

Novel Poly(*N*-substituted urethane): 1. Synthesis and Characterization of Liquid Crystalline Polyurethanes Pendant with Biphenyl Mesogenic Unit

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Received 21 December 2005; accepted 23 May 2006

ABSTRACT

Synthesis and characterization of new liquid crystalline poly(*N*-substituted urethane)s using 4-bromo-(4-hexyloxy-biphenyl-4'-oxy)butane (C6-C4Br) as mesogenic pendant group is described. The liquid crystalline polyurethanes were synthesized through *N*-substitution by a two-step process. First the polymer was dehydrogenated by sodium hydride, and then the prepared urethane polyanion was treated with C6-C4Br. The chemical structures were characterized by FTIR, ¹H NMR, and elemental analysis. The solubility and thermal properties of *N*-substituted polyurethanes were investigated in view of the *N*-substitution degree of mesogenic unit. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) in combination with polarizing optical microscopy (POM) were used to investigate the thermal properties of *N*-substituted polyurethane. As the degree of *N*-substitution increased, the solubility of polyurethane decreased in common organic solvents, and thermal stability increased from 285°C to 370°C because of different thermal-degradation mechanisms of parent and *N*-substituted polyurethanes. The glass-transition temperature (T_g) was shifted to higher temperature with an increasing degree of substitution due to the increasing rigidity of polymer chains. Optical microscopy showed focal conic texture characteristic of the smectic A phase for both C6-C4Br and *N*-substituted polyurethanes. DSC Experiments were also found in accordance with mesophase formation. The liquid crystalline properties were strongly dependent on the *N*-substitution degree with increasing mesogen content from 25 to 100%, the mesophase-transition and isotropization temperature increased. The minimum 25% amount of mesogen is necessary to exhibit a liquid crystal property in the polymer.

Key Words:

liquid crystalline polymers;
thermotropic polyurethanes;
mesogenic side group;
optical texture;
DSC.

INTRODUCTION

Side chain liquid crystalline polymers (SCLCPs) are an important class of materials that combine the properties of liquid crystals and classical polymeric materials [1,2]. SCLCPs comprise three structural units: a polymer backbone, a flexi-

ble spacer, and a mesogenic unit. Therefore, they combine the properties of polymers and conventional monomeric liquid crystals. In order to synthesize SCLCPs with desirable liquid crystalline properties, a great deal of research has

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been focused on the varying polymer chemical structure (the nature of the polymer backbone, the flexible spacer and its length, and the mesogenic unit), polymer molar mass, polydispersity, and tacticity [3-5]. Therefore, they have attracted more attention due to their potential application in numerous areas, e.g. in nonlinear optics, optical information storage devices, and piezo-, pyro- and ferroelectric devices [6-10].

Polyurethanes (PUs) are an important class of thermoplastic elastomers with many applications, such as coating, binder resins, fibres, and high-performance elastomeric products [11,12]. Thermotropic liquid crystalline polyurethanes (TLCPU)s are studied with much interest because of their application potential. As there is a strong intermolecular interaction arising from hydrogen bonding of the urethane linkage, the synthesis of TLCPU)s seems more difficult than the synthesis of other LC polymers. However, several of the main chain liquid crystal PUs have been developed, such as (i) insertion of flexible spacers into the mesogenic units, (ii) introducing substituted mesogenic segments or (iii) using secondary amines which have entered reaction with dichloroformates [13-15].

To our knowledge, side chain liquid crystalline polyurethanes (SCLCPU)s have not investigated as systematically as SCLCPs with acrylic, methacrylic, and siloxane backbones [16]. Conventionally SCLCPU)s have been prepared by polymerization of mesogen-containing monomers, i.e. mesogenic diol and diisocyanates [17-19]. One of the disadvantages of this polymer synthesis method is that the monomer and polymers often have low solubility in the reaction system and therefore a high degree of polymerization or low molar mass polydispersity (MMD) are not achieved. Also, the reactive centres in step polymerizations are liable to react with functional groups present on the mesogen. An alternative method for the synthesis of SCLCPs is through a polymer analogues reaction, whereby a polymer is synthesized and subsequently fitted with side groups. In this way the molar mass and MMD of the polymer can be controlled more conveniently. An additional advantage is that the LC properties of the side chain polymer can be tuned to a specific application by variation of the type of mesogen and the level of functionalization.

N-Substitution of PU has been used to improve various typically desired properties of the materials,

such as enhanced fire retardancy, flexibility, solubility, and so forth. However, most of the research works have been carried out with the *N*-substituted PU with methyl, polyether or azo-dye side chains [20-22]. This article presents the first series of our experiments dealing with the synthesis and phase behaviour of a side chain liquid crystalline poly(*N*-substituted urethane)s containing 4-bromo-(4-hexyloxy-biphenyl-4'-oxy) butane (C6-C4Br) moiety with different degrees of substitution. Thermotropic polyurethanes were prepared through *N*-substitution of prepared urethane polyanion from a well defined polyurethane with C6-C4Br mesogenic group in different mole ratios. The purpose of this study was to investigate the effect of the mesogenic unit on the liquid crystalline (LC) properties of the polyurethane. Also it is important to investigate as to what extent a mesogenic unit would be necessary to create the liquid crystalline properties.

EXPERIMENTAL

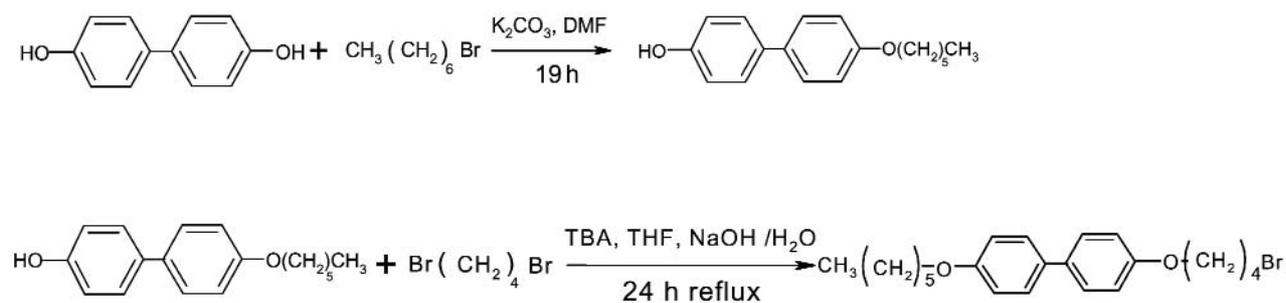
Materials

Dimethylformamide (DMF) was purified by distillation and stored over molecular sieves of 4 Å. Sodium hydride (NaH) purchased from Merck was 60 wt% in paraffin oil, and used as received. 4,4'-Biphenol, 1-bromohexane, 1,4-dibromobutane, tetra n-butylammonium fluoroborate (TBA) and sodium hydride were used as received. The used model of polyurethane was a thermoplastic polyurethane elastomer synthesized with polycaprolactone (CAPA 225) with a molecular weight of 2000 as a polyesterpolyol, toluene diisocyanate (TDI) constituting the mixed 2,4: 2,6 isomers in 80/20 ratio, and 1,4-butanediol (BD) as chain extender with a molar ratio of [23] and was purified dissolving in DMF and precipitation using methanol before use. The percentage of N atom in polyurethane sample was determined 6.311% by N analysis. The monomer and polymers were synthesized according to the route outlined in Schemes I and II, and further details are given below.

Synthetic Procedures

4-Hydroxy-4'-hexyloxybiphenyl (C6)

A solution of 4.09 g (23 mmol) 4,4'-biphenol and 1.52



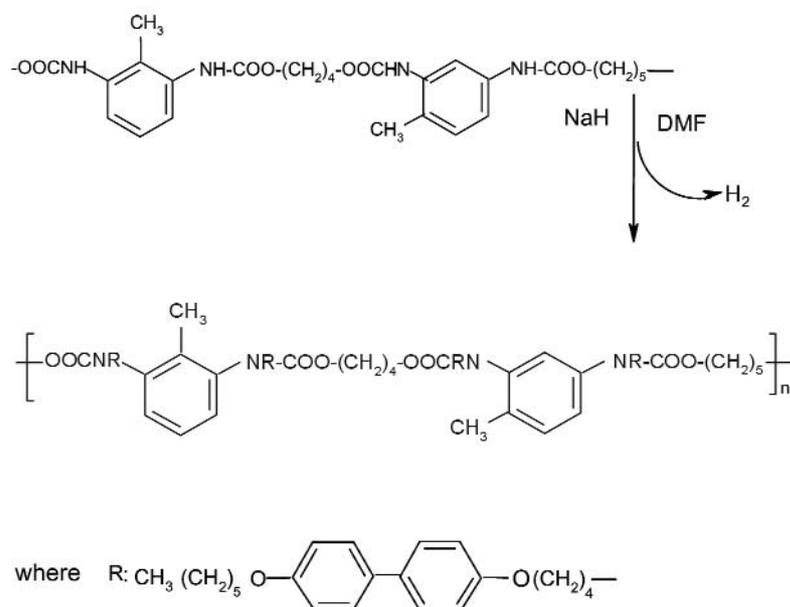
Scheme I. Synthesis of 4-bromo-(4-hexyloxy-biphenyl-4'-oxy)butane (C6-C4Br).

g (11 mmol) potassium carbonate in 50 mL of dry DMF was heated. 3.13 mL (23 mmol) of 1,4-dibromobutane was added dropwise, over a period of 30 min. The mixture was refluxed for approximately 12 h, after which the white precipitate was filtered hot to ensure the complete removal of any produced potassium bromide salt and side product. On cooling, the mixture was poured into the 10% NaOH aqueous solution, the precipitate was collected by filtration and dissolved in dichloromethane. The organic solution was washed with water and the solvent was removed. The crude product was collected and recrystallized twice from isopropanol and ethanol to give white crystals. Yield 72%, mp 158°C. FTIR (KBr):

$\bar{\nu}$ 3284 (OH), 3041 (C-H, aromatic), 2934 (CH₂), 1609 (aromatic), 1250 to 1177 (R-O-Ar) cm⁻¹. ¹H NMR (CDCl₃): δ 7.46-7.41 (m, 4H aromatic, ortho to -O), 6.96-6.87 (dd, 4H aromatic, meta to -O), 4.85 (s, OH phenolic), 3.99 (t, 2H, α to -O), 1.76 (m, 2H, CH₂, β to -O), 1.49-1.34 (m, 2H, CH₂, γ to -O) ppm.

4-Bromo-(4-hexyloxy-biphenyl-4'-oxy)butane (C6-C4Br)

A volume of 3.08 mL (24.5 mmol) 1,4-dibromobutane was added to a mixture of 1.4 g (4.9 mmol) of 4-hydroxy-4'-hexyloxybiphenyl, 0.13 g (0.24 mmol) TBA and 0.62 g (15 mmol) sodium hydroxide in 30 mL of THF-H₂O (1:1, v/v) over a period of 45 min



Scheme II. Synthesis of poly(*N*-substituted urethane)s with C6-C4Br mesogenic group.

under reflux condition. After 24 h the white precipitate was filtered out. The resulting mixture was concentrated, dissolved in chloroform and reprecipitated with excess of *n*-hexane. The product was recrystallized from ethanol. Yield 80%, FTIR (KBr): $\bar{\nu}$ 3041 to 3068 (CH, aromatic), 2872-2936 (CH₂), 1607 (C=C), 1241 (R-O-Ar), 589 (C-Br) cm⁻¹. ¹H NMR (CDCl₃): δ 7.47-7.43 (dd, 4H aromatic, ortho to -O), 6.96-6.91 (dd, 4H aromatic, meta to O), 4.02-3.97 (t, 4H, CH₂, α to O), 3.50 (t, 2H, CH₂, α to Br), 2.1-2.05 (m, 2H, CH₂, β to Br), 1.99-1.7 (m, 2H, β to -O), 1.48-1.32 (m, 6H, CH₂), 0.91 (t, 3H, CH₃) ppm. Calculated for C₂₂H₂₉BrO₂: C, 65.87%; H, 7.39%. Found: C, 65.45%; H, 7.34%.

Poly(N-substituted urethane)

Synthesis of poly(*N*-substituted urethane) with a calculated amount of sodium hydride for 100% level of substitution is described as a representative case. To a solution of 0.1 g polyurethane (N=6.31%) dissolved in 8 mL dry DMF, 0.025 g (0.61 mmol) of sodium hydride suspended in DMF was added with stirring, at a temperature not exceeding 0°C under inert conditions. The reaction mixture was kept at 0°C until evolution of H₂ ceased and 0.25 g of (0.61 mmol) C6-C4Br in DMF was added to the mixture. After another 4 h of stirring at 60°C, 40 mL hot water was added dropwise to the mixture to precipitate the polymer. The polymer was washed with ethanol repeatedly to remove DMF and unreacted starting material, and the product was dried in a vacuum. Yield 80%, FTIR (KBr): $\bar{\nu}$ 3334 (N-H), 3103 (C-H, aromatic), 2933 (CH₂), 1734, 1703 (C=O, urethane), 1200-1000 (C-N and C-O) cm⁻¹. ¹H NMR (CDCl₃): δ 7.4-6.8 (broad, H aromatic rings), 4.1-3.42 (broad, CH₂, α to -O and -N), 2.3-1.3 (broad, CH₂), 1.25 (s, CH₃, backbone), 0.90 (s, CH₃, side group) ppm.

Methods

Spectroscopic characterization was carried out by the following instrumentation: melting points were recorded with an electrothermal 9100 apparatus. FTIR Spectra were recorded on a Bruker PS-15 spectrometer. ¹H NMR Spectra were taken on a 400 MHz-Bruker SP-400 AVANC spectrometer using 50/50 chloroform as solvent with tetramethylsilane as internal standard. The inherent viscosity of the polymer

solution was measured in an Ubbelohde viscometer, at a concentration of 0.2 g/dL in DMF at 45°C. A differential scanning calorimeter Mettler 822 was used to determine phase transition temperatures at the heating and cooling rates of 10°C/min. The instrument was calibrated with indium regarding temperature and enthalpy. An optical Zeiss polarizing microscope equipped with long working distance objective was also used to observe phase transitions. The samples were heated and cooled with a TMS94 hot stage and associated temperature controller. Elemental analysis was carried out by a Hereaus, CHN analyzer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomer

4-Hydroxy-4'-hexyloxybiphenyl (C6) was synthesized via nucleophilic displacement of bromine from 1-bromohexane by potassium-4,4'-biphenoxide. A higher yield (72%) was obtained, as compared to 67% with the earlier reported route [24].

The mesogenic 4-bromo-(4-hexyloxy-biphenyl-4'-oxy)butane (C6-C4Br) was successfully synthesized by treating the C6 with 1,6-dibromobutane undergoing S_N2 substitution reaction with good yield (Scheme I).

The synthesized C6 and C6-C4Br were proved as their structures by using FTIR, ¹H NMR, and elemental analysis, etc. A POM with a heating stage and DSC



Figure 1. Optical polarized micrographs showing the focal conic texture formation of the S_A phase of C6-C4Br from isotropic phase on cooling at 114°C (magnification 200x).

were used for measuring the melting temperature (T_m) and isotropization temperature (T_i) of the compounds. The DSC thermogram of low molecular compound C6-C4Br, two overlapping exothermic transitions at 116°C and 119°C correspond to the crystal-mesophase transition and the second to the isotropization transition. On cooling of C6-C4Br one fairly small exothermic peak at 115°C ($H=24.28$ J/g) and a stronger exothermic peak at 111°C ($H=31.06$ J/g) appeared. The polarizing microscopic observation of C6-C4Br showed a S_A phase between the two DSC peaks on both cooling and heating processes. The focal conic texture formation of the S_A phase observes from isotropic phase in Figure 1.

Synthesis and Characterization of Polymers

Model polyurethane was used to carry out *N*-substitution according to Scheme II.

Sodium hydride was used in the first step as depicted in Scheme II. The catalyst abstracts the labile urethane proton and generates the active anionic sites on the polymer backbone. In the next step, the prepared urethane polyanion reacts as nucleophile in the bromine substitution in the molecule of the C6-C4Br to give *N*-substituted polyurethane with mesogenic group. Sodium hydride/DMF is commonly used as a catalyst/solvent in the *N*-substitution process of polyurethanes and polyanilines [22,25].

To compare the effect of substitution degree on the physical and thermal properties, four different levels of substitution were synthesized. The substitution degree represented in Table 1 was determined from ^1H NMR signals at 0.9 and 1.25 ppm, corresponding to the newly formed end substituted methyl group on the side chain and methyl protons of TDI moiety in

Table 1. Substitution degree and intrinsic viscosity of polyurethanes.

Samples	DS (mol%) ^a	ζ_{inh} (dL/g) ^b	Yield (%)
PU-0 ^c	0	0.635	-
PU-25	18	0.303	80
PU-50	32	0.487	80
PU-75	62	0.546	84
PU-100	80	0.607	85

(a) Degree of substitution, as determined from ^1H NMR analysis; (b) Solvent: DMF; 45°C; (c) Theoretical substitution degree (mol%).

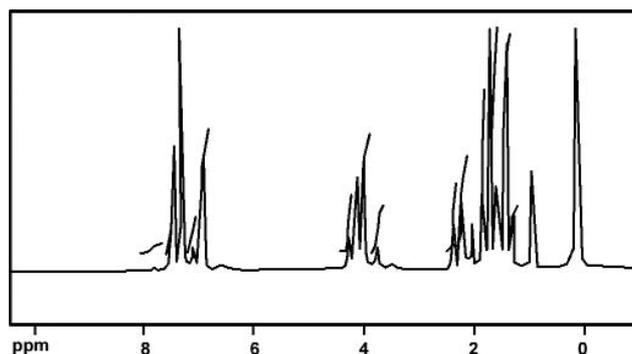


Figure 2. ^1H NMR Spectrum of the PU-25 in CDCl_3 .

polyurethane, respectively. The backbone methyl protons are not changed before and after the *N*-substitution reaction of polyurethane and can be used as the internal standard for the determination of the reaction degree (Figure 2). These amounts show that the theoretical *N*-substitution degrees were larger than those calculated from NMR spectra.

The inherent viscosity of poly(*N*-substituted urethane)s was determined by an Ubbelohde viscometer at 45°C in DMF and is listed in Table 1. As shown in Table 1, the viscosity of *N*-substituted polyurethanes slightly decreased as the substitution degree decreased presumably due to reduction of the molecular weight of polymer but the amount of viscosity for all synthesized poly(*N*-substituted urethane)s was lower than that of parent polyurethane. We thought that this was due to decreasing the interaction between the *N*-substituted polyurethanes chains. The increased rigidity of polymers leads to decreased solubility with increasing the substitution degree. The solubilities of the polyurethanes are presented in Table 2. The poly(*N*-substituted urethane) samples do not show elastic behaviour. Therefore, it was concluded that the content of mesogenic side group (hard segment) was the important factor to control the elastic behaviour.

FTIR Spectra of the parent polyurethane together with the poly(*N*-substituted urethane)s are shown in Figure 3. All polymers except for PU-0 exhibit characteristic absorption of urethane carbonyl at 1606-1734 cm^{-1} in addition to those for C-O-C bands at 1244 cm^{-1} , NH stretching of urethane linkages at 3333 cm^{-1} , CH stretching of alkylene chains at 2866-2934 cm^{-1} and of aromatic rings at 3038 cm^{-1} . The PU-0 shows no FTIR absorption for the mesogenic side

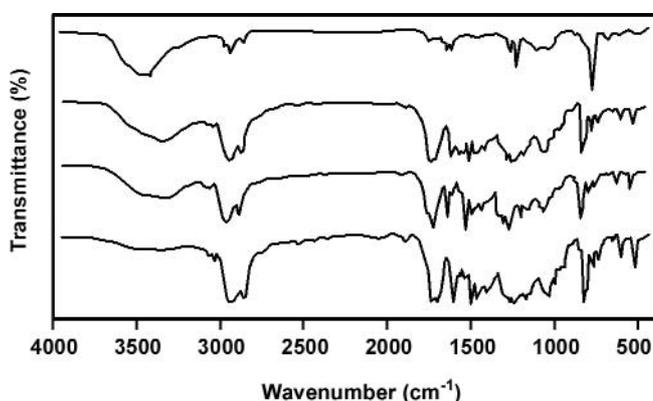
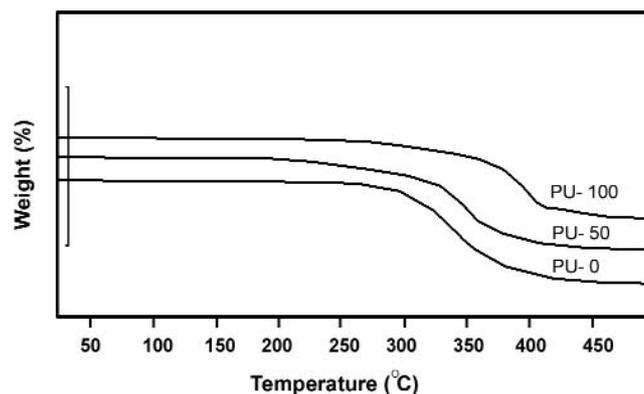
Table 2. Solubilities of polyurethanes.

Samples	Solubility					
	DMF	DMSO	CHCl ₃	EMK	THF	Acetone
PU-0	4	3	4	4	3	3
PU-25	4	3	4	4	3	3
PU-50	3	3	4	3	3	2
PU-75	2	2	4	3	1	1
PU-100	2	2	4	2	1	1

A scale for the different degrees of solubility is assigned as follows: (1) slightly soluble when hot; (2) soluble when hot; precipitate when cold; (3) soluble hot; (4) soluble cold.

chain. The bands at 1672 and 1727 cm⁻¹ are assigned to the hydrogen-bonded urethane carbonyl group and band at 1736 cm⁻¹ is based on the free carbonyl group. The absorption of the urethane carbonyl and the NH stretching weaken with the increase of the substitution degree. This means that the side chain hinders the formation of the hydrogen bonds based on intermolecular interaction of the urethane linkages.

TGA Thermograms of PU-0, PU-50 and PU-100 are shown in Figure 4. The results indicated that the pendant structures have an influence on the thermal decomposition of poly(*N*-substituted urethane)s. The thermal stability of the *N*-substituted polyurethanes increased as the C6-C4Br substitution degree increased. The different thermal degradation mechanisms of these PUs result in the higher thermal stability of the *N*-substituted polymer with respect to the unsubstituted polymer. The mechanism of thermal decomposition in *N*-alkylated PU is a hydrogen-transfer reaction that involves C-H transfer and requires

**Figure 3.** FTIR Spectra of the polyurethanes.**Figure 4.** TGA Thermograms of the PU-0, PU-50 and PU-100.

more energy than the N-H transfer that occurs in the case of PU [21].

Liquid Crystal Properties of Poly(*N*-substituted urethane)s

The transition temperatures of all synthesized poly(*N*-substituted urethane)s were determined by first DSC measurements at a heating rate of 10°C/min. The samples were also observed under an optical polarizing microscope to confirm the existence of the liquid crystalline phase. Figure 5 depicts the DSC thermograms of polyurethanes at the first heating cycle. DSC Curves of all polymers showed two step transitions corresponding to soft-segment glass transition and hard-segment glass transition that is derived from isocyanate and mesogenic units. The heating process of *N*-substituted polyurethanes showed three endothermic peaks owing to the melting transition temperature of soft segment, melting temperature of hard segment and isotropic transition temperature, respectively.

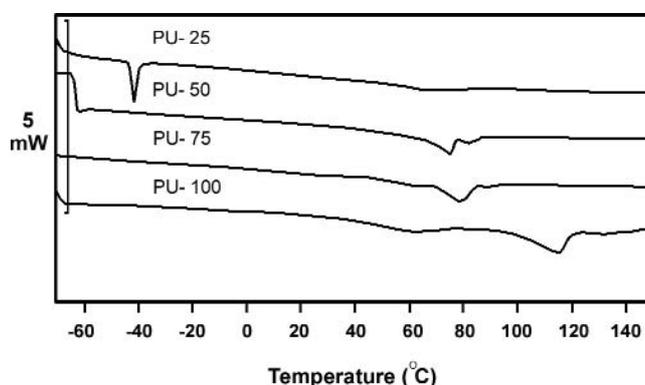
**Figure 5.** DSC Thermograms for polyurethanes.

Table 3. Thermal properties of the polyurethanes determined by DSC at scan rate 10°C/min on the first heating scan and microscopic observation.

Polymers	Thermal transition data from DSC (°C)					Phase transition from optical microscopy (°C)	
	T _{sg}	T _{sm}	T _m	T _{hg}	T _i	T _m	T _i
PU-0	-69	37	-30	-	-	-	-
PU- 25	-67	40	-18	50	-	52	-
PU- 50	-62	42	-	52	66	53	68
PU- 75	-44	62	0	80	90	81	92
PU-100	-38	68	8	114	130	115	133

T_{sg}: soft-segment glass transition temperature; T_{hg}: hard-segment glass transition temperature; T_{sm}: soft-segment melting temperature; T_m: melting temperature; T_i: isotropization temperature.

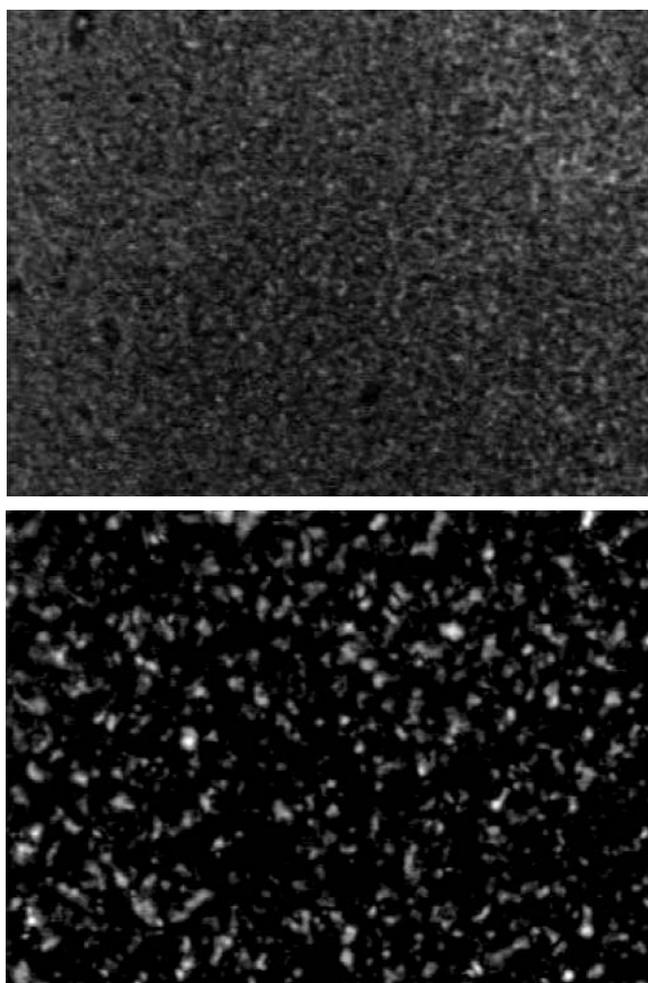


Figure 6. Optical polarized micrographs for (a) PU-100; and (b) PU-50 (magnification 200x).

As the active hydrogen in the urethane group of polyurethanes was replaced with the C6-C4Br group, the T_g of the soft segment and hard segment slightly increased. The thermal properties of polyurethanes are listed in Table 3. One can observe that from Table 3 with increasing mesogen content from 25 to 100%, the mesophase-transition temperature increased. It can be seen from the transition temperatures of *N*-substituted polyurethanes that an increase in mesogen content results in a higher T_g, and high T_m and T_i. The hydrogen bonding of the urethane to alkoxy side group restricts the segmental motion of the chain and increases the T_g of the chain [21].

The crystal-mesophase and isotropization transition were confirmed by polarizing optical microscope. Visual observations of the polyurethanes under microscope show that a minimum 25 mol% mesogen content is sufficient to impart an LC property to the polymers. Figure 6 shows polarizing optical microphotographs of PU-100 and PU-50. The textures seem to be of a smectic nature, but a correct liquid crystal phase assignment was not possible and further X-ray investigations have to be done. The texture of the mesophase did not vary as the mesogen content was varied.

CONCLUSION

The new series of thermotropic poly(*N*-substituted urethane)s containing biphenyl mesogenic side chain was synthesized through *N*-substitution of urethane polyanion. The effects of the *N*-substitution degree on their properties, such as spectroscopy, thermal stability, solubility, viscosity and thermal transition temperatures were observed. *N*-Substitution of polyurethane had significant impact on the thermal properties of the polymer. The higher melting point of *N*-substituted polyurethanes are due to the increasing the rigidity of polymer chains. Poly(*N*-substituted urethane)s showed a smectic texture under crossed polarizing optical microscope.

ACKNOWLEDGEMENTS

The authors express their appreciation to thank Research Vice Chancellor of Azarbaijan University of Tarbiat Moallem for financial support of this research

and Prof. A.A. Entezami for his useful help.

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