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Journal of Non-Crystalline Solids 353 (2007) 4293–4297

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Studies of molecular dynamics in polyurethane networks with hyperbranched polyester Boltorn®H30 as a crosslinker

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Available online 27 September 2007

Abstract

Several non-conventional polyurethane networks crosslinked with hyperbranched polyester (Boltorn®H30) were synthesised with an aim to determine an influence of the polyurethane linkage length on molecular relaxations in such systems. The polyurethane chain length was regulated by changing the macrodiol length or by changing the number of the repeating macrodiol-diisocyanate units. Molecular dynamics were investigated by dielectric spectroscopy and by dynamic mechanical analysis. It was found that the macrodiol length has a strong influence on the glass transition and the α-relaxation process correlated with it. By contrast, the changes of the repeating unit number practically did not affect the molecular relaxations. This effect was explained by the formation of a physical network by hydrogen bonds between urethane groups, controlling the molecular mobility. The distribution of the hydrogen bonds is controlled by the length of soft segment between the urethane groups. It means that in the polyurethanes based on the same macrodiol the distribution of the hydrogen bonds is similar, and what follows it, the molecular dynamics of such systems is very similar.

PACS: 77.22.Gm; 77.84.Jd

Keywords: Dielectric properties, relaxation, electric modulus; Mechanical; Stress relaxation; Polymers and organics; Glass transition; Structural relaxation

1. Introduction

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties [1]. PUs can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fibres, foams, and thermoplastic elastomers. Linear segmented PU elastomers can be considered as block copolymers, which consist of soft segments formed with polymer glycol and hard segments based on diisocyanate and chain extender. The properties of these PU elastomers are strongly dependent on molar mass and polydispersity of the soft segment component [2], as well as on the chemical structure of all components [3–6].

As far as the networks are concerned, one of the important factors used for changing their properties is the type of crosslinking agent. In PU systems two kinds of networks can be present: physical and chemical. The physical network is created by the H-bonds, which link the carbonyl and amine groups of adjacent chains [7]. Chemical network parameters depend on the crosslinker nature. Recently some papers dealing with the use of dendritic molecules as crosslinking agents were published. Especially random hyperbranched (HB) macromolecules, which can be easily obtained by one-pot synthetic methods, are very promising crosslinking materials [2,8,9].

In this work several PU networks based on hyperbranched polyester of 3rd pseudo-generation were investigated by means of dielectric spectroscopy and dynamic mechanical analysis, which give complementary information about the molecular dynamics. The polyurethane systems were

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doi:10.1016/j.jnoncrysol.2007.04.043

different in the length of the linear chain between the crosslinking points, which was regulated by using macrodiols of different molar masses or by changing the number of repeating macrodiol-diisocyanate units in the chain. The way of comparison of two techniques of molecular dynamics investigations – broadband dielectric spectroscopy and dynamic mechanical analysis was described well by Pakula [10].

2. Experimental details

2.1. Materials

Several PU networks crosslinked by HB polymer were synthesised in bulk using polytetrahydrofuran (Terathane®650, abbreviated as T_{650}, with $M_n = 650$ g/mole or Terathane®2900, abbreviated as T_{2900}, with $M_n = 2900$ g/mole) and 4,4′-diisocyanatodiphenylmethane (MDI with $M_w = 250$ g/mole) as monomers. As a crosslinking agent the hyperbranched polyester of 3rd pseudo-generation (Boltorn®H30 abbreviated as HB30) was used. According to the producer Boltorn®H30 has a molar mass $M_w = 3500$ g/mole with polydispersity $M_w/M_n = 1.5$ (i.e. Mn ∼ 2300 g/mol) and hydroxyl number 480–510 mg KOH/g. These data give at the average 20 primary –OH groups in the molecule. The substrates were used as supplied by the producer without additional purification. The hydroxyl number of Boltorn®H30 sample was checked by pH-metric titration and was the same as that given by the producer.

The aim of the synthesis presented in this paper was to obtain series of networks in which polyurethane linear chains are connected by the HB crosslinker. The PU linear chains in these series have different lengths, controlled by the molar mass (i.e. length) of the macrodiol, T_{650} and T_{2900}, or by the average number (*n* varying from 4 to 20) of the repeating macrodiol-diisocyanate units. The number of primary –OH functions present in the HB polymer controls the number of PU chains connected to the hyperbranched polyester.

The synthesis of polyurethane was carried out in bulk. Amounts of ingredients for synthesis of stoichiometric systems were calculated in accordance with the average numbers of the –OH groups in the HB crosslinker and with the projected length of the PU chains between the crosslinking centres [2,9]. A schematic road of the synthesis of the PU network crosslinked with the HB centres is shown in Fig. 1. The end of reaction was determined by FTIR spectroscopy. In the final PU networks the diisocyanate –N=C=O band (2250–2275 cm^{-1}) was absent in the spectra. The bands characteristic for the polyurethane formations appear at: 3320 cm^{-1} – urethane N–H stretching; 1731 cm^{-1} – urethane C=O without hydrogen bonding; 1710 cm^{-1} – urethane C=O with hydrogen bonding; 1535 cm^{-1} – urethane N–H bonding.

2.2. Measurements

The chemical structure of the synthesised materials was verified by FTIR absorption using Bio-Rad FTS 175 C spectrometer in the reflection mode with the Harrick IRS attachment.

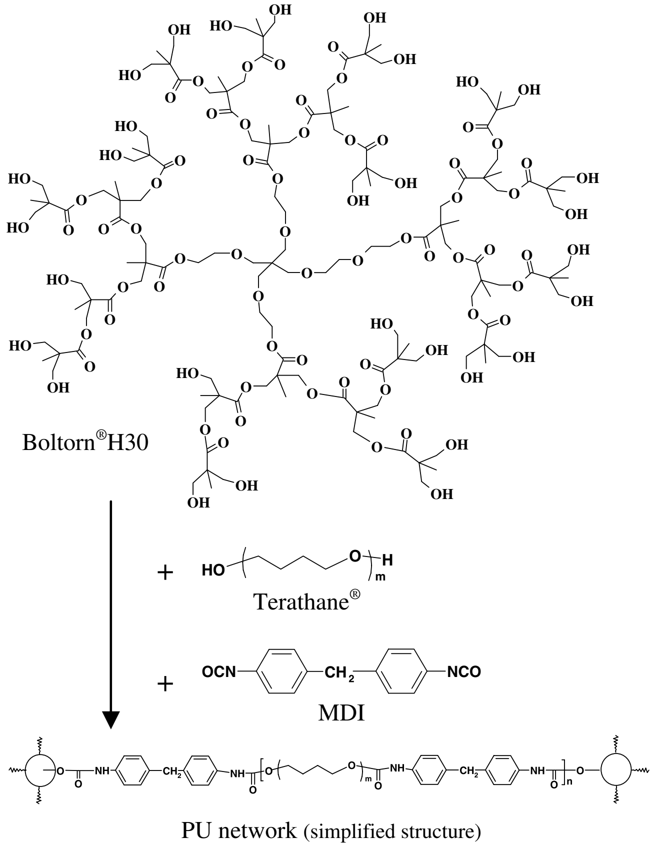

Fig. 1. Schematic representation of the synthetic route of PU network.

Differential scanning calorimetry (DSC) measurements were carried out using a 2920 TA Instrument. Samples of approximately 10 mg were sealed in aluminium pans and measurements were performed with a heating rate of 10 °C/min in the temperature range: −150 °C to 200 °C under a nitrogen atmosphere. The glass transition temperatures (T_g) were determined at the midpoint of the step.

Molecular relaxations were characterised in broad temperature range by dynamic mechanical analysis (DMA) using TA Instrument DMA 2980 dynamic mechanical analyser, and by dielectric relaxation spectroscopy (DRS) using Novocontrol Broadband Dielectric Spectrometer. DMA was performed in film tension mode in the temperature range from −130 up to 150 °C with a temperature ramp of 2 °/min using rectangular samples with the length 25 mm, width 5 mm and thickness 1 mm. Three frequencies were applied: 1, 5, and 10 Hz. DRS was performed in the frequency range 0.01 Hz–1 MHz and in the temperature range from −150 up to 130 °C with the step 5 °C. For the DRS measurements circular shape samples with diameter 20 mm and thickness up to 0.5 mm were used.

Dielectric results were presented in the classical representation of dielectric relaxations, i.e. dielectric losses, as well as in the electric modulus representation defined by Macedo et al. [11]. The real M' and imaginary M'' parts