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Synthesis of a novel comb-like poly(vinyl ether) with isopropylnaphthoxy pendant by cationic polymerization

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SUMMARY

A novel comb-like polymer having isopropylnaphthoxy pendant with the controlled molecular structure was synthesized by the cationic polymerization of 2-(6-isopropyl-2-naphthoxy)ethyl vinyl ether with $AlEtCl_2$ catalyst. Although the polymer's molecular weight (Mn: 4,000-17,000) could be controlled by the reaction conditions (sovent polarity, temperature and initial monomer concentration), the steric structure was not affected by them at all, giving almost the same amount of the meso and racemic diads irrespective of the conditions. The polymer showed only an amorphous character (Tg: 22-45 ℃) but not any liquid crystalline phase.

INTRODUCTION

One of the most important properties of the so-called comb-like polymers is their capacity to form a liquid crystalline (LC) phase by incorporating a rigid-rod mesogenic side chain into a polymer structure(1). And many types of side-chain liquid crystalline polymers (LCP), with different structures both of main chains and mesogenic side chains, have been synthesized and their properties have been investigated(2).

Since the first examples of LC poly(vinyl ether)s with narrow molecular weight distributions (MWD) by the use of living cationic polymerization were reported by Sagane and Lenz(3,4), several research groups in the world have been actively engaged in the living polymerization of mesogenic vinyl ethers(5,6), because the effect of the polymer's molecular weight on the phase transitions can be determined without the undue influence of the low and high molecular weight components. From the industrial point of view, however, the cationic polymerization using a conventional and inexpensive catalyst (for example, metal halides, alkyl metal halides and so on), though less controlled mannar, is also attractive, because the simplified polymerization process and catalyst system can be applied.

In the present study, we turned our attention to synthesis of a novel poly(vinyl ether) with an isopropylnaphthoxy pendant using ethylaluminium dichloride ($AlEtCl_2$), one of alkyl metal halides, as a catalyst. That is, polymerizations of 2-(6-isopropyl-2-naphthoxy)ethyl vinyl ether (I) were carried out with the catalyst, in order to extend the range of cationically obtained comb-like poly(vinyl ether)s with aromatic-rigid pendants. This 6-isopropyl-2-naphthoxy pendant structure was chosen, because there are some

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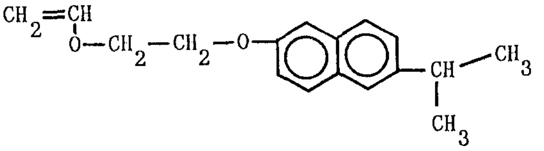
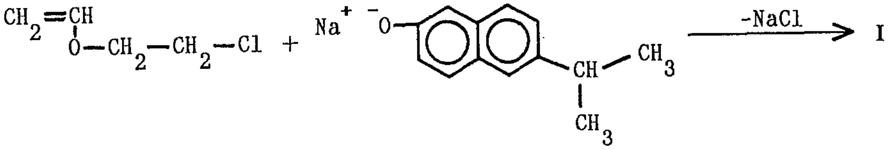
examples of the 2,6-naphthylene structure containing main-chain LCP's(7), and because 6-isopropyl-2-naphthol, the precursor of the monomer I, is available as a by-product of 2,6-dihydroxynaphthalene. Furthermore, the side-chain LCP with that structure as a pendant, to our knowledge, has not been reported so far. The first objective, therefore, was to examine whether the poly I could show a LC phase or not. And the second objective was to investigate the effect of polymerization conditions (solvent porality, temperature and so on) on the molecular weight, thermal properties and steric structure of the polymer. Unfortunately, this novel poly(vinyl ether) did not show any LC phase but only a glass transition as described below.



(I)

EXPERIMENTAL

Monomer Synthesis. 2-(6-isopropyl-2-naphthoxy)ethyl vinyl ether (I) was prepared by the phase-transfer-catalyzed condensation of 2-chloroethyl vinyl ether (Tokyo Kasei, purity 97%) with 6-isopropyl-2-naphthol (Mitsui Petrochemical, mp 112 ℃, purity 98%) in the presence of sodium hydroxide (equivalent to the naphthol) and a catalitic amount of tetrabutylammonium hydrogen sulfate(8), as shown below:



I was purified by recrystallization from ethanol three times; the isolated yield ca. 66% (based on the 6-isopropyl-2-naphthol charge), yellow needle-like crystal with mp 62 ℃ (by DSC), purity > 99 % by gas chromatography. The chemical shifts of the ^{1}H- and ^{13}C-NMR spectra of the monomer (I) are summarized in Table 1.

Procedures. Solvents were distilled over calcium hydride before use. $AlEtCl_2$ (Tosoh Akzo) was used as received. Polymerizations were carried out as reported(3,4). Polymer yield was determined by gravimetry. The molecular weight distribution (MWD) of the polymers was measured by gel-permeation chromatography (GPC) in chloroform solutions at room temperature on a Waters liquid chromatograph (150-C ALC/GPC) epuipped with a polystyrene gel column (7.5mmID × 60cm) and a UV detector (254nm). The $\overline{Mn}$ and $\overline{Mw}$ were calculated from GPC curves on the basis of a polystyrene standard calibration. ^{13}C- and ^{1}H-NMR spectra were recorded on a JOEL GX-500 spectrometer (125.8 MHz and 500 MHz, respectively) in $CDCl_3$ at 45℃.

Thermal analysis was carried out by differential scanning calorimetry (DSC) on a Seiko DSC-220C instrument with polymer samples of about 10mg under a nitrogen flow at a scanning rate of 10℃ per min.

Table 1.

^{1}H- and ^{13}C-NMR chemical shifts for the monomer (I) and the polymer.1)

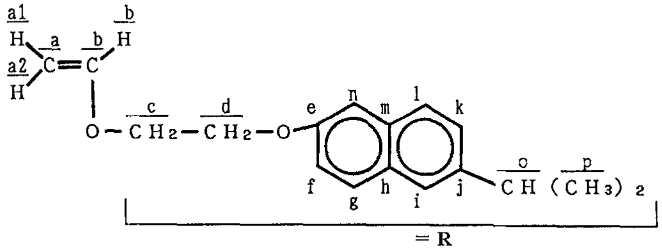
	^{1}H-NMR2)		^{13}C-NMR	
	δ (ppm)	proton	δ (ppm)	carbon
Monomer3)	1.35 (d)	p	23.9	p
	3.05 (septet)	o	33.9	o
	4.09 (d of d)	a1	66.4	c
	4.11 (t)	c	66.5	d
	4.29 (d of d)	a2	87.1	a
	4.33 (t)	d	107.0	n
	6.56 (d of d)	b	118.7	f
	7.14 (d)	n	123.9	i
	7.16 (d of d)	f	126.1	k
	7.36 (d of d)	k	126.8	l
	7.60 (d)	i	129.1	g
	7.67 (d)	l	129.4	h
	7.70 (d)	g	133.0	m
			144.1	j
			151.6	b
			156.2	e
Polymer4)	1.1-1.4	p	39.4, 41.1	a'
	1.6-2.1	a'	74.3	b'
	2.8-3.0	o		
	3.6-4.1	b', c, d	other carbons in R5)	
	6.8-7.6	f, g, i k, l, n		

1) Chemical shifts are given in ppm relative to TMS.

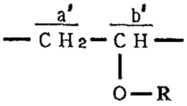
2) ^{1}H-^{1}H coupling constants (unit: Hz) are listed below:

$J_{a1,a2}$	$J_{a1,b}$	$J_{a2,b}$	$J_{c,d}$	$J_{f,g}$	$J_{f,n}$	$J_{i,k}$	$J_{k,l}$	$J_{o,p}$
2.2	7.0	14.3	6.8	8.9	2.5	1.7	8.4	7.0

3)



4)



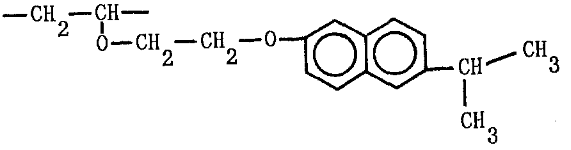
5) The signals of the pendant group (R) are at almost the same position as those of the monomer.

RESULTS AND DISCUSSION

1. Polymerization and Polymer Structure

Cationic polymerizations of the monomer **I** were carried out at 0 or -30 °C with $AlEtCl_2$ under various conditions. The results are listed in Table 2. The polymerization was relatively fast, reaching ca. 90 % polymer yield in 10-300 min, except for the samples obtained at the lower temperature and in CH_2Cl_2 solvent (samples D and E). All polymers were soluble in toluene and $CHCl_3$ at room temperature. The molecular weight distributions (MWD) of the polymers were shown in Figure 1. They exhibited wide MWD's, $\overline{Mw}/\overline{Mn}$ of 3.8-5.7, originating from $AlEtCl_2$ catalyst employed. As can be seen both in the $\overline{Mn}$ and $\overline{Mw}$ data in Table 2 and the MWD in Figure 1, a higher molecular weight was obtained in a more polar solvent, at a higher initial monomer concentration, $[M]_0$, and at a lower temperature, as normally observed in ionic polymerizations.

All the polymers (A - F) gave the expected comb-like structure **II**, formed only by the addition reaction of the double bonds in the vinyloxy groups, as shown by the NMR results in Table 1 and Figure 2.



(II)

Table 2.
Cationic polymerization of
2-(6-isopropyl-2-naphthoxy)ethyl vinyl ether (**I**) with $AlEtCl_2$

Sample code	Polymn. Conditions$^{a)}$				Polymer yield (wt%)	$\overline{Mn}^{c)}$	$\overline{Mw}^{c)}$	$\overline{Mw}/\overline{Mn}^{c)}$	$Tg^{d)}$ (°C)
	Solvent	$[M]_0$ (M)	Temp. (°C)	Time (min)					
A$^{b)}$	toluene	0.2	0	300	95	4,000	18,000	4.5	22
B	CH_2Cl_2	0.2	0	180	87	7,000	26,500	3.8	34
C	CH_2Cl_2	0.5	0	60	92	11,000	46,500	4.2	43
D	CH_2Cl_2	0.5	-30	180	53	14,100	73,700	5.2	43
E	CH_2Cl_2	1.0	-30	180	70	16,400	76,100	4.6	45
F	nitroethane	1.0	-30	10	97	16,900	96,800	5.7	41

a) $[AlEtCl_2]_0$ = 10.0 mM.

b) $[H_2O]_0$ = 5.0 mM.

c) Determined by GPC calibrated with standard polystyrene samples.

d) Taken from the second heating cycle (at 10°C/min).

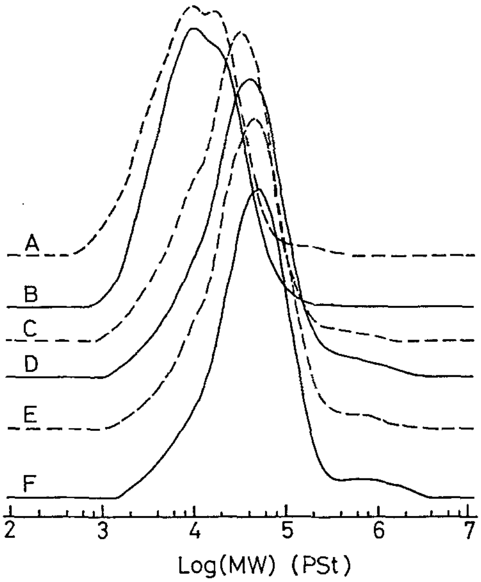


Figure 1. MWD's of the polymer obtained from **I**. Sample codes as indicated: see Table 2 for reaction conditions.

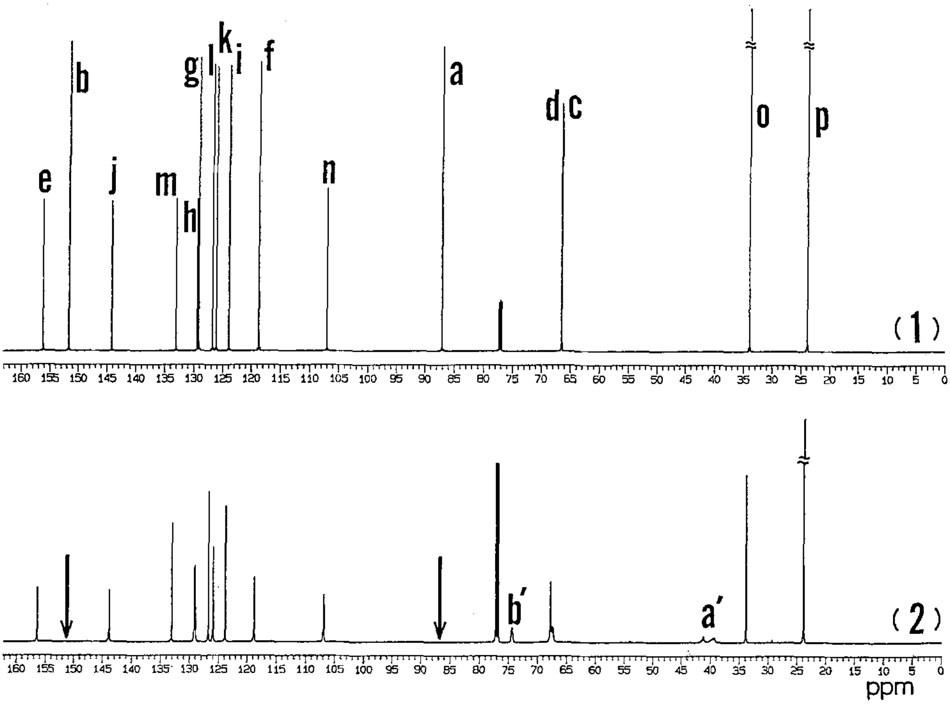


Figure 2. ^{13}C-NMR spectra of (1) **I** and (2) poly **I** obtained with $AlEtCl_2$ in CH_2Cl_2 at 0 ℃ (sample C): see Table 1 for designation of carbons.

2. Thermal Properties of the Polymers

The DSC thermograms of all the polymers showed only glass transitions but not any endo- nor exotherm peaks attributed to LC phases. To determine if there was any effect caused by the cooling rate on the thermal properties, a slow cooling rate of 2.0 ℃/min in the DSC measurement was also applied to all samples. No transition peaks, however, were observed for the samples, and their DSC thermograms were identical with those obtained at the higher scanning rate (10 ℃/min). The phenomenon that the poly **I** did not show any LC phase is consistent with the following fact. That is, the low molecular weight LC compounds with 2,6-disubstituted naphthalene ring gives lower isotropization temperature than the corresponding biphenyl compounds, because of the molecule's broadened structure against the long axis(9).

The Tg's of the polymers taken from the second heating cycle ranged from 22 to 45 ℃, depending on their molecular weight, as shown in Figure 3. As observed for other poly(vinyl ether)s with aromatic rigid pendants, which exhibited no LC phase, for example, polymers from 2-(4-biphenyloxy)-ethyl vinyl ether (Tg = 56 ℃)(3) and from 2-(4-biphenylcarboxyl)ethyl vinyl ether (Tg = 32 ℃)(3), introduction of a rigid-bulky isopropyl-naphthoxy pendant group into a polymer chain also increased the Tg of poly(vinyl ether)s, in comparison with flexible alkyl groups in poly(alkyl vinyl ether)s (Tg = -33 ℃ for ethyl, -49 ℃ for propyl, and -56 ℃ for butyl)(10).

3. Steric Structure of the Polymers

The polymer's molecular weight was found to be controlled by the polarity of the polymerization medium (temperature and solvent polarity) as described above. To investigate if there was any effect of the polarity on the propagating species derived from the monomer **I**, the steric structures of the polymers obtained by the different conditions were then compared by ^{13}C-NMR spectroscopy. Figure 4 shows the main-chain methylene signals, which consist of two peaks corresponding to the meso and racemic diads from the higher field(11).

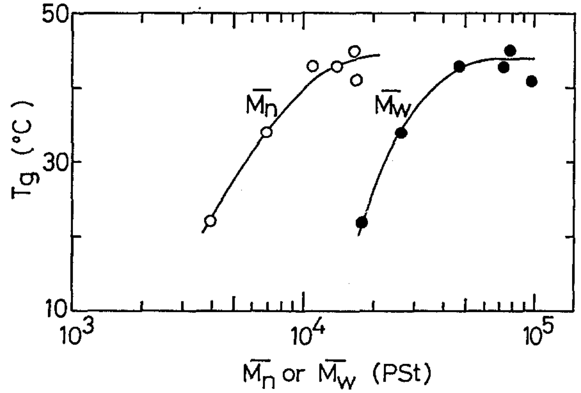


Figure 3. Tg of poly **I** as a function of $\overline{M}n$ and $\overline{M}w$.

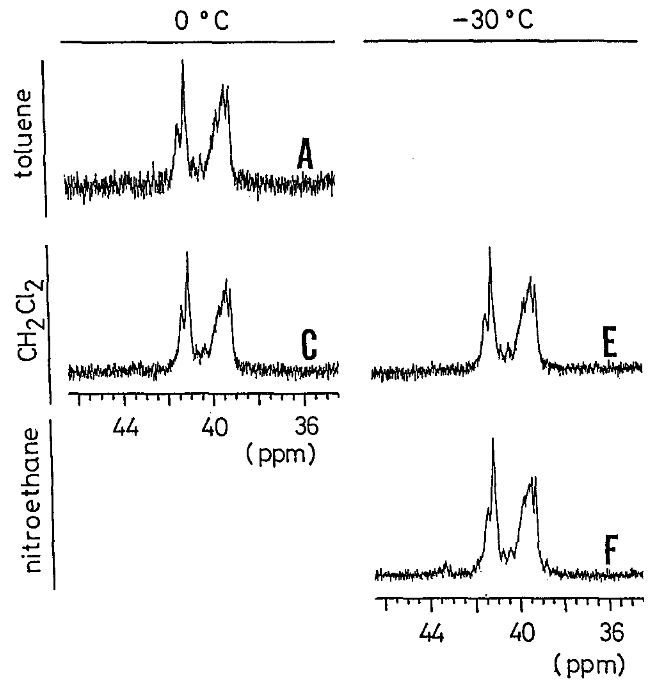


Figure 4. Partial ^{13}C-NMR spectra (main-chain methylene region) of poly I. Polymerization temperatures, solvents and sample codes as indicated: see Table 2 for reaction conditions.

The spectrum of the sample A [Figure 4(A)], obtained in nonpolar toluene solvent at 0 ℃, is similar to those of other samples C, E, and F [Figures 4(C),(E), and (F)] obtained in the higher polarity conditions, and all the samples had almost the same amounts of the meso and racemic diads. Poly(alkyl vinyl ether)s obtained cationically in a polar solvent were reported to be racemic-diad rich, where the active end should be highly dissociated, whereas that obtained in a nonpolar solvent had meso-rich diads(12,13). From the results that the polarity of the medium did not affect the steric structure of the polymer from I, it might be concluded that the propagating end derived from the monomer I is rather dissociated irrespective of the solvent polarity through the intramolecular self-solvation of the neighboring oxyethylene units in the 2-(6-isopropyl-2-naphthoxy)ethyloxy pendant, as proposed by Higashimura for the poly(vinyl ether)s with polyoxyethylene pendants(13).

In conclusion, a novel comb-like poly(vinyl ether) having isopropyl-naphthoxy pendant with the well-defined molecular structure could be synthesized from the monomer of 2-(6-isopropyl-2-naphthoxy)ethyl vinyl ether with $AlEtCl_2$ catalyst. Although the polymer's molecular weight could be controlled by the polarity of the medium, it did not affect the steric structure at all. Unfortunately, the polymer showed only an amorphous character (Tg: 22-45 ℃) but not any LC phase.

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