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PHASE SEPARATED POLYURETHANES WITH PENDANT MESOGENIC UNITS[†]

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Abstract

Polyurethanes containing polytetramethylene oxide soft segments and hard segments with azobenzene mesogenic groups were synthesized. Their thermal transitions were characterized by differential scanning calorimetry, while the dissociation of H-bonds with temperature was characterized by Fourier transform infrared spectroscopy. X-ra diffraction patterns at room temperature were also carried out.

INTRODUCTION

Polyurethanes are, in most cases, block copolymers composed of soft polyester or polyether segments and hard segments, formed by diisocyanates and low molar mass diols. These segments differ in polarity and, consequently, are more or less phase separated. The introduction of additional polar groups into the hard segments promotes phase separation even more. Due to their special mechanical properties, phase separated materials are indispensable in some areas of application.

Over the past few years, liquid crystalline materials have been studied extensively and have gained great importance due to their unique mechanical, rheological and optica

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[†] Dedicated to the memory of Professor Dr. Anton Šebenik

properties. Their special properties have been successfully employed, for example, in information technology. Side chain liquid crystalline polymers are processable and soluble as basic polymers, while the mesogenic units in the side chains can be ordered, *e.g.* by magnetic field. However, once the magnetic field has been switched of, they are prevented from moving out of alignment by the polymer backbone.

Three structural parts of side chain liquid crystalline polymers influence their properties: the polymer backbone, the flexible spacer and its length, as well the mesogenic unit and the end group in its para position. Several papers have been published which systematically investigate the influence of the above-mentioned structural parts on the liquid crystalline properties of side chain liquid crystalline polymers [1-4], although few of them refer to the polyurethane backbone. A systematic investigation of polyurethane side chain liquid crystalline polymers has been undertaken by this laboratory [5-10] and the present work is a part of this study.

As previously mentioned, microphase separation is known in some copolymers and polymer blends, but it is also characteristic of some liquid crystalline polymers as a consequence of differences in the chemical structure of individual structural parts of the polymer molecule, *i.e.* between the polymer backbone and mesogenic units. The driving force of microphase separation is the thermodynami immiscibility of the random coil of the polymer background (matrix) and the rigid mesogenic units tending to order. In side chain liquid crystalline polyurethanes, microphase separated materials show, besides other thermal transitions, two glass transition temperatures: one for the independen movement of soft segments of the polyurethane backbone and the other for the combined movement of hard segments and side chains.

In recent publications, we have described liquid crystalline side chain (LCSC) polyurethanes with hard segments only, prepared from diisocyanate and mesogenic diols [5-9]. In the present work, we report on the investigation of segmented LCSC polyurethanes with differing amounts of polytetramethylene oxide (PTMO) soft segments. By introducing soft segments into the polyurethane backbone, phase separation was expected to occur, while maintaining liquid crystalline properties in the hard segment part of the material.

EXPERIMENTAL

Synthesis

Polyurethanes (denoted as C6CNPTMOX polyurethanes), synthesized according to the scheme (PTMO-HDI)$_x$-(C6CNP0.95)-(HDI-PTMO)$_y$, were prepared from α-[bis(2-hydroxyethyl)amino]-ω-(4-cyanoazobenzene-4'-oxy)hexane (Cn6-diol), its synthesis has been described elsewhere [5]; hexamethylenediisocyanate (HDI), Fluka; and different amounts of polytetramethylene oxide (PTMO), BASF, M_n 1000 g/mol, in three steps.

In the first step, the hard segmented polyurethane C6CNP0.95 was prepared in the following way:
Cn6-diol was dried in vacuo at 40°C for 10 hours. 1.0609 g of dry Cn6-diol and 0.4129 g of HDI (mole ratio diol : HDI = 1 : 0.95) were weighed in a 50 mL round bottomed flask. The reaction mixture was diluted with dimethylformamide (DMF) to a 15 wt. % solution and the catalyst dibutyltin dilaurate (0.2 wt. % with respect to the diol) was added. All the reagents were weighed in a dry box to avoid water contamination. After removing of the dry box, the flask was equipped with a drying tube. The reaction mixture was stirred by a magnetic stirrer at 70 °C for 3 hours. The course of the reaction was followed by FTIR spectroscopy. The reaction was considered to be concluded when the NCO-band at 2274 cm^{-1} disappeared. Polyurethane was precipitated from the reaction mixture in ethanol and air dried. Its composition was examined by elemental analysis, while molar mass distributions and polydispersity were measured by size exclusion chromatography.

In the second step a NCO prepolymer of C6CNP0.95 was prepared:

1.4738 g of C6CNP0.95, 0.2696 g of HDI, catalyst (0.2 % with respect to C6CNP0.95) and DMF (15 wt. % solution) were weighed in a 50 mL round bottomed flask in a dr box and the reaction was performed at 70°C for 3 hours.

In the third step PTMO was added to the C6CNP0.95 prepolymer in molar ratios
prepolymer : PTMO = 1:1 (C6CNPTMO1),
prepolymer : PTMO = 1: 0.5 (C6CNPTMO0.5), or
prepolymer : PTMO = 1: 0.25 (C6CNPTMO0.25)
in a dry box and the reaction was run again at °C for 3 hours. The synthesized polyurethanes were dried in air for one month and then for an additional 48 hours at room temperature in a vacuum dryer. Their average molar masses and polydispersity are given in Table 1.

Table 1. Weight average molar masses ($\overline{M}_w$) and polydispersities ($\overline{M}_w / \overline{M}_n$) of C6CNPTMOX polyurethanes.

	$\overline{M}_w \times 10^{-3}$ (g/mol)	$\overline{M}_w / \overline{M}_n$
C6CNPTMO1	53	7.1
C6CNPTMO0,5	48	7.3
C6CNPTMO0,25	53	7.5

Methods

Size exclusion chromatography (SEC)

The measurements were performed on a modular Perkin Elmer liquid chromatograph with a UV detector. precolumn, a PL gel column Mixed (30 cm x 7 mm, particle size 4 - 5 mm, with a linear range of molar masses between 500 and $5 \cdot 10^6$ g/mol, Polymer Laboratories), and THF as an eluent (1 mL/min) were used. The calibration was performed with polystyrene standards (Toyo Soda Manufacturing) in the molar mass region of 500 - $3.7 \cdot 10^6$ g/mol.

Differential scanning calorimetry (DSC)

The measurements were made on a Perkin Elmer DSC 7 differential scanning calorimeter. All samples were treated in the same way: The sample was placed into the sample holder at °C, cooled to -50°C, maintained at -50°C for 3 min, heated to 150°C, maintained at 150°C for 3 min, cooled to -50°C, maintained at -50°C for 3 min, and then it was reheated once again, all at a scan rate of 10 K/min. Glass transition temperatures (T_g), all other transition temperatures, and the enthalpies given in the tables were average values of at least two measurements taken at the second heating and cooling cycle, respectively.

Fourier transform infrared spectroscopy (FTIR)

Infrared spectra at various temperatures were scanned by a Perkin Elmer FTIR 1725 X spectrophotometer equipped with a Spectra-Tech heating cell. The resolution was 4 cm^{-1}. The sample was pressed between two NaCl crystal plates and heated to the desired temperature in the heating cell.

X-ray diffraction

X-ray diffraction patterns were done on a Siemens D-5000 Diffractometer using a CuKα light (λ=1.54 Å) in 0.02° steps from 1-30° (in 2Θ) with 2 s and from 1-12° (in 2Θ) with 20 s. The measurements were carried out on free standing unoriented films, prepared by casting the samples in a 0.5 mm thick form at 150°C.

RESULTS AND DISCUSSION

The synthesized polyurethanes are phase separated compounds, so they show two T_g, one of the movement of the polymeric backbone (soft segments) and the other of the movement of the hard segments and the side chains. The DSC curves of the second heating of the samples at two heating rates (20 °C/min for the determination of T_g and 10°C/min for determination of other thermal data) are shown in Figure 1 with the corresponding temperatures and enthalpies given in Table 2. Glass transitions of PTMO soft segments (T_{g1}) occur in the temperature range between -74°C and -69°C, while the glass transitions of the hard polyurethane segments (T_{g2}) can be seen between 1°C and 10°C. This is followed by a weakly expressed endothermic transition (T_1 in Table 2), exothermic cold crystallization and endothermic transition, which could be due to the dissociation of H-bonds (FTIR measurements) and to the melting of hard segments of the polymer backbone.

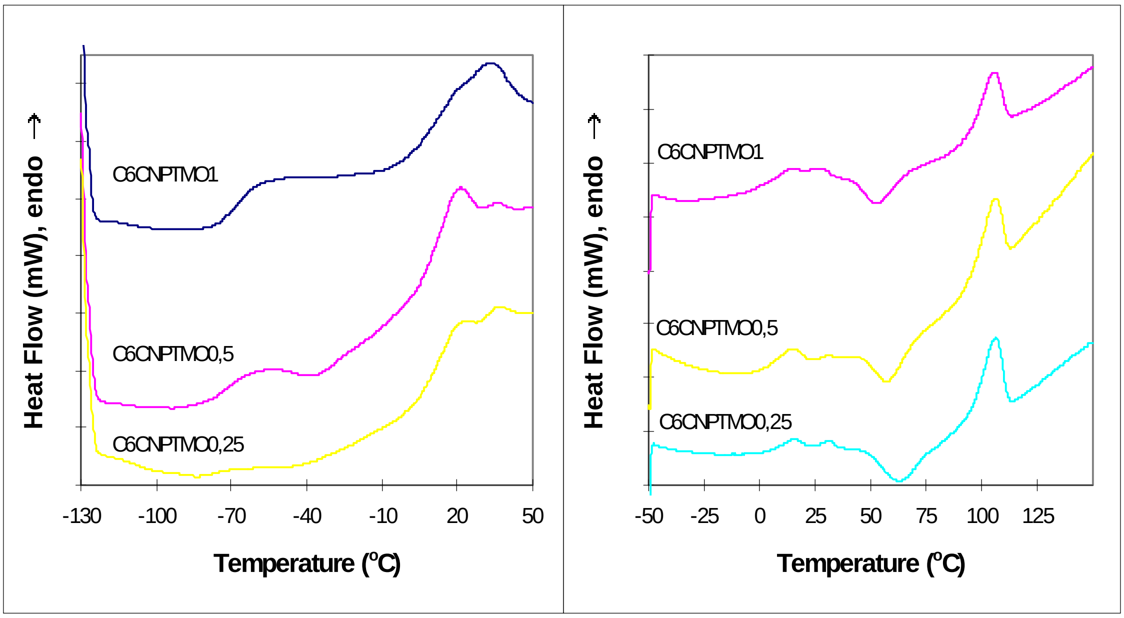

Figure 1. Normalized DSC curves of the second heating of C6CNPTMOX polyurethanes in two temperature ranges: A - heating rate of 20°C/min, B - heating rate of 10°C/min

Table 2. Temperatures (T) and enthalpies (ΔH) of the phase transitions of C6CNPTMOX polyurethanes at the second heating with a rate of 10°C/min. The shaded values (T_{g1}) were obtained at the second heating with a rate of 20°C/min.

	T_{g1} (°C)	ΔCp_1 (J/gK)	T_{g2} (°C)	ΔCp_2 (J/gK)	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)	T_3 (°C)	ΔH_3 (J/g)
C6CNPTMO1	-69	0.19	1	0.85	28	1.1	53	-11.5	106	12.9
C6CNPTMO0.5	-72	0.20	7	0.72	32	0.35	59	-12.5	107	15.6
C6CNPTMO0.25	-74	0.06	9	0.34	32	0.80	65	-18.5	107	17.2

The DSC curves of the thermally treated samples (held for 5 minutes at 150 °C, then cooled to room temperature where they were held for at least 7 days) are shown in Figure 2 and the corresponding temperatures and enthalpies of the phase transitions in Table 3. The endothermic transitions around 33 °C (T_1) are ascribed to the melting of soft segments; their enthalpy decreases with decreasing amounts of the soft segments in the C6CNPTMOX polyurethanes, as shown in Figure 3. The enthalpy of the endothermic phase transition around 51°C (T_2) increases with increasing amounts of hard segments. The transition could be ascribed to the isotropization of the mesogenic units and, possibly, to the melting of the side chains. The endothermic transition at the highes temperature (T_3) is ascribed to the melting of hard segments (dissociation of H-bonds).

Table 3. Temperatures (T) and enthalpies (ΔH) of the phase transitions of C6CNPTMOX polyurethanes at the second heating at a rate of 10 °C/min, followed by heating for 5 minutes at 150 °C, then cooling to room temperature where they were held for at least one week.

	T (°C)	ΔH (J/g)	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)	T_3 (°C)	ΔH_3 (J/g)
C6CNPTMO1	7	3.6	33	4.3	51	0.3	105	13.9
C6CNPTMO0.5	9	3.9	33	0.3	51	1.5	107	18.9
C6CNPTMO0.25	7	0.9			50	3.1	107	21.3

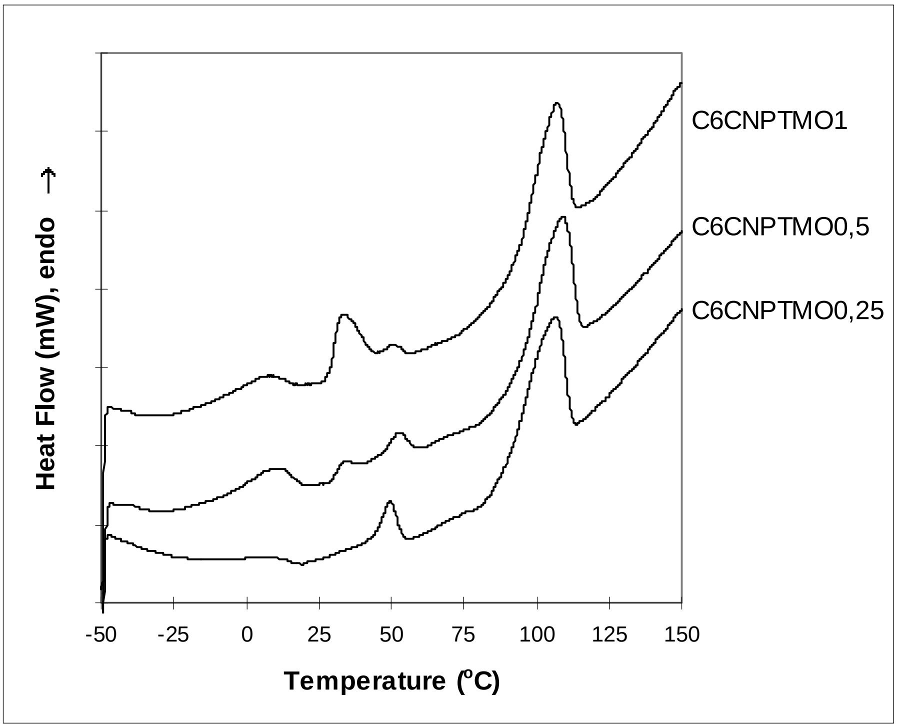

Figure 2. Normalized DSC curves (10 °C/min) of C6CNPTMOX polyurethanes with the following thermal history: heated for 5 minutes at 150 °C, then cooled to roo temperature where they were held for at least one week.

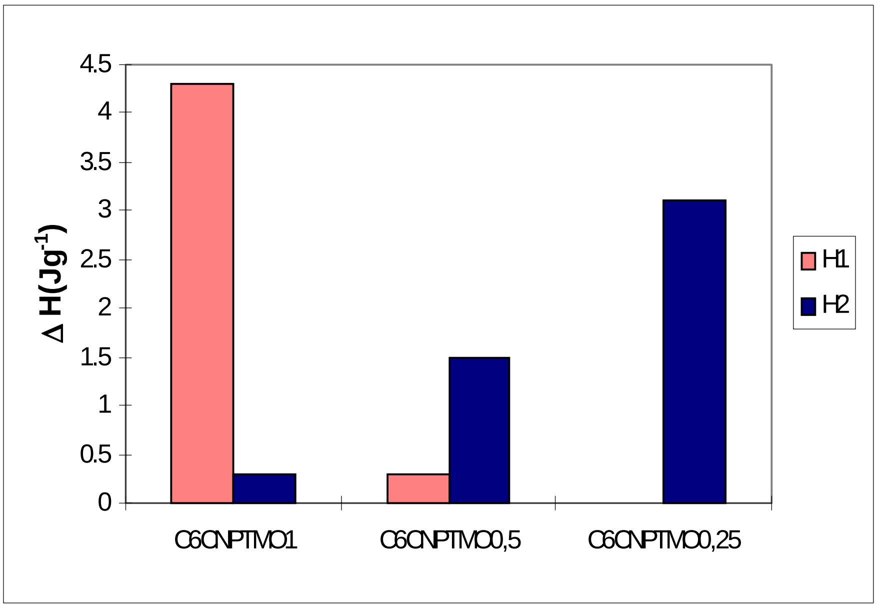

Figure 3. The dependence of ΔH_1 and ΔH_2 on the composition of C6CNPTMOX polyurethanes.

FTIR spectra of C6CNPTMO1 in the C=O stretching region, taken at different temperatures, are shown in Figure 4. Shifting of the wavenumber in the C=O stretching region (A) and in the N-H stretching region (B) for different C6CNPTMOX polyurethanes are shown in Figure 5. A large percentage of the H-bonds dissociates in the temperature range between 90 and 120°C.

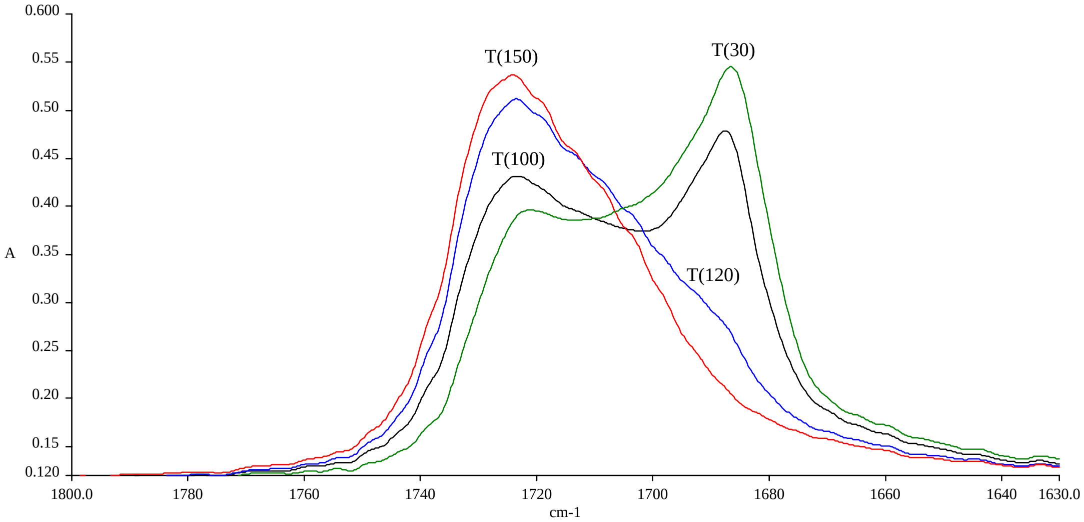

Figure 4. FTIR spectra of C6CNPTMO1 polyurethane at different temperatures T (°C) in the C=O stretching region.

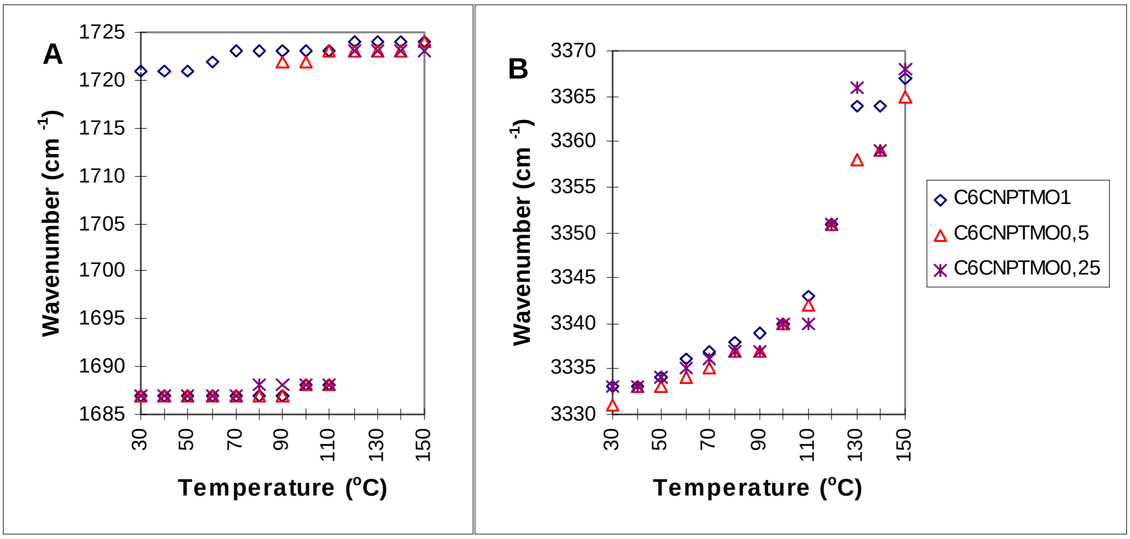

Figure 5: Shifting of the wavenumber in C6CNPTMOX polyurethanes: A - in the C=O stretching region and B - in the N-H stretching region.

In Figure 6 X-ray diffraction patterns of the samples are shown. As a comparison, the diffraction pattern of the sample without any soft segments, C6CNP, is given. In the small angle region, the diffractogram of C6CNP showed three Bragg reflections of the first, second and third order corresponding to the smectic layer spacing (d) 35.3 Å [6]. The value d was almost twice the length of the fully extended mesogenic unit together with the spacer (trans-planar conformation) indicating that smectic phase of a bilayer structure was formed. In the wide-angle region, a diffuse signal at the periodicity of 4.3 Å ascribed to the lateral disorder of mesogenic units withi smectic layers and a sharp signal at the periodicity 3.6 Å, which might be due t interchain distances of the side chains (side chain crystallization), was seen [6]. In the diffraction patterns of the samples containing PTMO (C6CNPTMO1, C6CNPTMO0.5, and C6CNPTMO0.25), the signals in the small angle region were not seen. This is not necessarily due to the loss of liquid crystallinity, but could also be due to the lower concentration of hard segments in the sample, which are associated in domains (PTMO has a high molar mass in comparison to the hard segment). In the wide angle region only the diffuse signals around 4.0 Å were found.

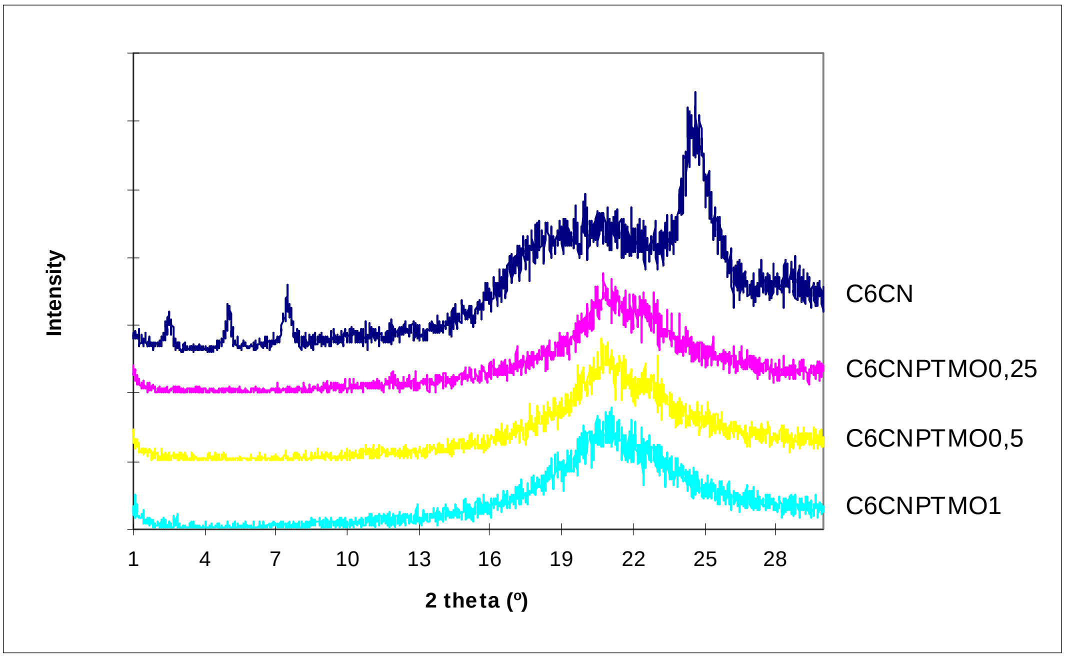

Figure 6: X-ray diffraction patterns of C6CNPTMOX polyurethanes at roo temperature.

SUMMARY

Phase separated polyurethanes containing hard segments wit azobenzene mesogenic groups in the side chain and PTMO soft segments have two glass transition temperatures, one between -74°C and -69°C for the PTMO soft segments and the other between 1°C and 10°C for the hard polyurethane segments. The endothermic transition around 51 °C could be ascribed to the isotropization of the mesogenic units and to the melting of the side chains. The endothermic transition around 107 °C are due to the melting of hard segments. The melting enthalpy increases with increasing amounts o hard segments in the sample. The dissociation of the H-bonds at this temperature is also seen in the FTIR spectra. The liquid crystallinity of the samples could not be confirmed by X-ray spectroscopy, which need not necessarily be ascribed to the loss of liquid crystallinity by the introduction of soft segments into the polyurethane. It could also be the consequence of the weakening of the signal by the dilution of hard segments domains in segmented polyurethanes (the molar mass of PTMO is large compared to the molar mass of the hard segment).

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Povzetek

Sintetizirali smo poliuretane iz trdih segmentov, ki vsebujejo azobenzenske mezogene enote, in politetrametilen oksidnih mehkih segmentov. Z diferenčno dinamično kalorimetrijo smo jim določili termične karakteristike, s FTI spektroskopijo pa smo opredelili disociacijo vodikovih vezi v vzorcih v odvisnosti od temperature. Posneli smo rentgenske difraktograme pri sobni temperaturi.