

Effects of Molecular Weight Distribution on the Thermal Properties of Side-Chain Liquid Crystalline Poly(vinyl ether)s

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ABSTRACT: Three biphenyl-containing vinyl ether monomers: 2-(4-biphenyloxy)ethyl vinyl ether (**I**), 2-(4-biphenylcarboxyl)ethyl vinyl ether (**II**), and 2-(4'-methoxy-4-biphenyloxy)ethyl vinyl ether (**III**), were cationically polymerized with the hydrogen iodide/iodine (HI/I₂) initiator system to form living polymers with narrow molecular weight distributions. The thermal properties of the polymers were determined by DSC and by visual observations of samples placed on a hot stage on a polarizing microscope. Polymer **I** and Polymer **II** formed only isotropic melts, but Polymer **III** showed enantiotropic, liquid-crystalline (LC) behavior, and formed both smectic and nematic phases after one heating and cooling cycle. For comparison, polymers were also prepared with boron trifluoride etherate (BF₃OEt₂) as the initiator. Polymer **III** obtained with this initiator had a much broader molecular weight distribution and formed only a nematic phase. At approximately the same molecular weight, this sample also had a much higher isotropization temperature than the narrow distribution sample of Polymer **III**.

KEY WORDS Side-Chain Liquid Crystalline Polymer / Poly(vinyl ether) / Cationic Living Polymerization / Biphenyl Group / 2-(4'-Methoxy-4-biphenyloxy)ethyl Vinyl Ether / Molecular Weight Distribution / Monodisperse Polymer / Hydrogen Iodide-Iodine Initiator /

Liquid-crystalline polymers (LCP) can contain mesogenic units either in the main chain or in the side chain, and both types are of theoretical and practical interest.¹ In contrast to the main chain LCP, the liquid-crystalline order of side chain LCP is generally closely related to that of the monomer,² so side chain LCP are of value for investigations on the relationship between mesogenic unit structure and mesophase type in polymers as compared to low molecular weight mesogens.

Side-chain LCP can be prepared by three different routes including addition polymerization, condensation polymerization and post-reactions of polymers.² Among the three

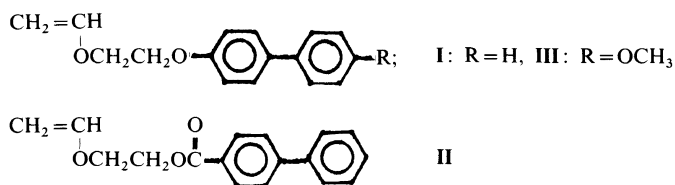
methods, the most convenient approach is to introduce the mesogenic unit beforehand into a reactive monomer capable of undergoing addition or chain-growth polymerization.² However, for the most part, the side chain LCP prepared by chain-growth polymerization have been limited to polymethacrylates,³ polyacrylates,³ and polystyrene derivatives,⁴ and very few of these investigations were concerned with the control and effect of molecular weight distribution on the properties of the LCP. One example of such control is the preparation of polymethacrylates by group-transfer polymerization,⁵ but the molecular weight distributions of these polymers

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were still quite broad ($\bar{M}_w/\bar{M}_n = 1.2-1.8$).

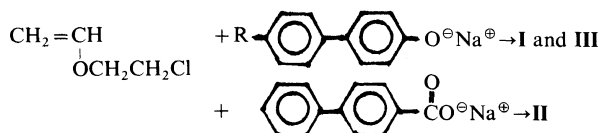
Recently, Higashimura and coworkers have developed a new living cationic polymerization procedure for vinyl ethers and propenyl ethers using an HI/I₂ initiator system.⁶⁻⁸ By this technique, in contrast to conventional cationic polymerization, even vinyl ethers containing polar groups can be polymerized in a polar solvent such as CH₂Cl₂ to form living polymers. Our goal, therefore, was to prepare side chain LC poly(vinyl ethers)s with con-

trolled molecular weight distributions by using this type of living cationic technique. If polymers with narrow distributions could be made in this manner, the effect of molecular weight on thermal properties could be determined without the undue influence of the component low and high molecular weight fractions. For this purpose, poly(vinyl ethers) were prepared by the living cationic polymerization of monomers containing biphenyl groups, including (I), (II), and (III) below:



The cationic polymerization reactions of (I) and (III)⁹ initiated with conventional Lewis acids were previously reported, and as expected, these reactions yielded polymers with broad molecular weight distributions. Living cationic polymerization reactions of (I), (II), and (III), which were carried out in the present study, gave narrow molecular weight distributions, as described below.

Monomers (I), (II), and (III) were prepared by the phase transfer-catalyzed condensation of 2-chloroethyl vinyl ether with 4-phenylphenol,⁹ sodium-4-phenylbenzoate,¹⁰ and 4-(4'-methoxyphenyl)phenol,⁹ respectively, in the presence of a catalytic amount of tetrabutylammonium hydrogen sulfate or tetrabutylammonium iodide as shown below:



The three monomers were purified by recrystallization from methanol, and the melting points and the chemical shifts of the ¹H NMR spectra of the monomers are summarized in Table I.

EXPERIMENTAL

The hydrogen iodide (HI), iodine (I₂), and boron trifluoride etherate (BF₃OEt₂) initiators and the solvents (toluene, dichloromethane, and *n*-hexane) were purified and used as pre-

viously reported.⁶

Polymerization Procedures

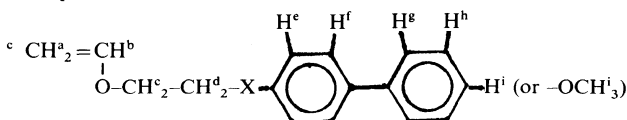
Cationic polymerization reactions were carried out in predried Schlenk tubes equipped with a three-way stopcock under a dry nitrogen atmosphere after the solid monomers were degassed. The reactions with BF₃OEt₂ were carried out by adding the initiator solution to the monomer solution, but for the HI/I₂ initiator, an HI solution in *n*-hexane was added to the monomer solution, and an iodine

Table I. Characterization of the monomers

Monomer	$T_m^a/^\circ\text{C}$	$T_d^b/^\circ\text{C}$	$T_c^b/^\circ\text{C}$	^1H NMR chemical shift		
				η/ppm	Proton ^c	Ratio
(I)	79	—	63	3.90—4.40 (m)	a, c, d	6
				6.55 (d of d)	b	1
				6.95—7.10 (m)	e	2
				7.25—7.70 (m)	f, g, h, i	7
(II)	76	—	37	4.05—4.25 (m)	a, c	4
				4.60 (m)	d	2
				6.53 (d of d)	b	1
				7.35—7.50 (m)	h, i	3
				7.60—7.70 (m)	f, g	4
(III)	121	109 ^d	105 ^d	3.82 (s)	i	3
				3.90—4.35 (m)	a, c, d	6
				6.55 (d of d)	b	1
				6.85—7.05 (m)	h, e	4
				7.40—7.55 (m)	f, g	4

^a Determined by DSC (taken from the 2nd heating cycle thermogram).

^b Determined by DSC (taken from the 1st cooling cycle thermogram). T_d , deisotropization temp; T_c , recrystallization temp.



I, X=O; II, X=OC(=O); III, X=O.

^d Monotropic liquid crystalline phase was identified with the polarizing microscope (mosaic texture characteristic of smectic phase was observed).

solution was then added to this mixture to initiate polymerization. The reactions were terminated with cold ammoniacal methanol. The quenched polymerization solution was washed as previously reported,⁷ and the conversion of monomer was determined by gel permeation chromatography (GPC, see conditions shown below). All polymers were purified by precipitation from CH_2Cl_2 solutions into methanol and were dried in vacuum.

Characterization of Monomers and Polymers

The molecular weight distribution of the polymer was measured by GPC on samples in CHCl_3 solutions on Waters Associates, Inc., liquid chromatograph equipped with five poly-

styrene gel columns (8 mm \times 23 cm each) and a refractive index (RI) detector. The number-average molecular weight (\bar{M}_n) was calculated with the use of a polystyrene calibration curve. ^1H and ^{13}C NMR spectra were obtained with Varian XL-200 and XL-300 spectrometers in CDCl_3 at room temperature. In the ^{13}C NMR spectra of the polymers, the absorptions of the methylene ($-\text{CH}_2-$) and the methine ($-\text{CH}-$) carbons in the main chain structure appear at 40.9, 39.2 ($-\text{CH}_2-$) and 74.9 ppm ($-\text{CH}-$) for Polymer I; 40.6, 39.2 ($-\text{CH}_2-$) and 74.1 ppm ($-\text{CH}-$) for Polymer II; 41.4, 40.8 ($-\text{CH}_2-$) and 74.1 ppm ($-\text{CH}-$) for Polymer III. The spectra also show that the signals of the pendant groups containing oxyethylene unit ($-\text{CH}_2-$

CH₂-O-), ethylene ester unit (-CH₂-CH₂-O-C(=O)-) and biphenyl group are exactly the same as those of corresponding monomers. All polymers also showed the expected ¹H NMR spectra.

Thermal analysis was carried out on a Perkin-Elmer DSC-2 instrument with polymer samples of about 10 mg under a nitrogen flow at a scanning rate of 10°C per min. Indium and naphthalene were used for the calibration of the temperature scale. The melt behavior of the polymers was visually observed using a capillary melting point apparatus and a polarizing microscope equipped with cross-polarizers and a hot stage.

RESULTS AND DISCUSSION

The possibility of carrying out a living cationic polymerization of the biphenyl-containing vinyl ethers [monomers (I), (II), and (III)] was investigated using the HI/I₂ initiator system. A conventional cationic initiator, boron trifluoride etherate (BF₃OEt₂), was also used as an initiator for comparison. The polymerization reactions of monomers (I), (II), and (III) by both initiators gave soluble polymers. Figure 1 shows the GPC plots of the

molecular weight distributions of the polymers thus obtained. As reported by Higashimura and coworkers, for other vinyl ethers,¹¹ the polymerization of monomers (I), (II), and (III) by BF₃OEt₂ gave broad distributions with \bar{M}_w/\bar{M}_n values ranging from 2.5 to 3.0, which are normal for cationic polymerization reactions. In contrast the HI/I₂ initiated polymers had very narrow distributions with \bar{M}_w/\bar{M}_n ratios ranging from 1.2 to 1.4.

Typical data for representative polymerization conditions and molecular weights of the polymers obtained are summarized in Table II. The living character of the polymerization reactions of (I), (II), and (III) initiated by the HI/I₂ system was indicated not only by the narrow distributions shown in Figure 1, but also by the relationship between polymerization reactants and number average molecular weight (\bar{M}_n) in many cases and the observation that \bar{M}_n of the polymers increased proportionally to the monomer-to-initiator feed molar ratio ($[M]_0/[HI]_0$) and to the molar ratio of monomer consumed-to-initiator, as shown by the data in Table II.

In spite of their bulky substituents, all three monomers could be readily polymerized by the HI/I₂ initiator system in the same manner as

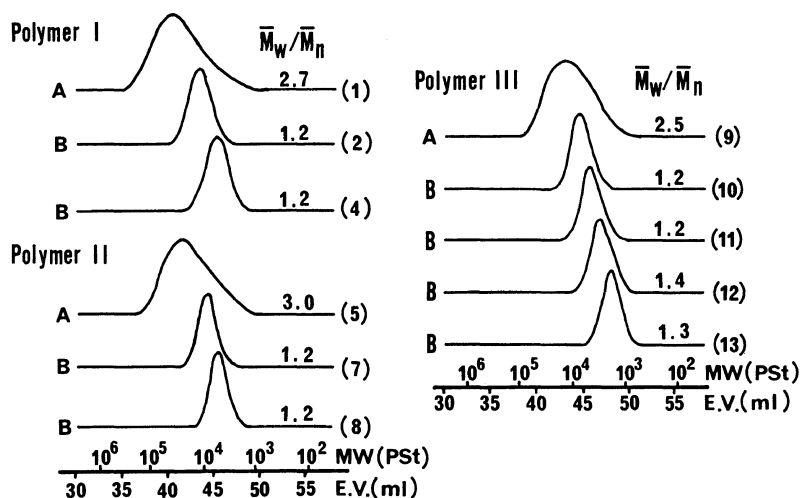


Figure 1. Molecular weight distributions of Polymers I, II, and III obtained by initiation with: (A) BF₃OEt₂ and (B) HI/I₂; numbers in parentheses indicate the reaction number in Table II.

Table II. Cationic polymerization of (I), (II), and (III) at $-15^{\circ}\text{C}^{\text{a}}$

Reaction No.	Monomer	Initiator (mM), solvent ^b	[M] ₀	Reaction time ^c	$\bar{M}_n \times 10^{-3}$		\bar{M}_w/\bar{M}_n
			M	h	Calcd ^d	Obsvd ^e	
(1)	(I)	BF ₃ OEt ₂ (10.0) <i>T</i>	0.17	1.5	—	18	2.7
(2)	(I)	HI/I ₂ (5.9/0.2) <i>D</i>	0.25	48	10.2	12	1.2
(3)	(I)	HI/I ₂ (8.4/10.0) <i>T</i>	0.20	18	5.7	6.5	1.2
(4)	(I)	HI/I ₂ (10.3/0.2) <i>D</i>	0.21	2	4.9	5.4	1.2
(5)	(II)	BF ₃ OEt ₂ (2.5) <i>T</i>	0.15	3	—	11	3.0
(6)	(II)	HI/I ₂ (8.9/0.2) <i>D</i>	0.21	70	6.3	8.5	1.3
(7)	(II)	HI/I ₂ (10.0/10.0) <i>T</i>	0.21	48	5.6	7.6	1.2
(8)	(II)	HI/I ₂ (20.0/20.0) <i>T</i>	0.21	48	2.9	4.8	1.2
(9)	(III)	BF ₃ OEt ₂ (2.5) <i>T</i>	0.06	3	—	6.7	2.5
(10)	(III)	HI/I ₂ (4.3/0.2) <i>D</i>	0.11	162	6.9	6.0	1.2
(11)	(III)	HI/I ₂ (2.9/3.0) <i>T</i>	0.06	408	4.8	4.3	1.2
(12)	(III)	HI/I ₂ (10.3/0.2) <i>D</i>	0.11	3	2.9	2.4	1.4
(13) ^f	(III)	HI/I ₂ (13.1/10.0) <i>T</i>	0.11	24	2.3	1.8	1.3

^a All reaction conversions were close to 100% except for Reactions 11, which was 85%.

^b Reaction solvents: *T*, toluene, *D*, dichloromethane.

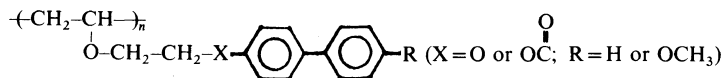
^c These values do not necessarily indicate the time when the monomer conversion reaches 100%, but represent the time between the initiation and the termination.

^d Calcd $\bar{M}_n = (\text{MW of monomer}) \times ([\text{M}] \text{ consumed}/[\text{HI}]_0)$.

^e Determined by GPC calibrated with standard polystyrene samples.

^f Reaction run at -5°C .

other vinyl ethers¹¹ to form polymers of the expected structure:



Thermal Properties of the Polymers

Typical DSC thermograms of Polymers I and II obtained by the HI/I₂ initiator are shown in Figure 2(A) and (B). Both polymers showed only T_g transitions; Polymer I at about 56°C and Polymer II at 32°C . Neither polymer showed any indication of the presence of a crystalline or liquid crystalline endotherm in the thermograms. The T_g of Polymer I was the same as that previously reported.⁹

In contrast, the thermograms of all samples of Polymer III showed at least one endotherm and in some cases two, as seen in Figure 2(C) and (D) for the DSC thermograms of Polymer III obtained by initiation with BF₃OEt₂ and HI/I₂, respectively. The thermal transition

data and calculated data for thermodynamic properties for all samples of Polymer III are collected together in Table III. The BF₃OEt₂-initiated polymer showed a glass transition at 157°C and an endothermic transition peak, T_1 , at 190°C in the first heating cycle and an exothermic transition peak, T_2 , at 160°C in the first cooling cycle in Figure 2. An endothermic transition peak, designated T_5 in Figure 2, at 185°C was also observed in the second heating cycle.

The transition values of the HI/I₂-initiated polymers were different from those of the former. A glass transition at 134°C and an endothermic transition peak, T_1 , at 174°C in the first heating cycle are seen in Figure 2,

Table III. Thermal properties of broad and narrow (10–13) distribution samples of polymer III

Reaction No.	Thermal transitions (°C) by DSC					Thermodynamic parameters ^c					
	Heating cycle ^a			Cooling cycle ^b		$\Delta H \times \text{cal g}^{-1}$			$\Delta S \times 10^2 (\text{cal g}^{-1} \text{K}^{-1})$		
	T_g	T_{s-n}	T_{n-i}	T_{i-n}	T_{n-s}	ΔH_{s-n}	ΔH_{n-i}	$\Delta H_{s-n} + \Delta H_{n-i}$	ΔS_{s-n}	ΔS_{n-i}	$\Delta S_{s-n} + \Delta S_{n-i}$
(9)	157	—	190 (185)	160	—	—	11.9	11.9	—	2.6	2.6
(10)	138	—	171 (149) (161)	130	123	5.3	6.9	12.2	1.3	1.6	2.8
(11)	134	—	174 (145) (160)	133	121	7.4	4.6	12.0	1.8	1.1	2.8
(12)	130	—	169 (143) (159)	138	123	8.1	3.9	12.0	1.9	0.9	2.8
(13)	128	—	170 (140) (160)	140	122	8.3	4.1	12.4	2.0	0.9	3.0

^a Taken from the first heating cycle; numbers in parentheses indicate the transition temperatures taken from the second heating cycle.

^b Taken from the first cooling cycle.

^c Taken from the second heating cycle.

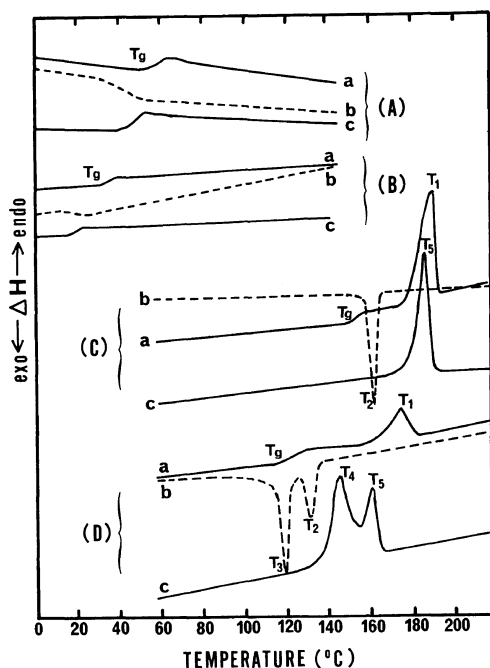


Figure 2. DSC thermograms of (A) Polymer I by HI/I₂, (B) Polymer II by HI/I₂, (C) Polymer III by BF₃OEt₂, and (D) Polymer III by HI/I₂. [(A) No. 4, (B) No. 6, (C) No. 9, (D) No. 11, in Table II; a) the first heating cycle, b) the first cooling cycle, c) the second heating cycle.]

while two exothermic transition peaks, T_2 and T_3 , at 133°C and 121°C, respectively, are evident in the first cooling cycle. Two endothermic transition peaks, T_4 and T_5 , are seen at 145°C and 160°C in the second heating cycle. After the first heating cycle, subsequent cycles on each polymer gave virtually identical DSC thermograms.

In order to identify the transition peaks T_1 to T_5 in the DSC thermograms of the polymer, texture observations were made of all samples of Polymer III with a polarizing microscope. The samples of the BF₃OEt₂-initiated polymer showed thread-like textures characteristics of the nematic phase¹² at the temperature just below T_2 in the cooling cycle and just below T_5 (or T_1) in the heating cycle, as shown in the photomicrographs in Figure 3. On the other hand, Polymer III samples obtained with HI/I₂ showed both nematic, thread-like textures between T_2 and T_3 (also between T_4 and T_5 and just below T_1) and focal-conic textures characteristic of the smectic phase¹² at temperatures just below T_3 (or T_4), as shown in the photomicrographs in Figure 4.

None of the samples of Polymer III ob-

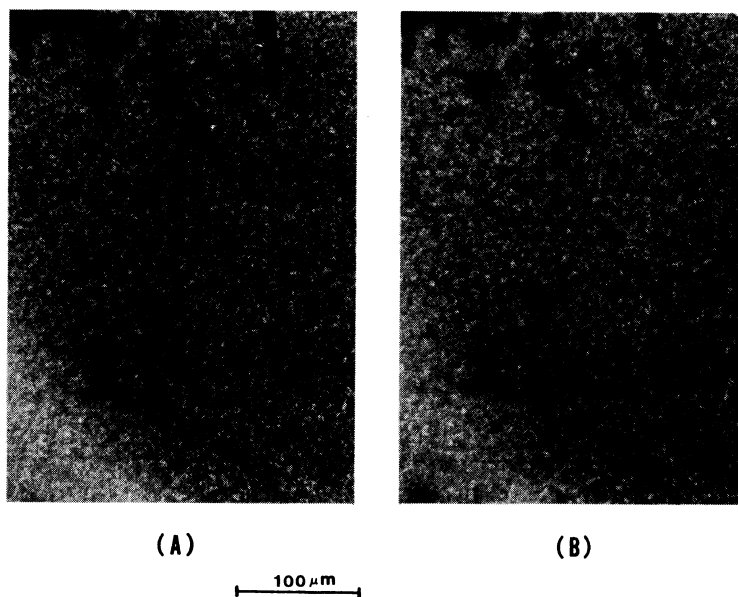


Figure 3. Micrographs of the nematic texture exhibited by Polymer III obtained by BF_3OEt_2 (No. 9 in Table II) in the first cooling cycle, (A) at 155°C (just below T_{i-n}), (B) after 30 min at the same temperature (original magnification: $320\times$).

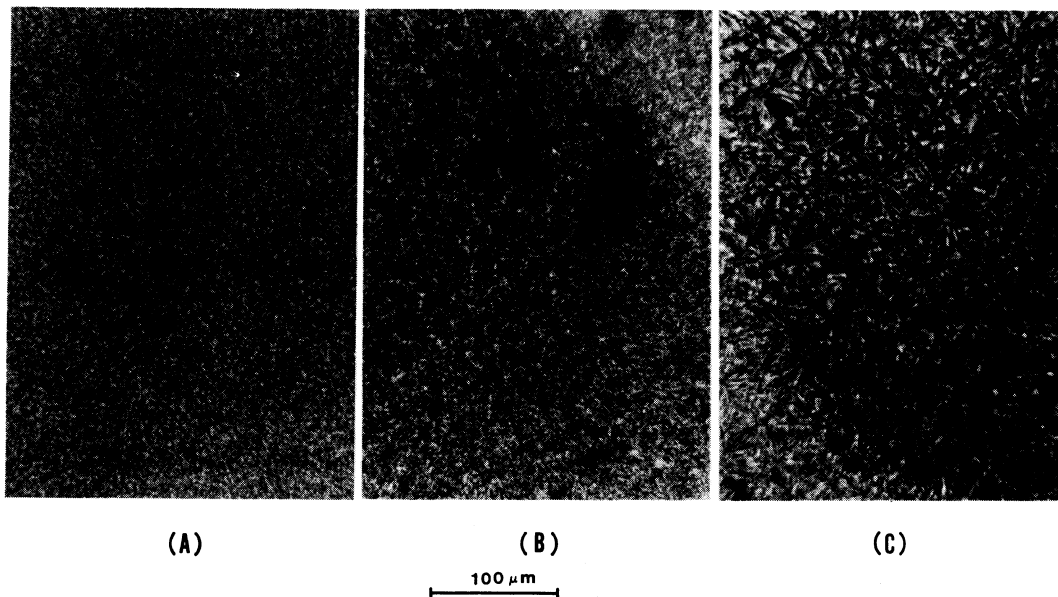


Figure 4. Micrographs of the nematic texture [(A), (B)] and the smectic texture [(C)] of Polymer III obtained with the HI/I_2 initiator (No. 11 in Table II) in the first cooling cycle, (A) at 130°C (between T_{i-n} and T_{n-s}), (B) after 30 min at the same temperature, (C) at 118°C (just below T_{n-s}); magnification is $320\times$.

tained with either BF_3OEt_2 or HI/I_2 showed glass transitions in the DSC thermograms after the first heating cycle. The virgin polymers,

which were obtained by precipitation from solution, were the only samples which showed a T_g . The T_g transition may overlap with the

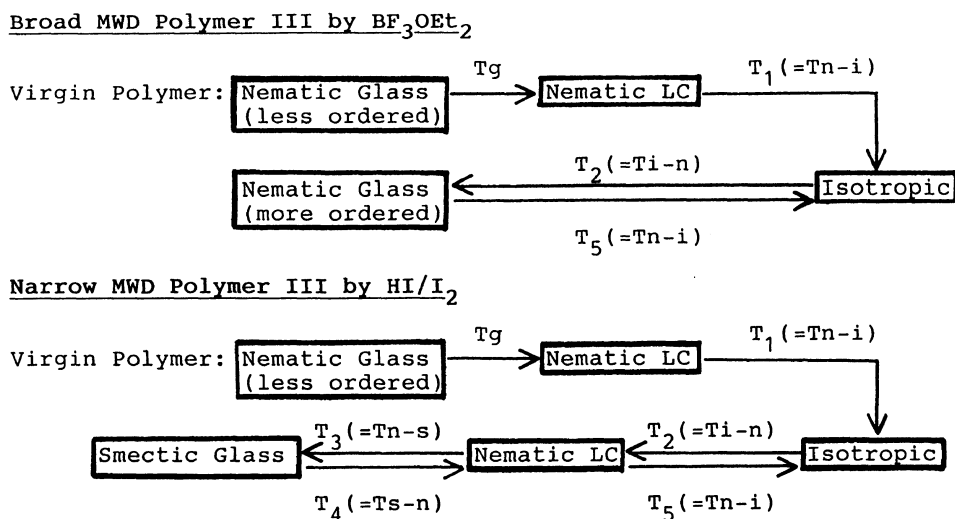


Figure 5. Schematic representations of the comparative thermal transitions of the broad and narrow distribution polymers.

T_2 (or T_5) transition in the BF_3OEt_2 -initiated samples and with the T_3 (or T_4) in the HI/I_2 -initiated samples after one heating cycle. That is, the T_g transition may have shifted to a higher temperature after the first heating and cooling cycle possible because the glassy state so formed differed from that of the virgin polymer. The virgin polymer as precipitated may have had either a poorly ordered nematic structure, or may have even been isotropic, while the glass formed after the first heating and cooling cycle may have been in an ordered nematic state (the BF_3OEt_2 -initiated samples) or in a smectic state (the HI/I_2 -initiated samples).

Each transition peak, and each phase before and after the peak, could be identified, and the transitions are represented in Figure 5, in which T_{x-y} indicates the transition temperature from the x -phase to the y -phase. The assigned transitions are also indicated in Table III. Observations on a capillary melting point apparatus gave the same results.

Molecular Weight Dependency

The molecular weight (\bar{M}_n) dependencies of the thermal transitions of Polymer III are

shown by the data in Table III. The narrow MWD samples of Polymer III in the molecular weight range of 1,800 to 6,000 showed only a slight effect of \bar{M}_n on T_g , T_{s-n} , and T_{i-n} . Thus, T_g and T_{s-n} increased and, surprisingly, T_{i-n} decreased with increasing \bar{M}_n , but T_{n-i} and T_{n-s} were not affected by this molecular weight variation.

The data in Table III also indicates that there is some molecular weight dependency on the thermodynamic parameters, ΔH and ΔS . That is, ΔH_{s-n} and ΔS_{s-n} decreased and ΔH_{n-i} and ΔS_{n-i} increased with increasing the \bar{M}_n , but the summations of $\Delta H_{s-n} + \Delta H_{n-i}$ and $\Delta S_{s-n} + \Delta S_{n-i}$ were not affected by changes in \bar{M}_n .

For the broad distribution sample of III, Polymer 9, obtained with the BF_3OEt_2 initiator, all of the observed transition temperatures were higher than those for the narrow distribution sample, but the ΔH and ΔS values for the transitions for the nematic glass phase to isotropic phase were almost the same level as the values of $\Delta H_{s-n} + \Delta H_{n-i}$ and $\Delta S_{s-n} + \Delta S_{n-i}$, respectively, of the latter. Possibly the T_g and T_{n-i} values are more strongly affected by the higher molecular weight frac-

tion of the broad distribution samples, and considering the inverse relationship for the narrow fraction polymers, perhaps T_{i-n} is affected more by the lower molecular weight fraction of the broad distribution. In contrast, the sum of the ΔH and ΔS value from the smectic to nematic to isotropic phases was not affected by the molecular weight of the polymer, as seen in the results for the narrow distribution polymer samples in Table III.

The possible sensitivity of the T_g transition of the broad distribution sample of Polymer 9 to the high molecular weight fraction may be responsible for the observation that it did not show a smectic phase. That is, the glass temperature of the nematic mesophase may be above the T_{s-n} temperature for this polymer so that on cooling the polymer becomes immobile before it can rearrange to form the smectic phase. Hence, the presence of a higher molecular weight fraction may cause the resulting increase of the T_g of the nematic phase preventing the formation of the smectic mesophase. If so, this polymer would have a monotropic smectic phase relative to T_g . Percec and coworkers reported⁹ that their sample of Polymer III, which was obtained with the BF_3OEt_2 initiator, showed a smectic texture below its isotropization temperature of 173°C , but they did not observe a T_g for their polymer, and they did not report a molecular weight for their sample.

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Chemistry, Kyoto University, Japan, and their help is gratefully acknowledged. Helpful discussions with Professor Jung-Il Jin of the Department of Chemistry, Korea University and technical support for the preparation of monomers from Mr. D. Hammel are especially appreciated.

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