

PROPERTIES OF POLYURETHANES BASED ON MESOGENIC DIOL AND 4,4'-METHYLENEBIS(CYCLOHEXYL ISOCYANATE)

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Abstract

New polyurethanes with mesogenic units in the main chain due to the use of a liquid crystalline chain extender were synthesized from 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) using diisocyanates of different *trans, trans* isomer content, a low molecular diol 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP) and a high molecular poly(hexamethylene adipate)diol (PHA). The growth of *trans, trans* isomer content in HMDI used to syntheses of PU induces monotonic growth of melting point, rectilinear growth of crystallization temperatures and the growth of crystallization enthalpy, both for hard segment polyurethanes and block polyurethanes. The increase of *trans, trans* isomer content in HMDI increases also glass transition temperatures and dynamic storage modulus of the polyurethanes.

Keywords: DMTA, DSC, HMDI, mesogenic chain extender, polyurethane

Introduction

New polyurethanes with mesogenic units in the main chain due to the use of a liquid crystalline chain extender were synthesized and investigated. Polyurethanes (PU) of different hard segment content synthesized from 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) of 16 mass% *trans, trans* isomer content exhibit relatively low melting point (110–120°C) [1]. The structure of isocyanate influences strongly the melting point of PU [2]. It was expected that increasing of the content of *trans, trans* isomer in HMDI used to the syntheses would increase thermal stability of the hard segments phase in investigated polyurethanes. The presented results of DSC and DMTA analyses confirm this anticipation.

Experimental

4,4'-Methylenebis(cyclohexyl isocyanate) containing 16 mass% of the *trans, trans* isomer was purified by vacuum distillation of commercial reagent (Aldrich). Enriched in the *trans, trans* isomer fractions were prepared by crystallization [3] of previously vacuum rectified HMDI. The first crystallization was carried out from melt at

the second – from melt at 20°C and the third – from cyclohexane solution. The content of *trans, trans* isomer in HMDI was analyzed by the use of gas chromatography. All fractions were vacuum distilled prior of use. Polyurethanes reported in this paper were synthesized from fractions containing following content of the *trans, trans* isomer: 97 mass% (U1A, U2A), 46 mass% (U1B, U2B), 16 mass% (U1C, U2C) and 12 mass% (samples U1D, U2D). The polyurethanes were obtained in a two-step reaction in the melt (U1C, U2C, U1D, U2D) or in concentrated *p*-dichlorobenzene solution (U1A, U2A, U1B, U2B). For synthesis of polyurethanes U1A, U1B, U1C and U1D only low molecular diol were used, but for syntheses of segmented polyurethanes U2A, U2B, U2C, U2D two diols were used: low molecular and high molecular one in the mass ratio 3:2. As a low molecular diol 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP) and as a high molecular diol poly(hexamethylene adipate) diol (PHA) of molar mass 3000 g mol⁻¹ were chosen. The choice of BHHBP as a chain extender enables safe processability of the PU due to relatively low melting point of hard segments which are built of short rigid mesogenic 4,4'-bis(oxy)biphenyl moieties separated from other rigid fragments by hexamethylene spacer. The presence of soft spacer facilitates ordering of polymer structure and the phase separation in segmented polyurethanes.

DSC measurements were performed using a Perkin Elmer DSC 7 instrument. The samples were sealed in aluminum pans and all scans were run under a nitrogen purge gas. The calorimeter was calibrated with pure indium and water. The 1st heating run was performed from 20 to 220°C. The sample was then quenched by cooling at 200°C min⁻¹ to 20°C and heated in the 2nd run. Prior to the crystallization scan the sample was annealed at 220°C for 3 min. Heating scans were performed at a scanning rate of 20°C min⁻¹ and crystallization scans at 10°C min⁻¹.

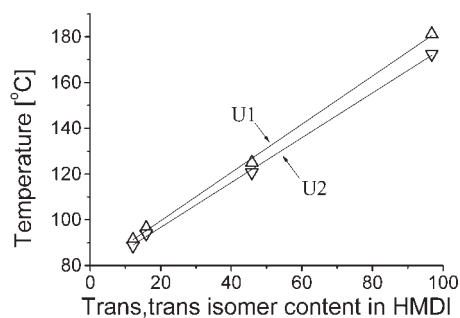


Fig. 1 The influence of the *trans, trans* isomer content in HMDI on crystallization temperatures of hard segment PU (U1A – 97 mass%, U1B – 46 mass%, U1C – 16 mass%, U1D – 12 mass% of the *trans, trans*-HMDI) and block PU (U2A – 97 mass%, U2B – 46 mass%, U2C – 16 mass%, U2D – 12 mass% of the *trans, trans*-HMDI)

Dynamic mechanical thermal analysis measurements were conducted using apparatus DMTA PL MkIII Standard (Polymer Laboratories) at the frequency of 1 Hz.

Liquid nitrogen was used as a cooling agent. Data were collected from -80 to 220°C at a heating rate of $4^{\circ}\text{C min}^{-1}$.

Results and discussion

The influence of *trans, trans* isomer content in HMDI on courses of melting and crystallization of hard segment polyurethanes (U1A, U1B, U1C, U1D) is shown in the Fig. 2 and for block polyurethanes (U2A, U2B, U2C, U2D) – in the Fig. 3. Appropriate enthalpy values are collected in the Table 1. The data in the Table 1 present results of the second run of heating and of the cooling run. The growth of *trans, trans* isomer content in HMDI used to syntheses of PU induces monotonic growth of melting point, rectilinear growth of crystallization temperatures (Fig. 1) and the growth of crystallization enthalpy, both for hard segment polyurethanes and block polyurethanes. Double peaks that occur during melting, result from recrystallization taking place during measurement, so obtained enthalpies are not a measure of crystallinity. Assuming that crystallization enthalpies of PU's do not depend on isomer distribution of HMDI, doubling of degree of crystallinity of the polymer would be induced by the growth of *trans, trans* isomer content from 12 to 97 mass%.

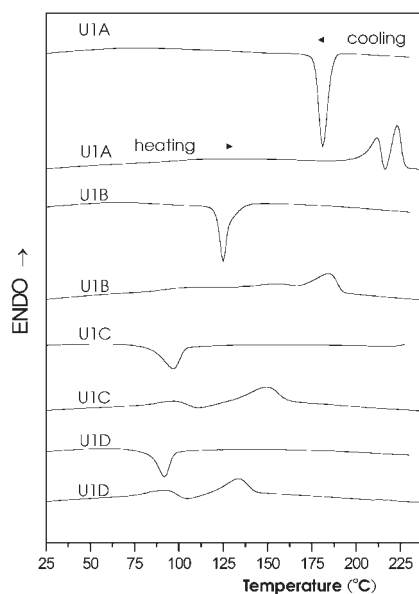


Fig. 2 DSC curves of melting after melt quenching (2nd run) and crystallization of the hard segment PU's (U1A – 97 mass%, U1B – 46 mass%, U1C – 16 mass%, U1D – 12 mass% of the *trans, trans*-HMDI)

Temperature dependencies of dynamic storage modulus E' and of the loss tangent $\text{tg}\delta$ (Figs 4 and 5) show the growth of thermal stability of the hard segment phase in PU's synthesized by the use HMDI of higher *trans, trans* isomer content. The glass

Table 1 DSC parameters of melting after melt quenching (*T2*) and crystallization (*CR*) of the hard segment and block polyurethanes according to *trans, trans* isomer content in HMDI

PU symbol	Hard segment content in polyurethane/mass%	<i>Trans, trans</i> isomer content in HMDI/mass%	Temp. maxima of melting and crystallization peaks/°C			Enthalpies/J g ⁻¹		
			<i>T2</i>		<i>CR</i>	<i>T2</i>	<i>CR</i>	
U1A	100	97	211.7	223.2	181.2	18.0	16.6	-35.6
U1B	100	46	154.2	184.8	125.0	14.8	16.6	-22.6
U1C	100	16	97.0	149.0	96.5	5.0	27.1	-20.0
U1D	100	12	92.0	134.0	91.3	4.7	17.4	-18.6
U2A	71.5	97	208.8	219.7	172.4	18.2	6.2	-27.3
U2B	72.2	46	144.3	185.1	120.6	5.5	11.4	-16.1
U2C	72.3	16	71.1	127.7	93.9	5.0	21.4	-15.8
U2D	72.2	12	75.1	132.3	88.6	5.1	18.3	-15.1

transition temperatures measured as maximum of $\text{tg}\delta(T)$ curve are following: 119.9, 103.7 and 99.6°C for hard segment polyurethanes U1A, U1B, U1C and 74.2, 73.3, and 69.7°C – for block polyurethanes U2A, U2B and U2C, respectively.

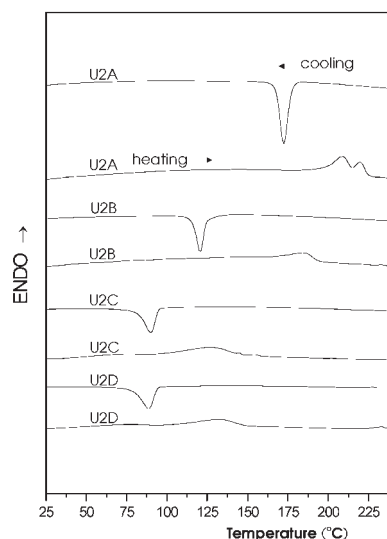


Fig. 3 DSC curves of melting after melt quenching (2nd run) and crystallization of the block PU's (U2A – 97 mass%, U2B – 46 mass%, U2C – 16 mass%, U2D – 12 mass% of the *trans, trans* HMDI)

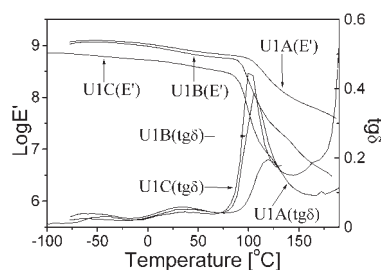


Fig. 4 Dynamic mechanical spectra of hard segment polyurethanes (U1A – 97 mass%, U1B – 46 mass%, U1C – 16 mass% of the *trans, trans*-HMDI)

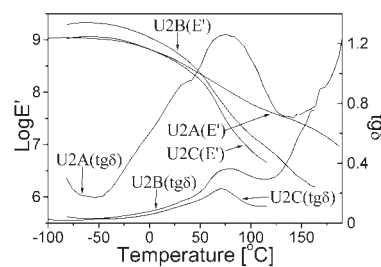


Fig. 5 Dynamic mechanical spectra of block polyurethanes (U2A – 97 mass%, U2B – 46 mass%, U2C – 16 mass% of the *trans, trans*-HMDI)

In consideration of high hard segment content in investigated block PU (U2A, U2B and U2C), glass transition temperatures refer only to hard segments. Glass transition for soft segments, built of PHA, was not visible for these polymers, probably because of the lack of big enough, separated soft segment domains. Therefore rubbery-like plateau of the storage modulus does not occur.

Conclusions

Polyurethanes synthesized from 4,4'-methylenebis(cyclohexyl isocyanate), mesogenic low molecular diol – 4,4'-bis(6-hydroxyhexoxy)biphenyl and – for block polyurethanes – poly(hexylene adipate) show linear dependencies of melting point, crystallization temperature and degree of crystallinity on *trans*, *trans* isomer content in isocyanate used for their syntheses.

For the investigated polyurethanes the increase of *trans*, *trans* isomer content in the isocyanate increases glass transition temperature and dynamic storage modulus in the temperature region above the glass transition.

The dynamic mechanical properties of the investigated block polyurethanes reveal behaviour typical for partially crystalline plastics, rather than for elastomers.

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