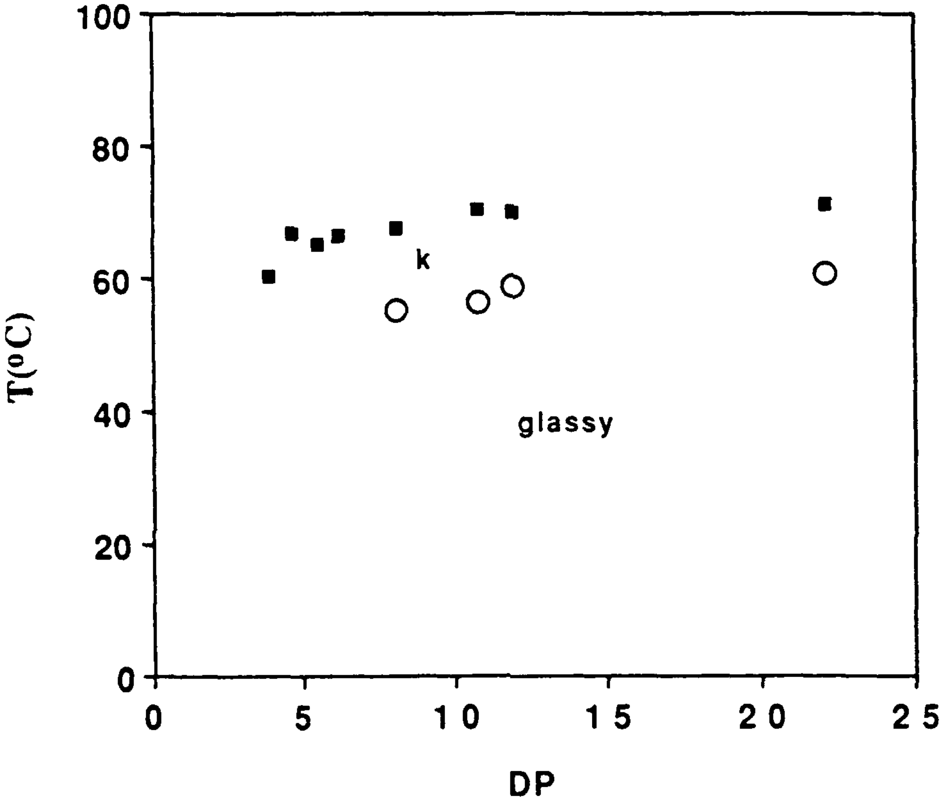

Figure 5a

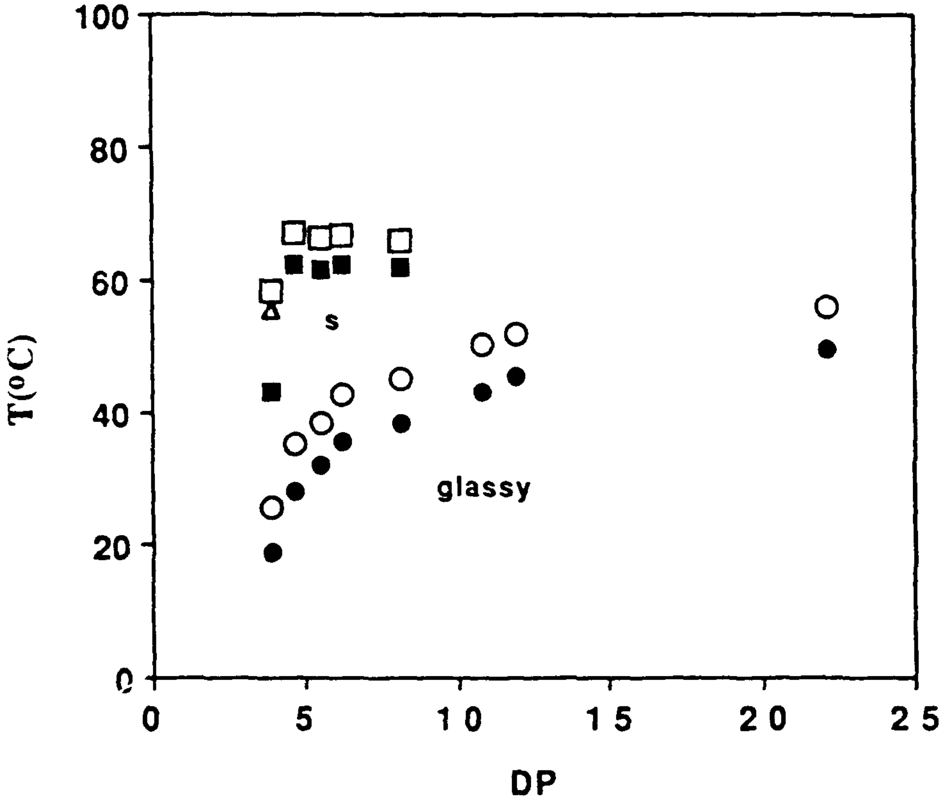

Figure 5b