Synthesis of Side Chain Liquid Crystal Polymers by Living Ring-Opening Metathesis Polymerization. 4. Synthesis of AB Block Copolymers Containing Amorphous and Side Chain Liquid Crystal Blocks

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ABSTRACT: This paper describes the synthesis of AB type block copolymers that contain a side chain liquid crystalline polymer (SCLCP) block and an amorphous polymer block by living ring-opening metathesis polymerization employing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) as the initiator. Norbornene, 5-cyano-2-norbornene, and methyltetracyclododecene were used for the amorphous polymer blocks and *n*-[((4'-methoxy-4-biphenyl)yl)oxy]alkyl bicyclo[2.2.1]hept-2-ene-5-carboxylates (1-*n*, *n* = 3, 6) were used for the SCLCP block. Block copolymers with monomer ratios from 75/25 to 20/80 (amorphous/SCLCP) and narrow molecular weight distributions (M_w/M_n = 1.06–1.25) were obtained in high yield. Glass transition temperatures of each block and the isotropization temperature of the mesophase are independent of the composition of the block copolymer and the same as those of the respective homopolymers. The enthalpy change of isotropization decreases significantly when the amorphous polymer block has a T_g higher than the isotropization temperature and the content of SCLCP is less than 60–70%.

Introduction

Diblock copolymers having well-defined block lengths often produce microphase-separated morphologies (lamellae, cylinders, or spheres) in cast films, the morphology type being determined primarily by the number of monomers in each block.[1,2] If one of the blocks is a side chain liquid crystalline polymer (SCLCP), then liquid crystalline (LC) microphases should form within one of the microdomains. One of the fundamental questions is the effect of the size and type of LC microphase on the phase transition.[3] Some segmented main chain liquid crystalline block copolymers have been prepared,[4,5] but they showed no evidence of phase separation, perhaps because the molecular weight distribution of the block copolymers was too broad.

In order to couple the motions of the main chain and the mesogens, SCLCPs must have a lower glass transition temperature (T_g) than isotropization temperature of the LC phase. Under these circumstances at the temperature at which the LC phase transition occurs, SCLCPs have rubber-like or liquid-like properties. Block copolymers containing an SCLCP block could display some interesting new properties. For example, if an amorphous block that has a higher T_g than the phase transition temperature of the LC phase is incorporated with the SCLCP block, the amorphous block should physically support the SCLCP microdomains throughout the LC phase transition. Such a material would be a "self-supported" SCLCP system.

Block copolymers can be prepared by anionic,[6] cationic,[7] group transfer,[8] or ring-opening metathesis[9,10] polymerization methods. Well-defined block copolymers with ordered morphologies have been prepared mainly by anionic polymerization methods.[1] Anionic polymerization methods have some limitations for preparing SCLCPs because the living anion often reacts with the polar functionalities used to connect the mesogenic side chain to the polymerizable group or with the mesogenic group itself. Liquid crystalline side chains have been introduced into block copolymers prepared by anionic polymerization methods.[11,12] These systems yielded lamellar structures in which the transition enthalpy change associated with isotropization decreased considerably. X-ray diffraction studies suggested that the mesogens were ordered parallel to the lamellae.

This paper presents a direct preparation of block copolymers using living ring-opening metathesis polymerization (ROMP) of nonmesogenic and mesogenic norbornene monomers using Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) as the initiator.[13,14] This type of molybdenum complex is known to tolerate many functionalities[15-20] and has been shown to polymerize mesogenic norbornenes to give well-defined SCLCPs.[21-23] The mesogenic norbornenes employed in this study are *n*-[((4'-methoxy-4-biphenyl)yl)oxy]alkyl bicyclo[2.2.1]hept-2-ene-5-carboxylates (1-*n*, *n* = 3, 6), the homopolymers of which are known.[21,22] The other monomers employed are norbornene (NBE), 2-cyano-5-norbornene (NBECN), and methyltetracyclododecene (MTD) (see Scheme I). All three are known to give amorphous homopolymers. Polynorbornene has a $T_g \sim 40$ °C, which is close to that of poly(1-6) and lower than that of poly(1-3), while the T_g's of the latter two homopolymers are higher than the isotropization temperatures of poly(1-6) and poly(1-3). The thermotropic behavior of these block copolymers will be the main focus of this paper.

Results

A Block Copolymer Containing NBE and 1-3 or 1-6. Synthesis of the mesogenic norbornenes (1-3 and 1-6) has been reported elsewhere.[21] The monomers were exo/endo mixtures (exo:endo = 1:3). As outlined in Scheme I, the nonmesogenic monomer was added to the initiator in THF to give a living polymer that subsequently was treated with 1-*n* to form the living block copolymer. After 1 h at room temperature, benzaldehyde was added to cleave off the polymer in a Wittig-like reaction. The block copolymer was then precipitated in methanol. Yields were quantitative and the polymers were free of unreacted monomers according to GPC studies.

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Scheme I

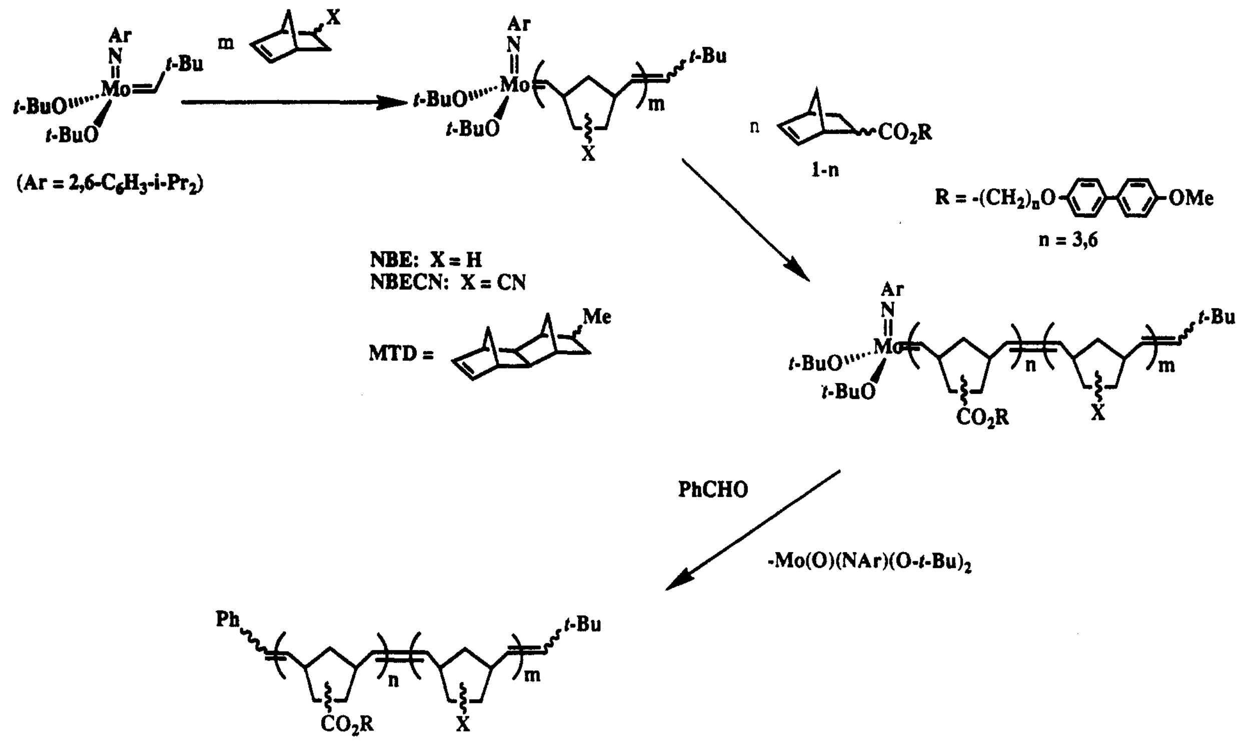

Table I
Properties of Block Copolymers Containing 1-*n* and Norbornene (NBE), Methylcyclododecene (MTD), or Cyanonorbornene (NBECN)

monomer			block ratio		GPC		DSC heating scan		
							phase transition temp (°C)	enthalpy changes	
first	second	equiv	theory	found	PDI	M_n		ΔH (J/g)[a]	ΔH (J/g, %)[b]
NBE	1-6	300 + 20	77/23	75/25	1.11	54 100	g 42 n 97 i	*c*	*c*
NBE	1-6	100 + 20	53/47	49/51	1.17	27 100	g 38 n 94 i	1.30	2.55, 75
NBE	1-6	100 + 50	31/69	30/70	1.25	38 000	g 38 n 91 i	2.30	3.29, 97
NBE	1-6	56 + 50	20/80	20/80	1.11	32 700	g 38 n 93 i	2.52	3.15, 93
NBE	1-3	300 + 20	79/21	79/21	1.06	88 900	g 44 g 58 n 84 i	*c*	*c*
NBE	1-3	100 + 20	55/45	53/47	1.10	37 600	g 39 g 55 n 92 i	0.47	1.00, 68
NBE	1-3	100 + 50	33/67	33/67	1.13	64 200	g 39 g 59 n 86 i	1.00	1.49, 101
NBE	1-3	50 + 50	20/80	20/80	1.16	50 800	g 36 g 60 n 87 i	1.10	1.38, 94
MTD	1-6	100 + 20	67/33	67/33	1.08	28 500	g 41 n 85 g 208 i	*c*	*c*
MTD	1-6	100 + 50	45/55	47/53	1.18	42 900	g 41 n 92 g 207 i	1.07	2.02, 59
NBECN	1-6	180 + 20	72/28	70/30	1.17	113 000	g 45 n 87 g 112 i	*c*	*c*
NBECN	1-6	180 + 50	50/50	52/48	1.13	145 900	g 43 n 93 g 114 i	0.98	2.04, 60
NBECN	1-6	89 + 50	34/66	38/62	1.16	79 300	g 43 n 91 g–[d] i	1.72	2.77, 82
NBECN	1-6	36 + 50	17/83	21/79	1.16	47 000	g 45 n 91 g–[d] i	2.17	2.75, 81
NBECN	1-3	180 + 20	74/26	72/28	1.09	66 200	(g – n –)[d] g 112 i	*c*	*c*
NBECN	1-3	180 + 50	53/47	54/46	1.17	108 700	g 67 n 86–91[e] g 119 i	*c*	*c*
NBECN	1-3	89 + 50	36/64	33/67	1.08	61 800	g 63 n 82 g –[d] i	0.52	0.75, 51
NBECN	1-3	36 + 50	15/85	23/77	1.15	46 600	g 63 n 82 g –[d] i	0.48	0.62, 42
—	1-6	0 + 20	0/100		1.16	6 740	g 35 n 87 i	3.40	3.40
—	1-6	0 + 50	0/100		1.15	24 100	g 42 n 93 i	3.38	3.38
—	1-3	0 + 20	0/100		1.08	7 630	g 57 n 79 i	1.61	1.61
—	1-3	0 + 50	0/100		1.12	20 200	g 61 n 86 i	1.47	1.47
NBE	—	100 + 0	100/0		1.04	18 726	g 40 i		
NBE	—	300 + 0	100/0		1.07	47 674	g 43 i		
MTD	—	100 + 0	100/0		1.07	19 995	g 214 i		
NBECN	—	180 + 0	100/0		1.06	82 079	g 116 i		

[a] Enthalpy based on a whole polymer. [b] Enthalpy based on a SCLCP part. Latter number shows proportion of enthalpy based on the corresponding homo SCLCP. [c] Too broad to determine a precise value. [d] Could not be detected. [e] Determined by polarized optical microscope analysis (see text).

The results of gel permeation chromatography (GPC) are summarized in Table I. In most cases the molecular weight distribution was relatively narrow, and polydispersities (PDI = M_w/M_n) were less than 1.2. The exception is the block copolymer of NBE and 1-6 (100/50; PDI = 1.25) where a small double molecular weight peak is observed along with a low molecular weight tail. (The formation of polymer with a doubled molecular weight is believed to result from the presence of traces of oxygen.[24]) Some other polymers show a small double molecular weight

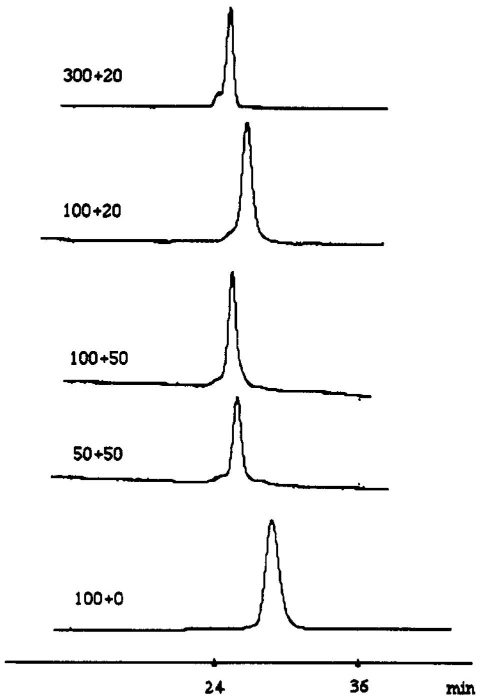

Figure 1. GPC traces of block copolymers prepared from NBE and 1-3.

shoulder also, but PDIs are still low. Representative GPC traces of the block copolymers containing NBE and 1-3 are shown in Figure 1.

Proton NMR spectra of the block copolymers are superpositions of spectra of each homopolymer; Figure 2 is an example. Although the olefinic proton resonances for poly(NBE) and poly(1-6) overlap, the aromatic proton resonances and resonances for protons α to the oxygen atoms that can be attributed to the SCLCP component are all observable. The ratio of the blocks can be measured by integrating these proton resonances and are listed together with the theoretical ratios in Table I. The measured ratios agree with theory, as one would expect in a controlled ring-opening reaction that yields polymer quantitatively.

The thermal behavior of the homopolymer components of the block copolymers prepared here was measured by differential scanning calorimetry (DSC). The T_g of poly(NBE) is 40–42 °C. Both poly(1-3) and poly(1-6) show only an enantiotropic nematic phase, as previously reported.[21] The T_g of poly(1-3) is higher than that of poly(1-6) and the isotropization temperatures are almost the same. It has been shown that T_g's and isotropization temperatures of these polymers become independent of molecular weight at approximately 30–50 repeat units.[21,22] Consequently, the transition temperatures of the 20-mers are somewhat lower than those of the 50-mers.

DSC analysis showed that the block copolymers of NBE and 1-6 have only one T_g at 38–42 °C, regardless of the ratio of the two components examined, since the T_g's of these two blocks are too close to be observed separately. Isotropization temperatures of the block copolymers are the same as those of homopolymer 1-6, which suggests that the blocks are phase separated. The block copolymers of NBE and 1-3 show two T_g's due to the slightly higher T_g of poly(1-3) than of poly(NBE), although again all T_g's and isotropization temperatures are essentially the same as those of the homopolymers. Examples of DSC traces of block copolymers of NBE and 1-3 or 1-6 (Figure 3) reveal the two T_g's and the *first-order transitions* of the LC phase clearly. Although the isotropization temperatures differ by ~6 °C in the two block copolymers, in general there does not appear to be any significant correlation of the isotropization temperature and the composition of the block copolymers. The T_g's of the poly(NBE) block and the poly(1-3) block both increase slightly with the average number of monomers in each block.

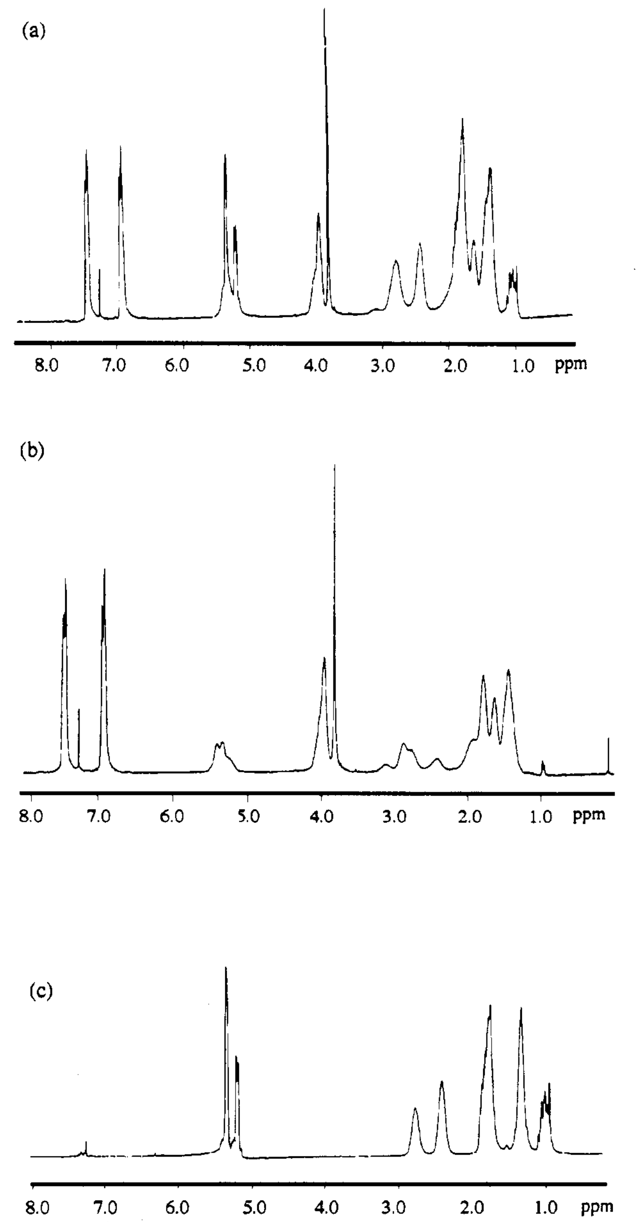

Figure 2. ^{1}H NMR spectra of (a) NBE and 1-6 block copolymer (100 + 50, 30/70 (w/w)), (b) poly(1-6) (57-mer), and (c) poly(NBE).

Enthalpy changes (by DSC analysis) are listed in Table I. Block copolymers that contain 70% or more of the SCLCP block have enthalpy changes very close to those found for the homo SCLCP. The isotropization peak for the polymer containing 25% of the SCLCP block was too small to measure. The block copolymers containing 51% (poly(1-6)) or 47% (poly(1-3)) showed a smaller enthalpy change than the corresponding homo SCLCP. Although the enthalpy changes are small, there is a tendency for the enthalpy to decrease as the content of the SCLCP block decreases. Optical polarized microscope studies indicated that all block copolymers exhibited an anisotropic phase below the isotropization temperature except for the block copolymer containing 72% NBECN and 28% 1-3. Although the homopolymer of 1-3 and 1-6 showed schlieren textures typical of a nematic mesophase, the block copolymers show either no textures or faint anisotropic

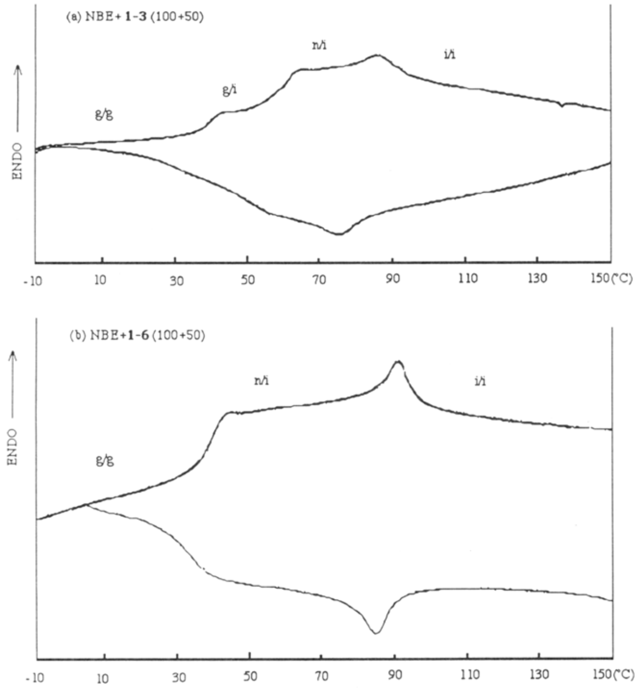

Figure 3. Normalized DSC thermograms of (a) NBE and 1-3 block copolymer (100 + 50, 33/67 (w/w)) and (b) NBE and 1-6 block copolymer (100 + 50, 30/70 (w/w)).

Figure 4. Polarized optical micrograph (magnification 80×) of the anisotropic texture observed on cooling NBE and 1-6 block copolymer (100 + 20, 49/51 (w/w)) at 87 °C.

textures. An optical micrograph of the poly(NBE)/poly(1-6) block copolymer (100/20; Figure 4) shows that the domain size of the separated microphase is too small to observe and to give clear textures.

Block Copolymers Containing MTD or NBECN and 1-3 or 1-6. The homopolymer of methyltetracyclododecene (MTD) has a T_g over 200 °C and therefore has been used as a relatively hard "host" polymer block in metal-containing block copolymers.[15,16] Two low-PDI samples of poly-MTD/1-6 block copolymers were synthesized. The two T_g's that are found correspond to the homopolymers of MTD and 1-6. The isotropization peak is also found at the same temperature as found in the homopolymer 1-6. The ratios of the two blocks calculated via integration of proton NMR spectra agree with theory. The enthalpy change associated with the isotropization of the LC phase in the SCLCP block is significantly smaller than that of the homopolymer 1-6, in contrast to the series of block copolymers containing a poly(NBE) block. The sample that contains MTD and 53% of 1-6 shows only 59% of the enthalpy change of homopoly(1-6), whereas the block copolymer containing NBE and 51% of poly(1-6) shows an enthalpy change that is 75% that of homopoly(1-6).

It is known that NBECN can be polymerized in a living manner using the molybdenum alkylidene complex in THF.[17] The homopolymer of NBECN has a $T_g \approx 116$ °C, which is much lower than that of poly(MTD), but still higher than the isotropization temperatures of poly(1-3) or poly(1-6). The block copolymers containing NBECN and 1-3 or 1-6 are included in Table I. Polydispersities are low, and the ratio of the two blocks determined by NMR integration agree with theory. All NBECN/1-6 block copolymers show a T_g corresponding to the poly(1-6) block and an isotropization peak for the LC mesophase. The block copolymers containing less than 38% NBECN did not exhibit clearly any T_g corresponding to the poly(NBECN) block. However, it seems unlikely that these polymers are homogeneous, because the T_g and isotropization temperature of the poly(1-6) block are independent of the percent composition of the block copolymers. Furthermore, the presence of anisotropic phase at temperatures below the isotropization temperature is confirmed by polarized microscopy. The enthalpy changes show the same trends as in block copolymers containing MTD and 1-6. For example, the block copolymer containing 52% NBECN exhibits only 60% of the enthalpy change compared to that of the homopoly(1-6). Even if the samples contain more than 60% of the SCLCP block, they show only 80% of the enthalpy change. The small enthalpy changes for the block copolymer containing 30% of the SCLCP could not be determined. Nevertheless, the small enthalpy change associated with the 48% of the SCLCP is the same as that seen for the NBE and 1-3 or 1-6 block copolymers. The DSC heating and cooling scans of the NBECN/1-3 (54/46 weight ratio) and NBECN/1-6 (52/48 weight ratio) block copolymers are shown in Figure 5. A polarized micrograph of the NBECN/(1-6) block copolymer is shown in Figure 6.

The NBECN/1-3 block copolymer also showed the expected proton NMR spectra. However, no sample exhibited all three DSC peaks for phase transitions (two T_g's and one isotropization temperature). For the block copolymers containing 33% and 23% NBECN, microphase separation is supported by the independence of the T_g for the poly(1-3) block and isotropization temperatures on polymer composition. The block copolymer containing 54% NBECN exhibits a broad isotropization transition in the DSC scans, as shown in Figure 5b. However, polarized optical microscopy of this sample clearly shows an anisotropic phase and shows a phase transition occurring at 86–91 °C. The enthalpy change could not be determined because of the very broad transition and the small amount of heat exchanged. The block copolymer containing 28% of the poly(1-3) block does not show a T_g ascribable to the poly(1-3) block nor an isotropization temperature. In this particular sample, polarized optical microscopy provided no evidence for an anisotropic phase. This sample contains a poly(1-3) block, according to NMR spectra, and the presence of a phase-separated morphology

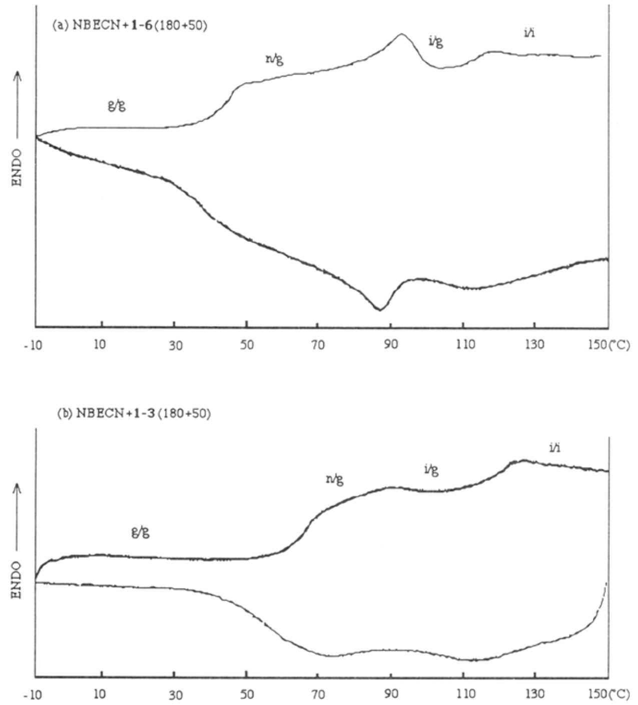

Figure 5. Normalized DSC thermograms of (a) NBECN and 1-6 block copolymer (180 + 50, 52/48 (w/w)) and (b) NBECN and 1-3 block copolymer (180 + 50, 53/47 (w/w)).

Figure 6. Polarized optical micrograph (magnification 80×) of the anisotropic texture observed on cooling NBECN and 1-6 block copolymer (89 + 50, 38/62 (w/w)) at 50 °C.

is suggested by the fact that the T_g is the same as the T_g of NBECN homopolymer. If this sample has a phase-separated morphology, the absence of anisotropic phase could be ascribed to SCLCP domains that are smaller than a critical value.[25,26] Consequently, the poly(1-3) microphase may not be able to form a LC phase. The change of enthalpy corresponding to the SCLCP block is only 42–51% that of the homopolymer of 1-3, even when the copolymer contains more than 60% of 1-3, in significant contrast to the results obtained for block copolymers containing NBE and 1-3.

Discussion

How the thermodynamic parameters of the phase transition vary with the size and type of LC microphase has been an important question in LC studies.[11,12] We have found that the phase transition temperatures of all the block copolymers examined in this study do not depend on the percent composition of the blocks; i.e., all LC phase transition temperatures and T_g's are the same as for the homopolymers. We have found also that the enthalpy change does depend on the composition of the block copolymer. Block copolymers containing ~50% of an SCLCP block show smaller enthalpy changes than those with >60% of an SCLCP block. Although we have no information on the morphology of the phase separation at this stage, we believe the dependence of the enthalpy change on diblock composition can be attributed to the restricted size of the LC microphase.[15,16] A change in the block ratio leads not only to a change in the size of the separated domain but also to a change in morphology, as evidenced by a sudden decrease in the enthalpy change of the block copolymers containing ~50% SCLCP.

If the size of the microdomain is less than a critical value required to form the mesophase, then the SCLCP will not form any LC phases. This effect is realized in the case of the block copolymer of 72% NBECN and 1-3, which shows no evidence of a mesophase, either by DSC analysis or by polarized microscopy, while the T_g of poly(NBECN) is still observed. Further investigations will be necessary, preferably direct observation of the microdomain in which the LC microphase forms.

The block copolymers with a non-LC block that has a higher T_g than isotropization temperature of the SCLCP block exhibit a much smaller change of enthalpy than the block copolymers with poly(NBE), which has lower T_g than the isotropization temperature. The value of the enthalpy change of the block copolymer containing MTD and 1-6 is 59% of the homopolymer of 1-6 and those of the block copolymer containing NBECN and 1-6 are 60–82%. For the block copolymers containing NBECN and 1-3, the enthalpy values are only 42–51% of that of the homopolymer of 1-3. In contrast, the block copolymers containing NBE show 93–100% of the enthalpy change when the block copolymers contain more than 67% of SCLCP. It seems that poly(1-3) is more sensitive to the high-T_g amorphous block than poly(1-6).

The decrease of the enthalpy in the block copolymer, which has a high-T_g amorphous block, cannot be explained solely in terms of the size of the separated LC phase. Since a microphase-separated block copolymer has a relatively sharp boundary between the two incompatible blocks, the orientation of the polymer main chain with respect to the interphase may alter the orientation of the mesogens at the boundary. If the polymer main chain of the amorphous phase is in a glassy state, movement of the mesogens at the boundary will be more restricted compared to the amorphous phase in a rubbery state. Therefore, the LC microphase near the boundary is relatively disordered. The interior of the SCLCP microphase forms a LC phase like the SCLCP homopolymer does. On the whole, the crystallinity of the LC phase decreases. When the mesogens are connected through long flexible spacers, the amorphous polymer block will be less influential, compared to the situation in which the mesogens are connected through a short flexible spacer. This must be the explanation as to why the poly(1-3) block is more sensitive to the poly(NBECN) block than is the poly(1-6) block. If this is the case, an increase in molecular weight of each component at a fixed ratio of the two blocks should yield large domains in which the surface area that is influenced by the state of amorphous block is relatively small. Ideally, the amorphous block part will not affect the thermal behavior of the SCLCP microphase, yet will support the system physically.

Experimental Section

Materials and Methods. All polymers were prepared in THF under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran was vacuum transferred from sodium benzophenone ketyl just before use. Ether and THF used for monomer synthesis were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane used for purification of monomers was distilled from calcium hydride under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Norbornene and MTD were doubly distilled from molten sodium. Commercially available 5-cyano-2-norbornene (60:40 mixture of exo and endo isomers) and benzaldehyde were distilled under nitrogen and stored under nitrogen. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_3$[13,14] and *n*-[((4′-methoxy-4-biphenylyl)oxy]alkyl bicyclo[2.2.1]hept-2-ene-5-carboxylates (1-*n*, *n* = 3, 6)[17,21] were prepared as described in the literature. All other reagents and solvents were commercially available and used as received.

All NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. Molecular weight was determined by gel permeation chromatography (GPC) at room temperature using a set of Shodex KF802.5, -803, -804, -805, and -800P columns (700 Å, 2×10^3 Å, 2×10^4 Å, 1×10^5 Å, and a precolumn, respectively), a Knauer differential refractometer, and a Spectroflow 757 absorbance detector set at 300 nm on 0.1–0.3% (w/v) samples in THF. The GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03×10^6 MW. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions, which were read as the maxima and minima of the endothermic or exothermic peaks, respectively. All heating and cooling rates were 20 °C/min. Glass transition temperatures (T_g's) were read as the middle of the change in the heat capacity. All second and subsequent heating scans were identical. A Nikon optical polarized microscope (magnification 80×) equipped with a Mettler FP82 hot stage and a Mettler FP800 central processor was used to observe the thermal transitions and to analyze anisotropic textures.

Polymerization Procedure. A solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_3$ (0.2 mL, 0.0205 M) in THF was added in one portion to a rapidly stirred solution of nonmesogenic monomer (3 mL, 0.137 M, 100 equiv) in THF, and the mixture was then stirred for 30 min. A solution of the mesogenic monomer was added as rapidly as possible to the reaction solution and the reaction was stirred for 1 h. The polymerization was quenched by adding 20 μL of benzaldehyde (0.19 mmol). After 30 min, the solution was added dropwise to methanol (~50 mL), and the precipitated polymer was isolated by centrifugation, washed with methanol, and dried in vacuo. In all cases, polymer yields were >90% and GPC analyses showed no traces of monomer. Further purification of samples by reprecipitation had no effect on their thermotropic behavior. When 20 equiv or less of monomer was used, the catalyst concentration was adjusted to 0.205 M.

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