Synthesis of aromatic polyethers by Scholl reaction

X. Synthesis and cation-radical polymerization of 1,5-bis(1-naphthoxy)-3-oxapentane*

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ABSTRACT
This paper describes the synthesis and cation-radical polymerization of 1,5-bis(1-naphthoxy)-3-oxapentane. This monomer contains a flexible diethylene oxide unit between two 1-naphthalene rings. The FT-IR analysis of the resulted polymer indicates that it contains 1,4-disubstituted naphthalene structural units, i.e. 4,4'-disubstituted-1,1'-binaphthalene units. The polymer is crystalline with a melting point of 236 °C.

INTRODUCTION
Functional aromatic polyethers such as polyether sulfones and polyether ketones are conventionally synthesized by variants of aromatic nucleophilic substitution or aromatic electrophilic substitution reactions.[1-9] Two novel approaches to the synthesis of these functional aromatic polyethers have been demonstrated by cation-radical polymerization of bisaryloxy derivatives by Scholl reaction[10-19] and by the homocoupling of aryl halides by Ni^0 catalyzed reactions.[20,21]

The cation-radical polymerization of 4,4'-bis(phenoxy)diphenyl sulfone, 4,4'-bis(phenylthio)diphenyl sulfone, and 4,4'-bis(phenoxy)diphenyl sulfone substituted with various electron-donating groups leads to polyether sulfones of only low molecular weight.[11] This is caused by the low polymerizability of these monomers. The polymerization of 1,5-bis(phenoxy)pentanes substituted with methyl groups is also accompanied by proton transfer reactions from the benzylic groups.[18] The cation-radical polymerization of bis(1-naphthoxy) monomers leads to high molecular weight polymers when tne starting monomers are 4,4'-bis(1-naphthoxy)diphenyl sulfone,[10] 4,4'-bis(1-naphthoxy)benzophenone,[10] α,ω-bis[4-(1-naphthoxy)phenylsulfonyl]perfluoroalkanes,[13] bis[4-(1-naphthoxy)phenyl]-methane,[14] 1,3- and 1,4-bis[4-(1-naphthoxy)phenylmethyl]-benzene,[14] 2,2'- and 3,3'-bis(1-naphthoxy)biphenyl,[15] 1,3-bis(1-naphthoxy)benzene,[15] and α,ω-bis(1-naphthoxy)alkanes.[12,22] However, the cation-radical polymerization of 4,4'-bis(2-naphthoxy)diphenyl sulfone led to polymers of multi-modal molecular weight distribution. The bis(1-naphthoxy) and bis(2-naphthoxy) monomers investigated so far are summarized in Scheme 1.

This communication presents some preliminary results on the synthesis and the cation-radical polymerization of the first monomer containing a flexible diethylene oxide central unit, i.e. 1,5-bis(1-naphthoxy)-3-oxapentane.
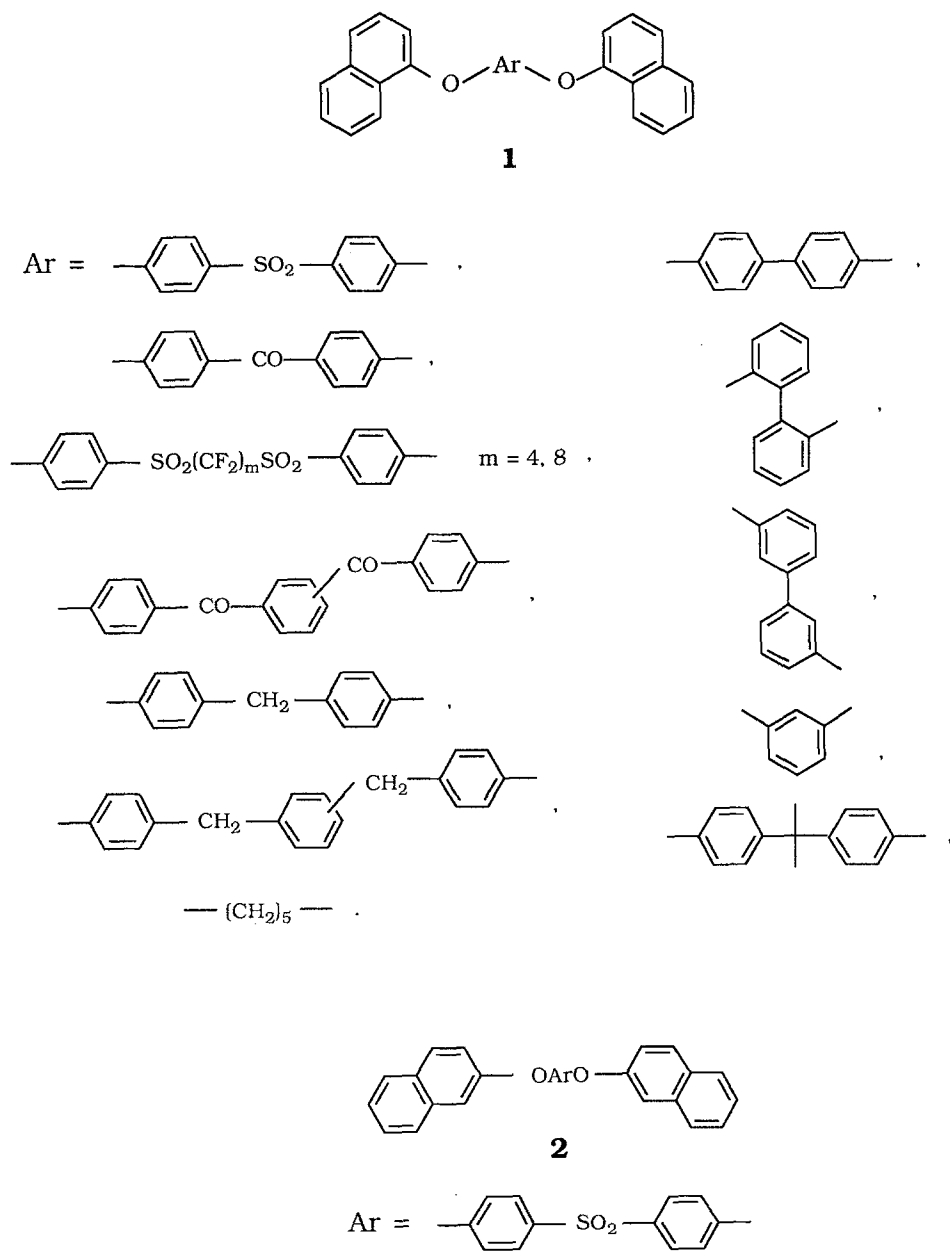
EXPERIMENTAL
Materials
1-Naphthol (3) (99%, Aldrich), FeCl3 (anhydrous, Aldrich), Bis(2-chloroethyl) ether (4, 99%, Aldrich), and K_2CO_3 (Fisher) were used as received. Dimethyl sulfoxide (DMSO, Fisher) was distilled from CaO. Nitrobenzene (PhNO2, Fisher) was distilled from CaH_2 under nitrogen. Other solvents were used as received.

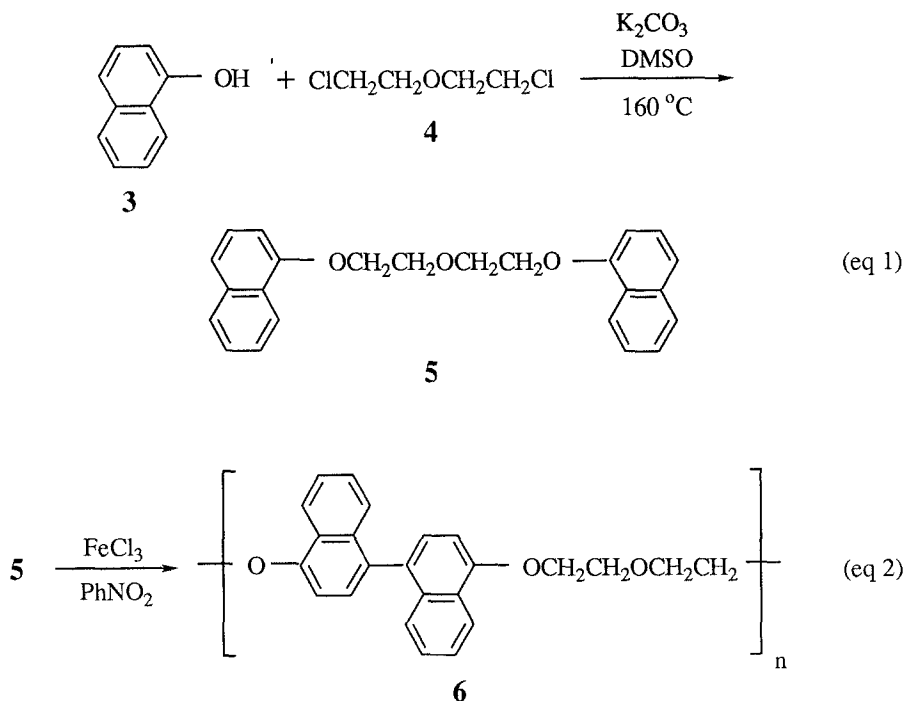*Part IX: V. Percec and J. H. Wang: J. Mater. Chem., in press
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1

Ar = (structures shown)

$-SO_2-$

$-CO-$

$-SO_2(CF_2)_mSO_2-$ m = 4, 8 ,

$-CO- \ CO-$

$-CH_2-$

$-CH_2- \ CH_2-$

$-(CH_2)_5-$.

$OArO$

2

Ar = $-SO_2-$

Scheme 1. Structure of bis(1-naphthoxy) and bis(2-naphthoxy) monomers polymerized by cation-radical reactions.

Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in CDCl$_3$ with TMS as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Bomen Michaelson 110 spectrometer equipped with a liquid nitrogen cooling and purging system and a mercury-cadmium-telluride detector. The spectra were recorded on neat samples using a diffuse reflectance (DRIFT) unit (Spectra-Tech), in the range of 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Purity was determined by high performance liquid chromatography (HPLC) performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven, an LC 600 autosampler, and a Nelson Analytical 900 series data station. The measurements were made using a UV detector set at 254 nm, chloroform as solvent (1 mL/min, 40°C), and a PL-gel column of 100 Å. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal properties of the polymers at a heating rate of 20°C/min. The inherent viscosity of the polymers was determined with an Ostwald viscometer in N-methyl-2-pyrrolidinone at a concentration of 0.5 g/dL at 50 $^{\circ}$C.

$$\text{3} \quad \text{OH} + \text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl} \xrightarrow[160\,^{\circ}C]{\substack{K_2CO_3 \\ DMSO}} $$

<center>4</center>

$$\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O} \qquad \text{(eq 1)}$$

<center>5</center>

$$\text{5} \xrightarrow[\text{PhNO}_2]{\text{FeCl}_3} \left[O \text{—} \text{—} OCH_2CH_2OCH_2CH_2 \right]_n \qquad \text{(eq 2)}$$

<center>6</center>

Scheme 2. Synthesis and cation-radical polymerization 1,5-bis(1-naphthoxy)3-oxapentane (5).

Synthesis of 1,5-Bis(1-naphthoxy)-3-oxapentane (5)

1-Naphthol (10.0 g, 69.4 mmol) was dissolved in a mixture of 80 mL dry dimethyl sulfoxide and 30 mL dry toluene. K$_2$CO$_3$ (12.5 g, 90.2 mmol) was subsequently added. The reaction flask was equipped with a nitrogen inlet, a thermometer, and a Dean-Stark trap equipped with a condenser. The reaction mixture was heated at 160 $^{\circ}$C until no more water was collected in the Dean-Stark trap. Then the mixture was allowed to cool to 70 $^{\circ}$C, and bis(2-chloroethyl) ether (3.3 g, 23.1 mmol) was added. The reaction mixture was stirred at

160 °C for 6 h. The cooled reaction mixture was poured into 800 mL cold water. The mixture was acidified with 5 N aqueous HCl, and the precipitate was collected by filtration. The resulting solid was dissolved in 100 mL toluene and washed three times with 2N aqueous NaOH, and then with water until neutral, dried over anhydrous $MgSO_4$, and decolored by activated carbon. The evaporation of toluene led to a dark brown oil. The oil crystallized upon the addition of 3 mL methanol. The crude crystalline solid was recrystallized in methanol/chloroform = 9/1 (v/v) and was subsequently purified by column chromatography (basic alumina, chloroform) yielding 5.2 g (62%) of white crystals. Purity (HPLC): 99.3%, mp. 85-86 °C. ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 4.13 (t, J = 5.0 Hz, -OC$\underline{H}_2$CH$_2$OAr), 4.35 (t, 4H, J = 5.0 Hz, -OCH$_2$C$\underline{H}_2$OAr), 6.82 (d, 2H, 2-$\underline{H}$ of the naphthalene unit), 7.31-7.50 (m, 8H, 3-, 4-, 6-, and 7-$\underline{H}$ of the naphthalene unit), 7.79 (m, 2H, 5-$\underline{H}$ of the naphthalene unit), 8.31 (m, 2H, 8-$\underline{H}$ of the naphthalene unit).

Polymerization Experiments

All polymerizations were performed under nitrogen in dry nitrobenzene, using FeCl$_3$ as oxidant. The detailed polymerization conditions are summarized in Table I. A typical polymerization example is provided below. 1,5-Bis(1-naphthoxy)-3-oxapentane (5, 0.36 g, 1.0 mmol) was dissolved in 1.0 mL dry nitrobenzene placed in a 25 mL three-neck flask equipped with a nitrogen inlet-outlet, and an addition funnel. A solution of 0.65 g FeCl$_3$ dissolved in 2.0 mL dry nitrobenzene was added dropwise under a stream of nitrogen over 20 min period. The reaction mixture was stirred at room temperature for 3 h. The content was precipitated into 200 mL methanol acidified with 2% HCl. The precipitate was dissolved in warm N-methyl-2-pyrrolidinone and precipitated into methanol. The precipitate was dried *in vacuo* to yield 0.33 g (92%) of polymer. The inherent viscosity of the polymer was 0.53 dL/g.
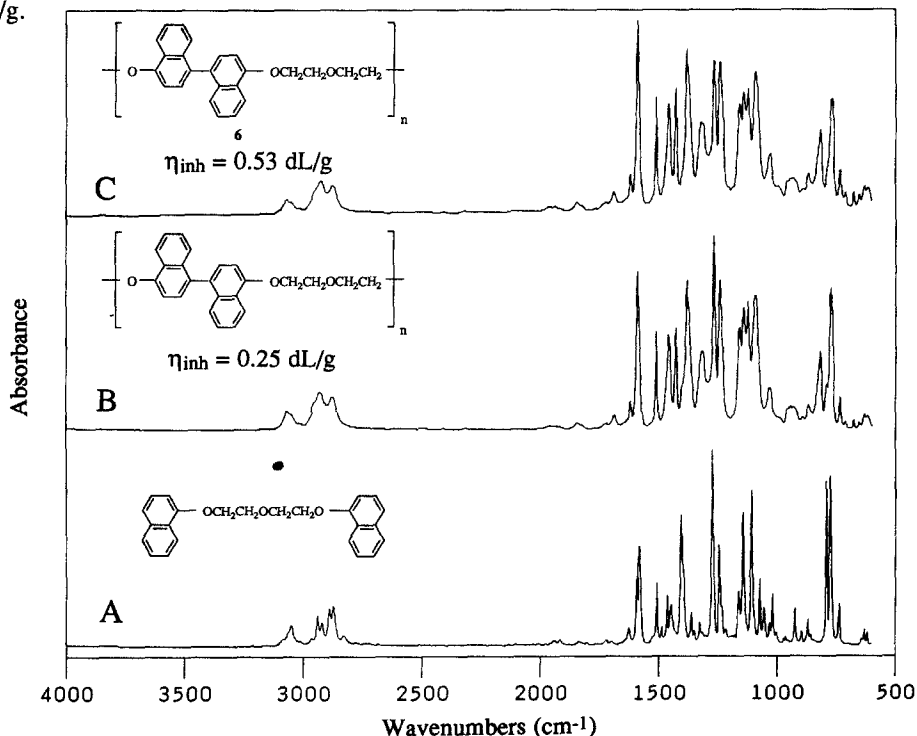

Figure 1. FT-IR spectra of 1,5-bis(1-naphthoxy)-3-oxapentane (**5**) (spectrum A) and polymers derived from **5**: spectrum B for sample 1 from Table I and spectrum C for sample 2 from Table I.

Table 1. Polymerization of 1,5-Bis(1-naphthoxy)-3-oxapentane (**5**). Polymerization Time, 4 h; Polymerization Temperature, 25°C.

Experiment No.	Monomer Solution		FeCl$_3$ Solution		Polymer			
	Monomer (mmol)	PhNO$_2$ (mL)	FeCl$_3$ (mmol)	PhNO$_2$ (mL)	Yield (%)	η_{inh}[a] (dL/g)	Tg (°C)	Tm (°C)
1	1.0	1.0	2.2	2.0	85	0.25	112	196
2	1.0	1.0	4.0	2.0	98	0.53	-	-

a) η_{inh} values were determined at 50 °C in N-methyl-2-pyrrolidinone at a concentration of 0.5 g/dL.

RESULTS AND DISCUSSION

The synthesis of 1,5-bis(1-naphthoxy)-3-oxapentane (5) is presented in eq 1 from Scheme 2. It is a   nucleophilic substitution of bis(2-chloroethyl) ether (4) by 1-naphthol (3).

The cation-radical polymerization of 1,5-bis(1-naphthoxy)-3-oxapentane (5) is presented in eq 2 from Scheme 2. The polymerization reactions were performed in nitrobenzene and were initiated by $FeCl_3$ oxidant. The results of the polymerization experiments are summarized in Table I. The polymerization performed at a $FeCl_3$/monomer molar ratio of 2.2/1.0 (experiment 1, Table I) produced 85% yield of polymer. The polymer has an inherent viscosity of 0.25 dL/g. A higher $FeCl_3$/monomer molar ratio (4.0/1.0) increased both the polymer yield (98%) and the inherent viscosity (0.53 dL/g) of the polymer. The polymers samples synthesized from 1,5-bis(1-naphthoxy)-3-oxapentane (5) are insoluble in boiling chloroform and tetrahydrofuran, consequently we are unable to determine the molecular weight distribution of the polymers. However, these polymers are soluble in N-methyl-2-pyrrolidinone in which the viscosity data were successfully determined at 50 °C.

The FT-IR spectra of neat 1,5-bis(1-naphthoxy)-3-oxapentane (5) and of the two polymers synthesized from 5 are presented respectively as spectra A, B and C in Figure 1. An expansion of the 600 to 1800 cm^{-1} region of the infrared spectra is shown in Figure 2. The most obvious change from the monomer 5 to polymers occurs in the region from 750 to 850 cm^{-1} region which corresponds to the aromatic C-H out of plane bending vibration modes. The substitution patterns of the naphthalene ring can be determined by both the frequences and the relative intensities of the bands in this region.
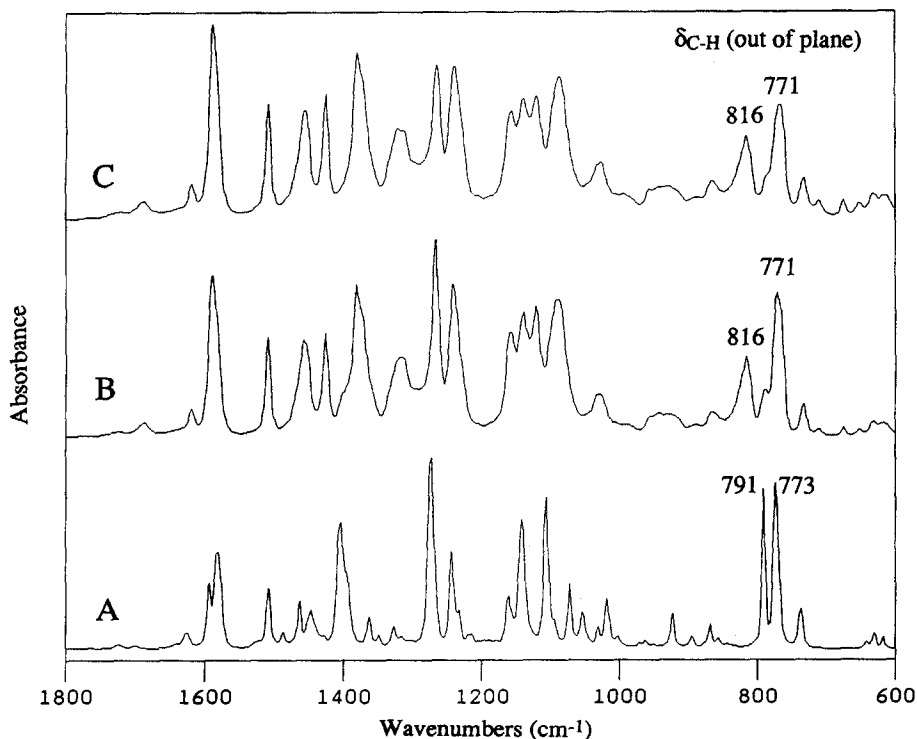

Figure 2.   An expansion of the 600 to 1800 cm^{-1} region of the FT-IR spectra of samples from Figure 1.

Spectrum A exhibits two bending absorption bands at 773 and 791 cm^{-1} with the band at 773 cm^{-1} slightly stronger in intensity than that of the band at 791 cm^{-1}. This pattern is characteristic of the 1-alkoxynaphthalene.[23] In the same spectral region, both polymers display two bands at 771 and 816 cm^{-1}. The frequences of these two bands and their relative intensities resemble closely those of 1,4-disubstituted naphthalene. For example, 1,4-dimethylnaphthalene and 1-bromo-4-methylnaphthalene have two bands at about 820 and 750 cm^{-1} with similar relative intensities.[24] Therefore, these polymers contain 1,4-disubstituted naphthalene structural units, i.e. 4,4'-disubstituted-1,1'-binaphthalene units, as expected from the polymerization reaction (eq 2, Scheme 2). The amount of the less favorable 1,2-disubstituted naphthalene structural unit is below the detection limit of the FT-IR technique, since this type of structure should have three bands at 805, 770 and 740 cm^{-1} of about similar intensities.[25]

The insolubility of the polymers containing flexible diethylene oxide unit is caused by their crystalinity. This is demonstrated by the DSC trace of the polymer (experiment 1, Table I) shown in Figure 3. The polymer exhibits a small melting endotherm at 168 °C and a major endotherm at 196 °C. The initial melting was followed by a recrystallization exotherm at 209 °C and a second melting at 236 °C. Therefore the crystallinity of the polymer limits the solubility of the polymers. The glass transition temperature of the polymer is 112 °C.
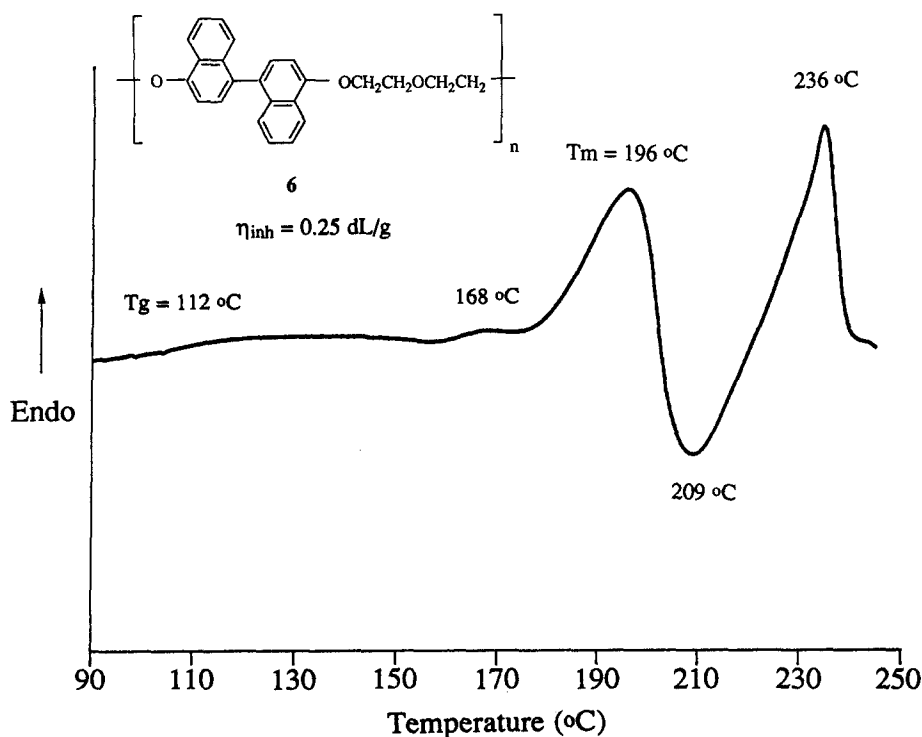

Figure 3. DSC trace of the polymer synthesized from 1,5-bis(1-naphthoxy)-3-oxapentane (5) (sample 1 from Table I).

The polymers synthesized from the monomers listed in Scheme 1 with a rigid central group are amorphous.[10-19] As the rigidity of the polymer backbone decreases by the introduction of $-(CH_2)_n-$ groups, crystalline polyethers are obtained.[22] The glass transition temperature of polymer containing diethylene oxide unit is lower than the corresponding temperature of polymers containing a $-(CH_2)_5-$ group ($Tg = 143^\circ C$).[22] This is as expected since the diethylene oxide unit is more flexible than the $-(CH_2)_5-$ group.

ACKNOWLEDGMENT

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