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

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

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Abstract

The synthesis of AB type block copolymers comprising side chain liquid crystalline polymer (SCLCP) block and amorphous polymer block by living ring opening metathesis polymerization with $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ ($Ar=2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) is described. Norbornene, 5-cyano-2-norbornene, and methyltetracyclododecene were used for amorphous polymer block and 5-carbo{n-[(4'-methoxy-4-biphenylyl)oxy]alkyl}bicyclo[2.2.1]hept-2-ene (**1-n, n = 3,6**) were used for SCLCP block. The block copolymers with ratios of the components from 75/25 to 20/80 and narrow molecular weight distributions (Mw/Mn=1.06-1.25) were obtained in high yield. The glass transition temperatures for both components and isotropization temperature of mesophase are independent of the composition of the block copolymer and the same as those of each homopolymer suggesting microphase separated morphology. The change in

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enthalpy of isotropization decreases significantly when the amorphous polymer block has Tg higher than the isotropization temperature.

Introduction

Diblock copolymers with well defined block length yield ordered phase separation. Morphology of the microphase separation is controllable by varying the weight ratio of the two blocks and the length of each block.[1] If one of the blocks is a side chain liquid crystalline polymer (SCLCP), microphase separated systems with liquid crystalline microphases may be realized. Such systems are of fundamental as well as practical interest. The effect of size and type of the liquid crystalline microphase on the phase transition is one of the fundamental questions. This effect is recently investigated by the polymer system in which low molecular weight liquid crystals are dispersed.[2] Different from the low molecular weight liquid crystals dispersed systems, the block copolymer can give several types of microdomains (lamellae, cylinders, or spheares). The effect of the microphase separation on the liquid crystalline order is also a subject of interest. In the case of main chain liquid crystalline polymer, some of the segmented block copolymers were prepared.[3,4] However, because of the broad distribution of the blocks, they showed no phase separated behavior. A practical interest arises from the assembling of two different features of each block. For the incomplete separation of the motions of main chain and mesogens, SCLCPs must have low glass transition temperature (Tg) so that the orientation of mesogens and isotropization of liquid crystalline phase become possible at proper temperature. As the result, at the temperature at which the phase transition occurs, SCLCPs have rubber like or liquid like properties. If the amorphous block which is incorporated with a SCLCP block has a high Tg, this amorphous block will physically support the SCLCP microdomains. This system allows to prepare self-supported SCLCP system.

So far the block copolymers are usually prepared by living anionic polymerization. However, because of the highly reactive living anion toward a number of functionalities, this polymerization system is not suitable for the block copolymers containing side chain mesogenic groups. Another synthetic strategy using modification of the block copolymers prepared by anionic polymerization with liquid crystalline side chains was introduced, and the resultant diblock copolymers were investigated.[5] These systems presented lamellae structure and considerable decrease of the transition enthalpy change associated with the isotropization. X-ray diffraction studies suggested a parallel orientation of the mesogens to the lamellae layers.

This paper presents a direct preparation of the block copolymers using living ring opening metathesis polymerization (ROMP) of non mesogenic and mesogenic norbornene monomers using $Mo(CHMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$ as an initiator.[6] This type of molybdenum complexes are known to tolerate functionalities[7] and has been used for the preparation of several types of well defined SCLCPs.[8,9]

The mesogenic norbornenes used in this study were 5-carbo{n-[(4'-methoxy-4-biphenylyl)oxy]alkyl}bicyclo[2.2.1]hept-2-enes (**1-n, n = 3 and 6**) whose homopolymers were studied previously. The polymerization of **1-n** was initiated with living polymer of norbornene (NBE), 2-cyano-5-norbornene (NBECN), and methyltetracyclododecene (MTD).[10] These non mesogenic norbornenes are known to give a amorphous homopolymers with different Tgs. Polynorbornene has Tg ~ 40°C which is close to that of poly(**1-6**) and lower than that of poly(**1-3**). On the other hand, Tgs 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 discussed.

RESULTS

Block copolymer of NBE and 1-3 or 1-6

The synthesis of the mesogenic norbornenes (**1-3** and **1-6**) was reported elsewhere.[8] The monomers were used as an exo-endo isomeric mixture (exo:endo = 1:3).

The block copolymerization was initiated with $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ because of its high tolerance to various functional groups. As outlined in scheme I, a non mesogenic monomer was polymerized in THF first. The resultant living polymer was reacted with mesogenic **1-n** to form a block copolymer. After 1 hour at room temperature, benzaldehyde was added to give a benzylidene terminated polymer. The block copolymer was separated by precipitation into methanol. Yields were quantitative and the polymers were practically free from unreacted monomers.

The gel permeation chromatography (GPC) analysis of the polymers are summarized in Table I. In most of the cases, the molecular weight distribution was fairly narrow, and polydispersities (PDI = Mw/Mn) are lower than 1.2 except the block copolymer of NBE and **1-6** (100+50) which is PDI = 1.25 due to the presence of a double molecular weight peak and low molecular weight tailing. Although some polymers show a small double molecular weight peak, PDIs are still low. Representative GPC traces of the block copolymer of NBE and **1-3** are shown in Figure 1.

The ^{1}H NMR spectra of the block copolymers are in a complete superimposition of those of corresponding each homopolymer. Figure 2 presents an example of the ^{1}H NMR spectra of block copolymer (100+50) of NVE and **1-6** and homopolymers of each component. Although olefinic protons of poly(NBE) and poly(**1-6**) overlap completely, aromatic protons and protons α to the oxygen atoms which are all attributed to SCLCP component are isolated from other protons. Using these protons, the ratio of the components can be estimated. There was no difference in the observed ratio of the block copolymers whether it is based on the aromatic protons or on the protons adjacent to the oxygen atoms. The weight ratio obtained by NMR analysis are listed together with theoretical values in Table I. The observed values show very good agreement with the theoretical ones. This is not surprising considering quantitative yields of block copolymers and supports he formation of block copolymers.

Thermal behavior of homopolymers of NBE was characterized by differential scanning calorimetry (DSC). Tg of poly(NBE) is 40-42°C and high molecular weight polymer gives a higher value. Both poly(**1-3**) and poly(**1-6**) show only enantiotropic nematic phase as reported. Tg of poly(**1-3**) is higher than that of poly(**1-6**) and isotropization temperatures are almost the same. However, it has been shown that Tgs and isotropization temperatures of these polymers become independent of molecular weight at approximately 30-50 repeat units, the transition temperatures of 20eq polymers are somewhat smaller than those of 50eq polymers.

The DSC analysis showed that the block copolymers of NBE and **1-6** have only one Tg at 38-42°C regardless of the ratio of the two components examined. Tgs of these two blocks are too close to have separate Tgs. Nonetheless, isotropization temperatures of the block copolymers are the same as those of homopolymer of **1-6** suggesting a phase separated morphology. In the case of the block copolymers of NBE and **1-3**, they show two Tgs due to the slightly higher Tg of poly(**1-3**) than that of poly(NBE). Again, all Tgs and isotropization temperatures are essentially the same as those of homopolymers. Some representative DSC traces of block copolymers of NBE and **1-3** or **1-6** are shown in Figure 3. The two Tgs and the first order transitions of liquid crystalline phase can be seen clearly. Although isotropization temperatures scattered in the range of 6°C for both series of block copolymers, no significant relationships between isotropization temperature and the composition of the block copolymers can be seen. Tgs, however, show good correlation with the molecular weight of each components. The polymerization using 300eq of NBE produces a polymer with slightly high Tg. The same tendency can be seen for the Tg of the block of poly(**1-3**).

The enthalpy change accompanying with the isotropization of LC phase is also a subject of interest. The enthalpy changes based on the whole polymer sample and based on the content of SCLCP block of block copolymers are listed in Table I. The block copolymers containing NBE block less than 50% by weight are very close to that of homo SCLCPs. Because of the very small enthalpy change, the values are subject of experimental error. Especially the samples of the block copolymers containing less than 25% of SCLCP block showed too small isotropization peak due to the low content of SCLCP block that it was impossible to determine definite value of the enthalpy. However, there may be a tendency that the enthalpy decreases as the decrease of the content of SCLCP block. The optical polarized microscope analysis of the block copolymers indicated the presence of anisotropic phase under the isotropization temperature. Although the homopolymer of **1-3** and **1-6** showed schlieren textures typical for nematic mesophase, the block copolymers do not show any clear textures which can be used for the identification of the mesophase other than dimmed anisotropic textures. However, it is clear that on cooling or on heating of the samples, formation or isotropization of anisotropic phase is taking place at the phase transition temperature. A picture obtained from the cooling scan of poly(NBE) and poly(**1-6**) block (100+20) is presented in Figure 4. It is obvious that the domain size of the separated microphase are too small for the observation of optical microscope and to give clear textures.

Block copolymers of MTD, NBECN and 1-3, 1-6.

The next series of the block copolymers consist of a non LC block with Tg higher than both Tg and isotropization temperature of a SCLCP block. The homopolymer of MTD has quite high Tg over 200°C and has been used for an amorphous component for metal containing block copolymers which have a good physical strength as the films.[11] Two samples of the block copolymer with MTD and **1-6** were synthesized. The GPC analyses indicted narrow PDIs of these polymers. They exhibit two Tgs corresponding to homopolymer of MTD and **1-6** respectively. There is also an isotropization peak at the same temperature as being found for the homopolymer of **1-6**. The ^1H NMR spectra of the blocks presented a completely overlapped shape of each blocks and the ratios of two components calculated from the NMR spectra have an excellent agreement with the theoretical values. These observations again support the formation of phase separated block copolymers. The enthalpy change of the isotropization of LC phase based on the SCLCP block is significantly smaller than that of the homopolymer of **1-6** different from the series of the block copolymers containing poly(NBE) block. This tendency is much clearer in the case of the block copolymer of NBECN and **1-3** or **1-6**. It is known that NBECN can be polymerized in a living manner using the molybdenum alkylidene complex in THF.[7(a)] The homopolymer of NBECN has Tg~116°C which is much lower than that of poly(MTD) but still higher than the isotropization temperatures of SCLCPs.

The results of the block copolymerization of NBECN and **1-3** and **1-6** are included in Table I. The GPC analyses show fairly good polydispersity despite some samples indicated a formation of a small amount of double molecular weight polymer. The ^1H NMR spectra of the block copolymers are again in a superimposition of those of composing homopolymers. The observed ratios of the two blocks are in a good agreement with the theoretical values. All of the samples of the block copolymer of NBECN and **1-6** show Tg corresponding to the poly(**1-6**) block and isotropization due to the transition of the mesophase. For the Tg of the poly(NBECN) block, the blocks containing less than 38% NBECN block did not exhibit any clear Tg corresponding to the poly(NBECN) block. However, it is less likely to estimate these polymers are homogeneous because of the independency of Tg and isotropization to the composition of the blocks. Furthermore, the presence of anisotropic phase at temeratures under the isotropization temperature is confirmed by polarized microscopic analysis. The enthalpy change of the block copolymers are in the same tendency as seen in the case of blocks of MTD and **1-6**. The values of enthalpy based on the SCLCP block are considerably lower than that of homopolymer of **1-6** and comparable as that of MTD containing block copolymer. Because of very small change of enthalpy, the value of the block copolymer with 30% of SCLCP part could not be determined. Nevertheless, the relatively small value of the block with 48% SCLCP block implies the dependence of the enthalpy on the composition of the block copolymers as seen in the case of the NBE and **1-3** or **1-6** block copolymer. The DSC heating and cooling scan of NBE and **1-3** or **1-6** block copolymers with the weight ratio of 54/46 and 52/48 are presented in Figure 5. A picture obtained by polarized microscopic analysis of the block copolymer of NBECN and **1-6** is presented in Figure 6.

The block copolymer of NBECN and **1-3** also show expected ^{1}H NMR spectra which give observed ratio of the components of the blocks. Despite the ^{1}H NMR spectra, no samples exhibited all three phase transition temperatures such as two Tgs and one isotropization temperature. For the block copolymers containing 33% and 23% of poly(NBECN), the phase separated character is supported by the independency of the Tg of poly(**1-3**) block and isotropization temperature. In the case of the block copolymer with 54% poly(NBECN), it exhibits very broad isotropization transition on DSC scans as shown in Figure 5. However, the observation of polarized optical microscope of this sample clearly indicated the presence of anisotropic phase and the transition occurred at 86-91°C. The enthalpy change could not be determined because of the very broad transition peak and small exchange of the heat. The block copolymer containing 28% of SCLCP block does not show Tg of SCLCP block nor isotropization temperature. For this particular sample, the polarized optical microscope analysis does not give any evidence of the formation of anisotropic phase. It is clear that this sample contains poly(**1-3**) block by NMR analysis and it is also likely to estimate the presence of phase separated morphology because of the same Tg as the Tg of NBECN homopolymer. If this sample has a phase separated morphology, the absence of anisotropic phase may be due to the very small size of SCLCP domains which may be smaller than a critical value to form anisotropic phase predicted by theoretical considerations.[12] As a result, the SCLCP microphase may not be able to form LC phase. The change of enthalpy corresponding to the SCLCP block is much smaller than that of homopolymer of **1-3** and block copolymer of NBE and **1-3**.

DISCUSSION

It has been a subject of interest that the effect of the size and type of LC microphase on the thermodynamic parameters of the phase transition.[5] The phase transition temperatures of all the block copolymers examined in this study show no dependence on the composition of the blocks. The theoretically predicted change of the transition temperature may be too small to detect by conventional methods as pointed out by Adams and Gronski.[5] All of the phase transition temperatures and Tgs observed for the block copolymers are the same as those of homopolymers and this fact supports the phase separated morphology. Another important parameter is the change of enthalpy associated with the phase transition. It is obvious that the block copolymers with a non LC block with higher Tg than isotropization temperature of an SCLCP block exhibit much smaller change of enthalpy than that of the homopolymer of SCLCP. The value of the enthalpy change of block copolymer of MTD and **1-6** is 59% of the homopolymer of **1-6** and those of block of NBECN and **1-6** are 60~80%. For the block copolymers of NBECN and **1-3**, the enthalpy values are only 47% of that of the homopolymer of **1-3**. It seems that poly(**1-3**) is more sensitive to the high Tg amorphous block than poly(**1-6**). On the other hand, the block copolymers made from NBE and **1-n** show only slightly smaller value of the enthalpy than the homopolymer of their components. The decrease of the enthalpy can be explained either by a thermodynamic effect or by a disordering of the mesogens at the phase boundary. The thermodynamic effect is originated from the restricted size of the LC microphase.[12] However, only the size of the microphase is not enough to explain the difference of the block copolymers with NBE and with NBECN or MTD. Since a microphase separated block copolymer has sharp boundary between two incompatible blocks which are coupled through polymer main chain, the orientation of the polymer main chain respect to the interphase may disturb the orientation of the mesogens at the boundary. If the polymer main chain of amorphous phase is in a glassy state, the restriction on the movement of the mesogens at the boundary will increase compared to the amorphous phase in a rubbery state. Therefor, LC microphase near the boundary is much disordered by the influence of the limited mobility of amorphous polymer phase and the interior of the SCLCP microphase forms LC phase like homopolymer of the SCLCP does. When the mesogens are connected through long flexible spacers, the influence from the amorphous polymer block will be less effective compared to the mesogens connected through short flexible spacer. This consideration also explains the high sensitivity of the poly(**1-3**) to the poly(NBECN) block compared to the poly(**1-6**). If this is the case, the increase of the molecular weight of each component without changing the ratio of the components will give large domains in which there are much less quantity of surface area under the influence of the state of amorphous block. This illustration give a way to the practical application of this type of block copolymers. In an ideal case, the amorphous block part will not affect the behavior of the SCLCP microphase and will support the system physically.

It is not completely clear, but there may be another effect on the enthalpy changes. As described above, the enthalpy change may have a tendency to decrease as the decrease of the content of the SCLCP block. This effect can be explained by the thermodynamic effect based on the limited size of the microphase. The change of the ratio of components leads the change of morphology such as from lamellae to droplets accompanying the decrease of the distance of the boundaries. This will give rise not only the decrease of the enthalpy change but finally, disappearance of the mesophase under a critical distance of the boundaries. This effect may be realized in the case of the block copolymer of NBECN and **1-3** with 72% of poly(NBECN) which doesn't show any evidence of the presence of the mesophase. To confirm this speculation, further investigation especially including the direct observation of the morphology which enable to measure the size of microphase and the change of the overall molecular weight will be necessary.

CONCLUSION

Living metathesis polymerization system initiated by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was successfully applied to the synthesis of the AB type block copolymer comprising SCLCP block and amorphous polymer block. The SCLCP block was made from 5-carbo{n-[(4'-methoxy-4-biphenylyl)oxy]alkyl}bicyclo[2.2.1]hept-2-ene with n = 3,6 and the amorphous block was made from NBE, MTD, and NBECN. All the block copolymers with the composition ranging from 75/25 to 20/80 in weight and narrow molecular weight distribution show Tgs and isotropization temperatures independent of the composition. These transition temperatures are essentially the same as those of the homopolymers of the components. They also give ^{1}H NMR spectra in a complete superimposition of the spectra of homopolymers of each block. These facts suggest the phase separated morphology of the block copolymers. The polarized microscopic analysis doesn't give well defined texture but indicates the formation and isotropization of an anisotropic phase upon cooling or heating the samples. The enthalpy change associated with isotropization is smaller than that of homopolymers of **1-3** and **1-6** especially the amorphous polymer block has higher Tg than the isotropization temperature. The decrease of the enthalpy change is rationalized in terms of the disturbance of the orientation of the mesogens at the boundary of microphase caused by the coupling of two phases through polymer main chain.

EXPERIMENTAL

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-nrobornene (60:40 mixture of exo and endo isomers) and benzaldehyde were distilled under nitrogen and stored under nitrogen. 5-carbo{n-[(4'-methoxy-4-biphenylyl)oxy]alkyl}bicyclo[2.2.1]hept-2-ene (**1-n, n = 3,6**)[8(a)] were prepared as described in the literature. All other reagents and solvents were commercially available and used as received.

300MHz ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard. Obvious multiplicities and routine coupling constants are usually not listed. Molecular weight was determined by gel permeation chromatography (GPC) at room temperature using a set of Shodex KF802.5, 803, 804, 805, 800P columns (700, 2×10^3, 2×10^4, 1×10^5Å, and a precolumn, respectively), a Knauer differential refractometer, and a Spectroflow 757 absorbance detector set at 300nm 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 (Tgs) 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 $Mo(CHCMe_3)(NAr)(OCMe_3)_3$ (0.2 ml, 0.0205 mol/l) in THF was added in one portion to a rapidly stirred solution of non mesogenic monomer (3 ml, 0.137 mol/l, 100eq) in THF and the mixture was then stirred for 30 min. The solution of the second mesogenic monomer was added as rapidly as possible to the reaction solution and stirred for 1 hour. 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 more than 90% and GPC analyses showed no traces of monomer. Further purification of samples by reprecipitation had no effect on their thermotropic behavior. When 20eq or less of monomer was used, the catalyst concentration was adjusted to 0.205 mol/l.

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Table I

Block copolymerization of 1-n and norbornene(NBE), methylcyclododecene(MTD), and cyanonorbornene(NBECN) and characterization of the resultant block copolymers

monomer					GPC		DSC heating scan		
1st	2nd	eq	weight ratio		PDI	Mn	phase transition temperature(°C)	enthalpy changes	
			theor.	found				ΔH(J/g)[a]	ΔH(J/g)[b]
NBE	**1-6**	300+20	77/23	75/25	1.11	54067	g 42 n 97 i	-[c]	-[c]
NBE	**1-6**	100+20	53/47	49/51	1.17	27092	g 38 n 94 i	1.30	2.55
NBE	**1-6**	100+50	31/69	30/70	1.25	38035	g 38 n 91 i	2.30	3.29
NBE	**1-6**	56+50	20/80	20/80	1.11	32739	g 38 n 93 i	2.52	3.15
NBE	**1-3**	300+20	79/21	79/21	1.06	88937	g 44 g 58 n 84 i	-[c]	-[c]
NBE	**1-3**	100+20	55/45	53/47	1.10	37574	g 39 g 55 n 92 i	0.47	1.00
NBE	**1-3**	100+50	33/67	33/67	1.13	64169	g 39 g 59 n 86 i	1.00	1.49
NBE	**1-3**	50+50	20/80	20/80	1.16	50782	g 36 g 60 n 87 i	1.10	1.38
MTD	**1-6**	100+20	67/33	67/33	1.08	28537	g 41 n 85 g 208 i	-[c]	-[c]
MTD	**1-6**	100+50	45/55	47/53	1.18	42850	g 41 n 92 g 207 i	1.07	2.02

(Continuation of Table I)

NBECN	**1-6**	180+20	72/28	70/30	1.17	113224	g 45 n 87 g 112 i	-^{c}	-^{c}
NBECN	**1-6**	180+50	50/50	52/48	1.13	145898	g 43 n 93 g 114 i	0.98	2.04
NBECN	**1-6**	89+50	34/66	38/62	1.16	79331	g 43 n 91 g -^{d} i	1.72	2.77
NBECN	**1-6**	36+50	17/83	21/79	1.16	46991	g 45 n 91 g -^{d} i	2.17	2.75
NBECN	**1-3**	180+20	74/26	72/28	1.09	66185	(g - n -)^{d} g 112 i	-^{c}	-^{c}
NBECN	**1-3**	180+50	53/47	54/46	1.17	108655	g 67 n 86-91^{e} g 119 i	-^{c}	-^{c}
NBECN	**1-3**	89+50	36/64	33/67	1.08	61751	g 63 n 82 g -^{d} i	0.52	0.75
NBECN	**1-3**	36+50	15/85	23/77	1.15	46624	g 63 n 82 g -^{d} i	0.48	0.62
-	**1-6**	0+20	0/100		1.16	6739	g 35 n 87 i	3.40	3.40
-	**1-6**	0+50	0/100		1.15	24067	g 42 n 93 i	3.38	3.38
-	**1-3**	0+20	0/100		1.08	7633	g 57 n 79 i	1.61	1.61
-	**1-3**	0+50	0/100		1.12	20172	g 61 n 86 i	1.47	1.47

(Continuation of Table I)

NBE	-	100+0	100/0	1.04	18726	g 40 i
NBE	-	300+0	100/0	1.07	47674	g 43 i
MTD	-	100+0	100/0	1.07	19995	g 214 i
NBECN	-	180+0	100/0	1.06	82079	g 116 i

[a] Enthalpy based on a whole polymer. [b] Enthalpy based on a SCLCP part. [c] Too broad to determine a pricise value. [d] Could not detected. [e] Determined by polarized optical microscope analysis (see text).

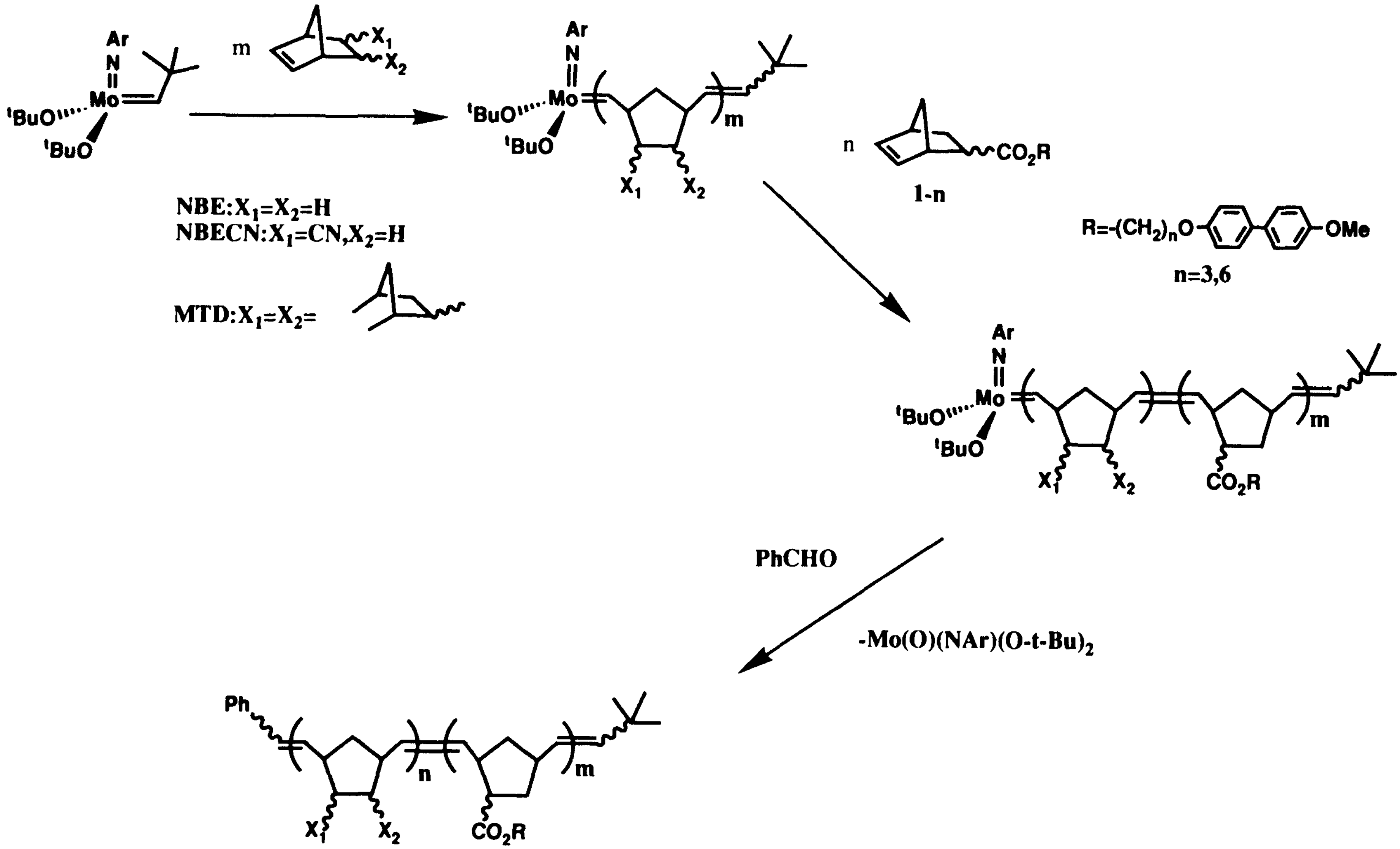

m
n
1-n
NBE:$X_1=X_2=H$
NBECN:$X_1=CN,X_2=H$
MTD:$X_1=X_2=$
R=-$(CH_2)_n$O-
n=3,6
PhCHO
-Mo(O)(NAr)(O-t-Bu)$_2$

Figure Captions

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

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

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.

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

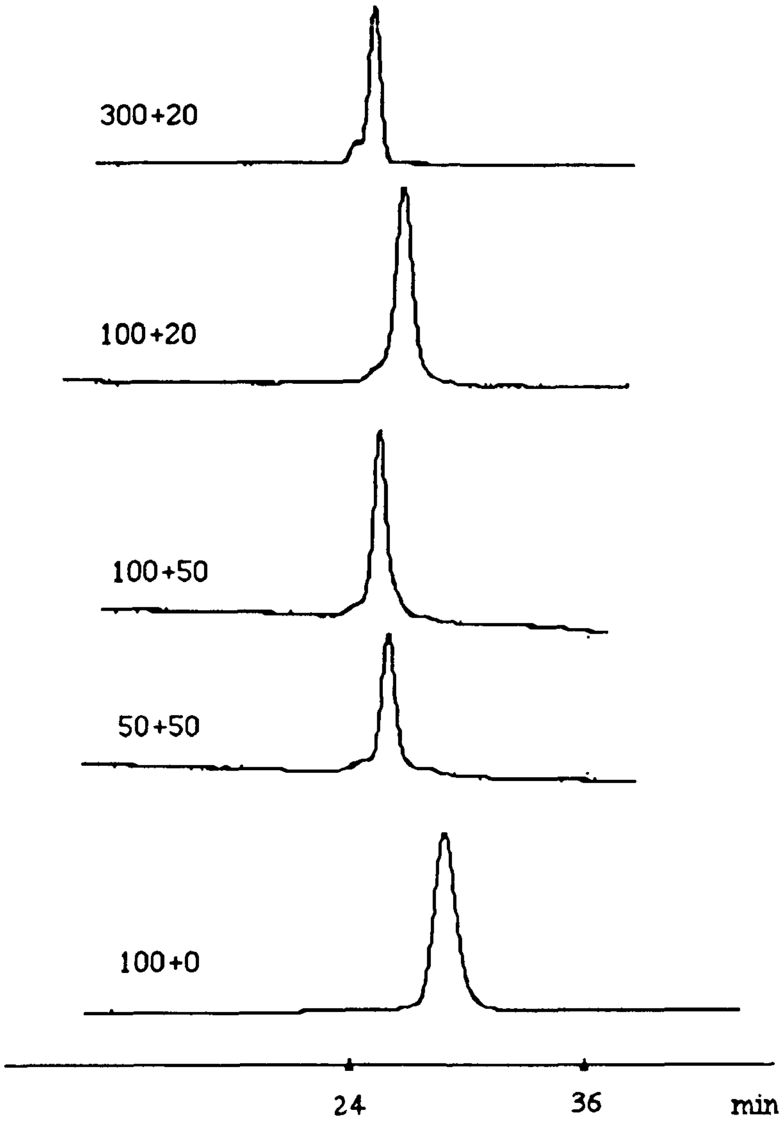


Figure 1. GPC traces of NBE and 1-3 block copolymers.

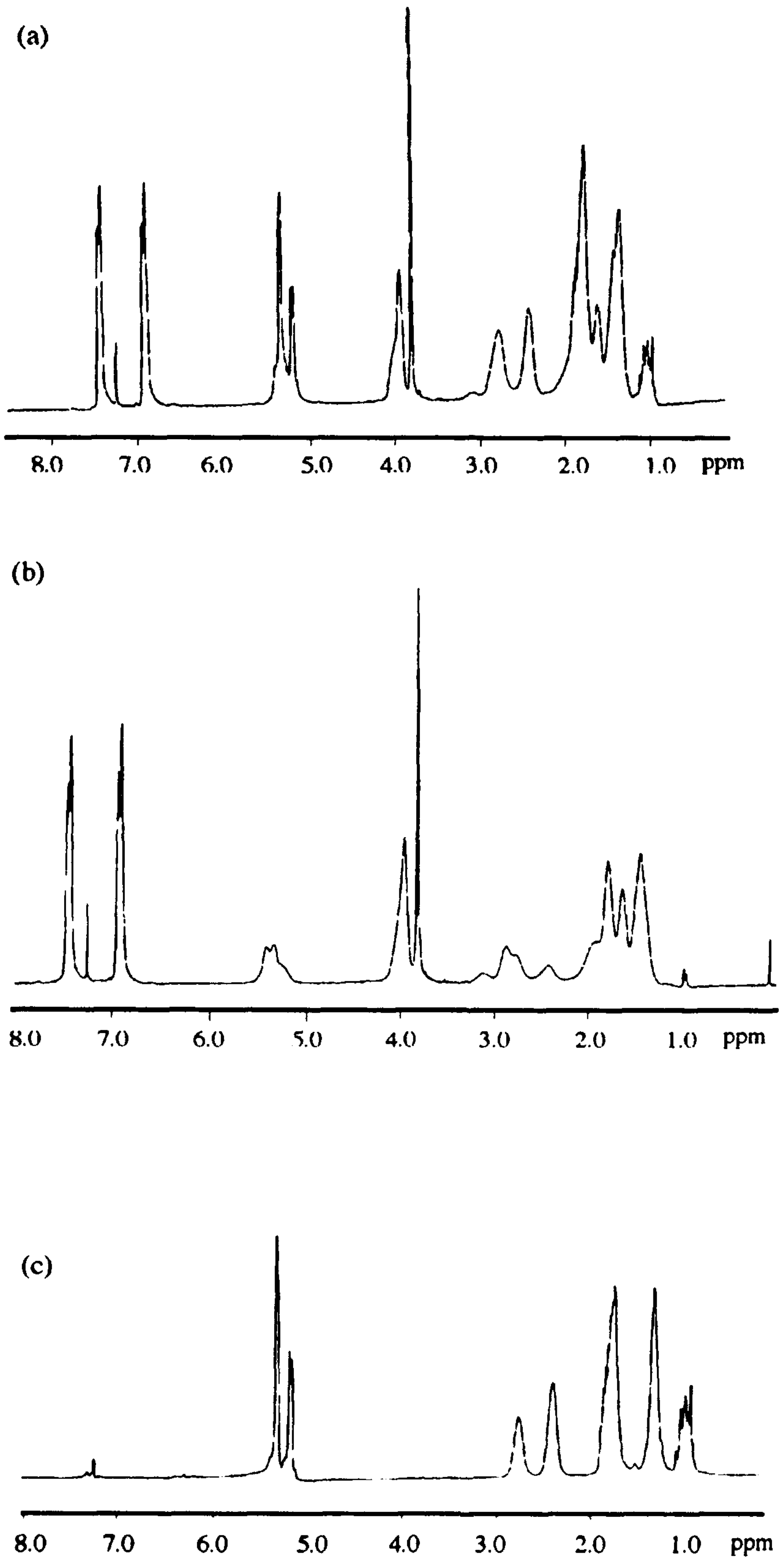
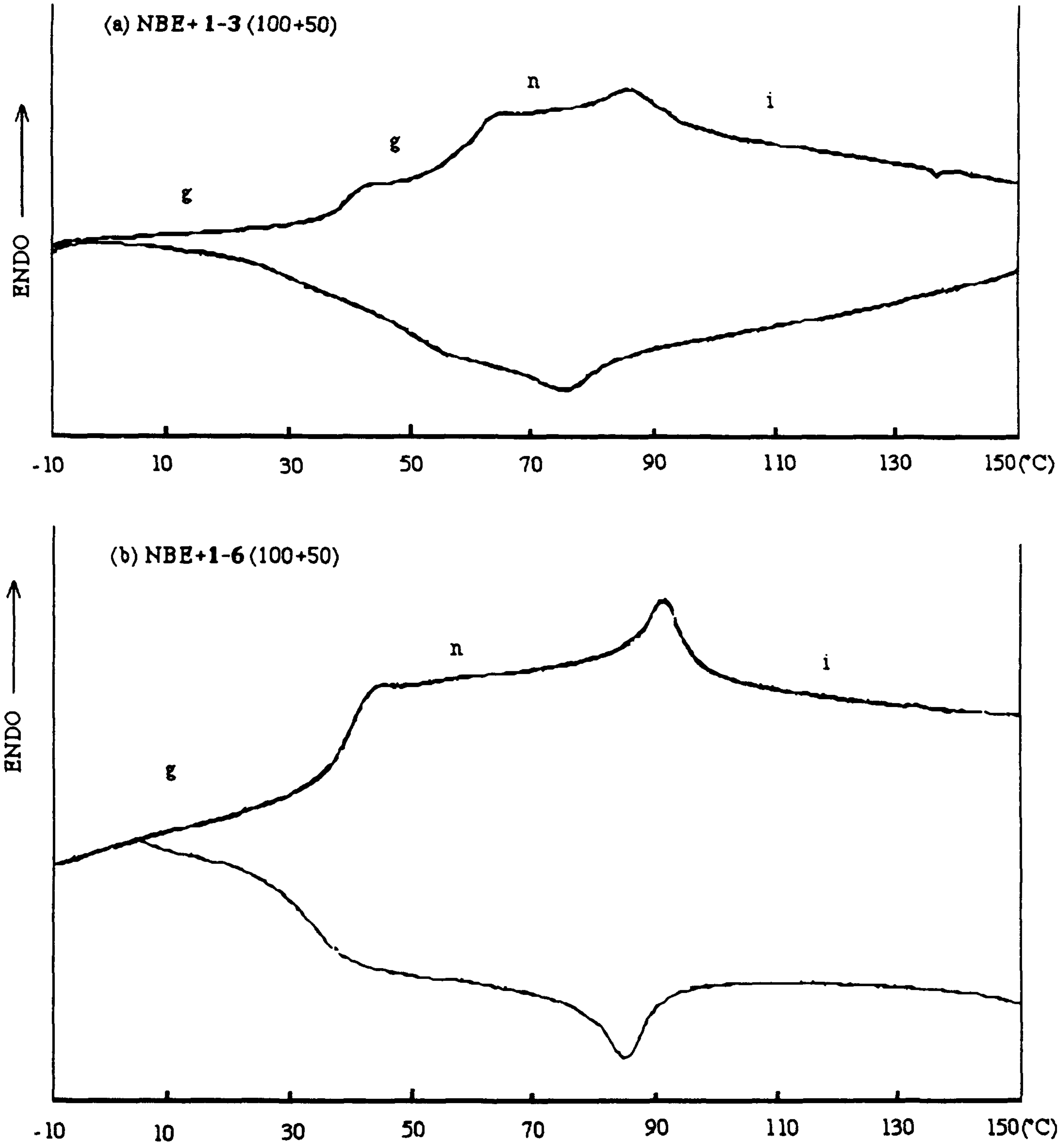


Figure 2. NMR spectra of poly(NBE+1-3), poly(NBE), and poly(1-3).



(a) NBE+ **1-3** (100+50)

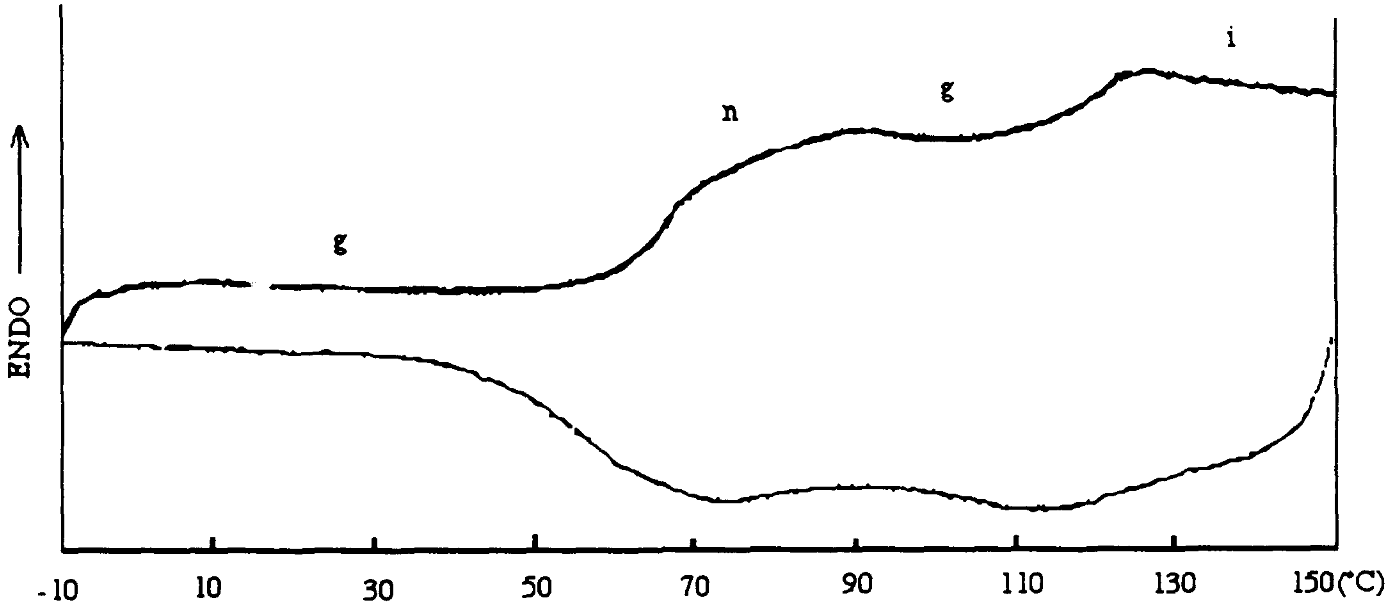
(b) NBE+**1-6** (100+50)

Figure 3.DSC traces of block copolymer containing poly(NBE) block.

NBE+C6
100+50 82°c. 80x

Figure 4

(a) NBECN+**1-3**(180+50)



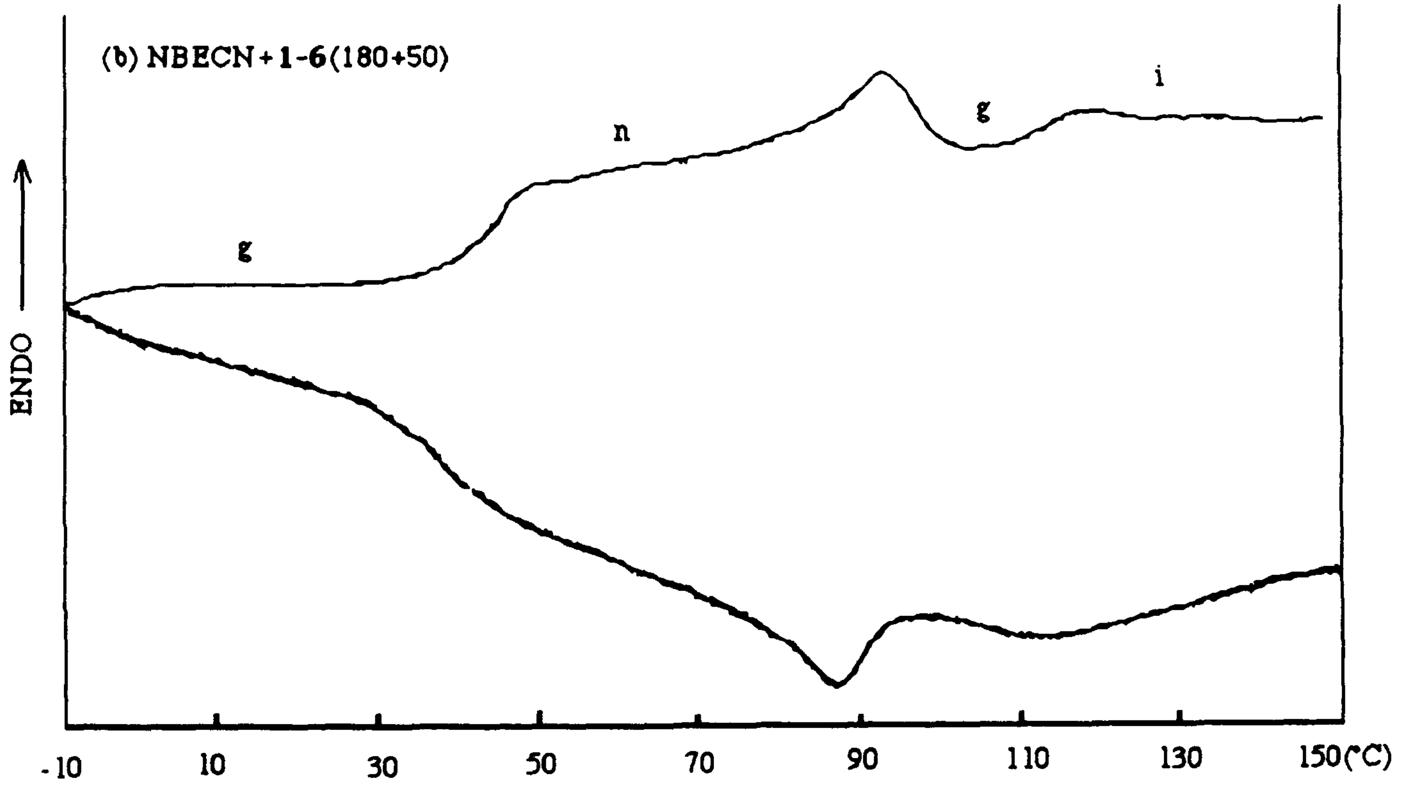
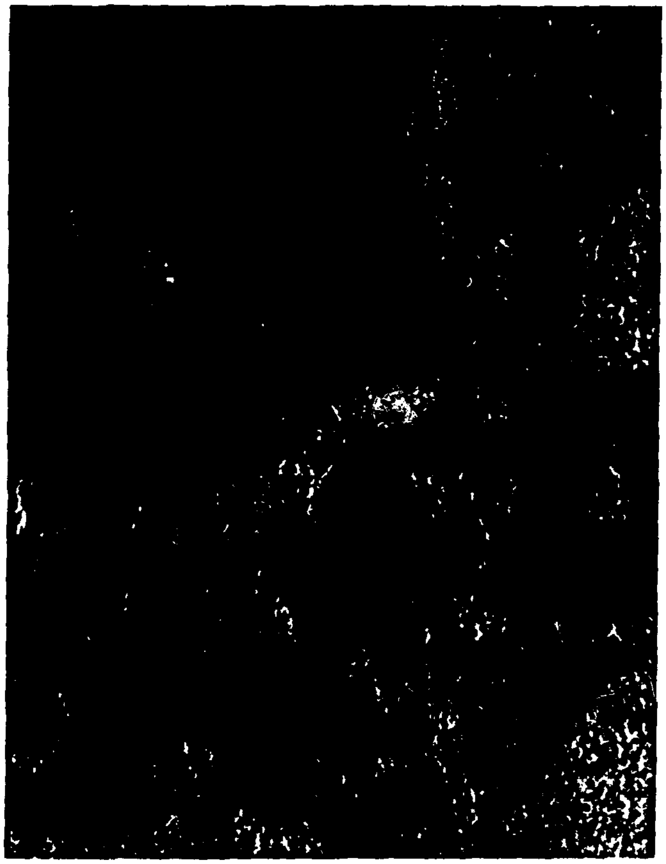

(b) NBECN+**1-6**(180+50)

Figure 5



NBECN
~~[illegible]~~ + Et 89tn 80x, 50°c

Figure #6

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