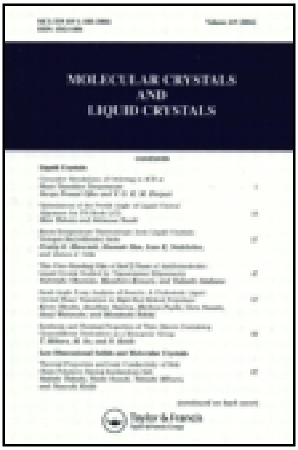

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Experimental and Theoretical Aspects of Segmented Poly(ester urethane)s properties. Conformational Transitions in Solid State and Solution

Doina Macocinschi [a], Silvia Ioan [a], Mihaela Lupu [a] & Andcristian Grigoras [a]
[a] “Petru Poni” Institute of Macromolecular Chemistry, Iasi, RO, Romania

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EXPERIMENTAL AND THEORETICAL ASPECTS OF SEGMENTED POLY(ESTER URETHANE)S PROPERTIES. CONFORMATIONAL TRANSITIONS IN SOLID STATE AND SOLUTION

Doina Macocinschi, Silvia Ioan, Mihaela Lupu, and
Cristian Grigoras
"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Grigore Ghica Voda Nr. 41A,
RO-700487 Iasi, Romania

Segmented poly(ester urethane)s containing hard and soft segments, were obtained from aromatic diisocyanates with 4,4′-dihidroxydiethoxydiphenyl sulphone as chain extender, and poly(ethylene glycol)adipate using a multi-step polyaddition process. Transition temperatures by differential scanning calorimetry and thermo-optical analysis were employed to characterize polyurethane materials. Changes in the conformation of these polyurethanes were analyzed also, by viscometer measurements in N,N-dimethyl-formamide. The obtained data revealed that the thermal curves are influenced by the soft and hard segment structures in the temperature range studied.

Keywords: conformational transition; poly(ester urethane)s; thermo-optical analysis; viscosity measurements

INTRODUCTION

Different properties of polyurethanes show the existence of highly flexible chains, i.e. a low degree of intermolecular interaction, and the presence of crosslinks, which can be of a chemical or physical nature. Thus, the studied polyurethanes are block copolymers, consisting of alternating rigid and flexible blocks. Due to the different polarity and chemical nature of both blocks they separate into two phases designated as soft and hard. Hard blocks also associate into domains because of rigidity and hydrogen

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Address correspondence to Dr. Doina Macocinschi, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda Nr. 41 A, RO-700487 Iasi, Romania. E-mail: mcdoina@icmpp.ro

bonding and act as physical crosslinks. Studied segmented polyurethanes are, thus, two-phase polymers and their properties in solution are strongly affected by the amount of phase separation [1–6].

The purpose of the present study is to obtain information about the conformational behavior of segmented copolymers containing aromatic diisocyanates with chain extenders and poly(ethylene glycol)adipate as a function of the temperature. The copolymers were characterized by thermo-optical and viscosity measurements.

EXPERIMENTAL

Structure and Compositional Parameters of Poly(ester urethane)s

The samples containing segmented block copolyurethanes were obtained from aromatic diisocyanates (4,4′-methylene diphenylene diisocyanate (MDI) or 2,4-tolylene diisocyanate (TDI)), with 4,4′-dihidroxydiethoxydiphenyl sulphone (DEDS, our synthesis [7]) as chain extenders and poly(ethylene glycol)adipate (PEGA, $M_n = 2000\,g/mol$) using a two steps polyaddition process in DMF [8].

The general chemical structure of the segmented poly(ester urethane)s studied in this work is illustrated in Scheme 1:

Sample1: $-(O-R_3-O-CO-NH-R_1-NH-CO-O-R_4-O-CO-NH-R_1-NH-CO-)_{q1}-$

Sample 2: $-(O-R_3-O-CO-NH-R_2-NH-CO-O-R_4-O-CO-NH-R_2-NH-CO-)_{q2}-$

where:

$R_1 = -C_6H_4-CH_2-C_6H_4-$ derived from MDI
$R_2 = -C_6H_3(CH_3)-$ derived from TDI
$R_3 = -(CH_2)_2-O-C_6H_4-SO_2-C_6H_4-O-(CH_2)_2-$ derived from DEDS
$R_4 = [(CH_2)_2-O-CO-(CH_2)_4-CO-O]_n-(CH_2)_2-$ derived from PEGA

SCHEME 1 Chemical structure of segmented poly(ester urethane)s

and subscripts q1, q2, and n are the polymerization degrees.

Table I presents the compositional parameters [9] obtained for studied samples of poly(ester urethane)s.

Experimental Procedures

The thermo-optical measurements (TOA) were realized with the thermo-optical analyzer (TOA), which consists of an optical microscope equipped

TABLE 1 Compozitional Parameters of Soft and Hard Segments and Number Average Molecular Weights, M_n, Polydispersities, M_w/M_n, and Intrinsic Viscosities, $[\eta]_{Huggins}$, in DMF at 25°C of Segmented Poly(ester-urethane)s

Sample	Soft segment	Hard segment		Weight ratio (%) $R_4:(R_{1\ or\ 2}:R_3)$	M_n	M_w/M_n	$[\eta]_{Huggins}$ (dL/g)
MDIDEDS	PEGA	MDI	DEDS	69.26:(18.33:12.41)	47993	1.56	0.474
TDIDEDS	PEGA	TDI	DEDS	73.18:(13.57:13.25)	25863	1.55	0.210

with a hot stage programmed by a control unit. The light that was transmitted through the sample was picked up by a photocell. The amplified photocurent was fed through a voltage divider and the voltage difference was plotted continuously against temperature (time) on a strip chard recorder. The normal heating rate was 9.6°/min in the temperature ranges 20–150°C.

The viscosity measurements were carried out in DMF in the 20–45°C temperature range (±0.01°C), by use an Ubbelohde suspended-level viscometer. Plots of η_{sp}/c vs. c were extrapolated to zero concentration to obtain intrinsic viscosity $[\eta]$ according to Huggins equation.

RESULTS AND DISCUSSION

Conformational Transition from TOA Investigations

The poly(ester urethane)s based on PEGA in soft segments and MDI or TDI/chain extender in hard segments exhibit the two melting temperatures associated with the melting of soft segments, T_{mss}, and a melting of hard segments, T_{mhs}.

Figure 1 presents TOA curves to detect a chain mobility transition temperature for MDIDEDS and TDIDEDS samples in the temperature range 20–100°C. In this interval the melting temperatures of soft segments, T_{mss}, are observed. The vertical scale represent transmitted light intensity by heating samples, although actually a voltage reading from the photoelectric circuit is arbitrary. It is obvious that there is a close correlation between the chain mobility transition temperature observed in the temperature range studied and the structure of studied samples. Thus, Figure 1 indicate that melting temperature of soft segments for TDIDEDS sample is about 43°C and for MDIDEDS samples is about 48°C. The transition phenomenon is abrupt at TDIDEDS sample and slower at MDIDEDS sample.

These results indicate that MDI/chain extenders segments contributed to a higher T_{mss} than TDI/chain extenders. So, it would be expected for

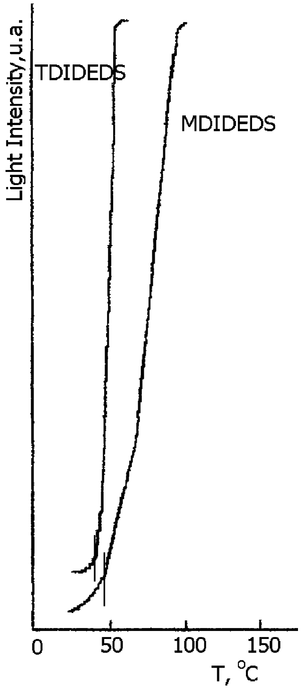

FIGURE 1 TOA curves for segmented poly(ester urethane)s in the temperature range 20–100°C. Vertical lines indicate the melting point of the soft segment, T_{mss}.

MDI to shift T_{mss} to higher values than TDI due to a higher cohesive energy and bulkiness because of their benzene rings. Such behaviour may be attributed to the crystalline structures that could form because of the interactions (hydrogen bonding) between MDI-PEGA.

The literature [10] and previous our studies [4] indicate that at about 230°C the segmented polyurethane materials exhibit the melting transition of the hard segments, T_{mhs}. Also, the T_{mhs}values of samples with symmetrical hard segments, MDI, are higher, thus, higher crystallinity, than the segmented polyurethane materials with asymmetrical hard segments, TDI.

Conformational Transition from Viscosity Measurements

The studied segmented polyurethanes are two-phase polymers and their properties in solution are strongly affected by the amount of phase separation. The polyurethane-solvent interaction parameter can be analyzed by a simplistic two parameters model, where effective interaction parameter is supposed to be the sum of two interaction parameters, coming from solvent-soft segment and solvent-hard segment interactions, or by the complicated multiple-parameters models which take into consideration more interaction parameters [9]. In the present work the studied polyurethanes are multicomponent compounds and the determination of the interactions that may occur is very complicated, the methods of investigation of conformational transition in solution being limited to intrinsic viscosity measurements [11].

The variation of η_{sp}/c and $[\eta]$ versus temperature for poly(ester urethane)s samples from Table 1 is shown in Figures 2 and 3.

Generally, an inflexion in the η_{sp}/c and $[\eta]$ versus temperature plot can be seen, indicating the temperature range where the conformational changes take place. The explanation of the conformational transition is not easy; a tentative for the interpretation of these phenomena is due to differences of penetration of solvent in soft (more flexible) and hard (with physical crosslinks) segments versus temperature, which modifies the conformation of chain in solution. Moreover, there are preferential interactions between DMF and soft segment, due to the carbonyl groups.

In function of the chemical composition, the polyurethanes possess different global flexibility. It is known that the diisocyanates with methyl

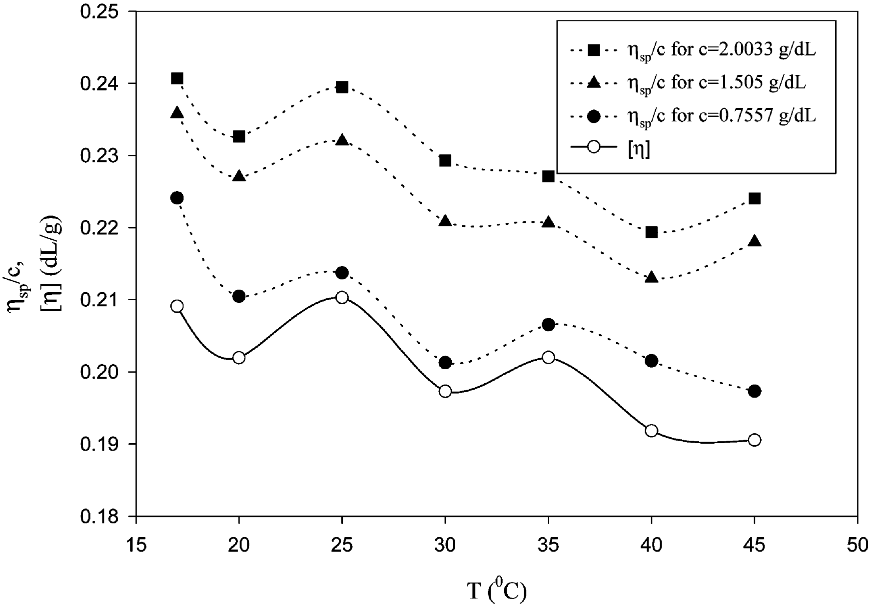

FIGURE 2 Variation of reduced viscosity $\eta_{sp/c}$ and intrinsic viscosity $[\eta]$ with temperature for TDIDEDS sample in DMF.

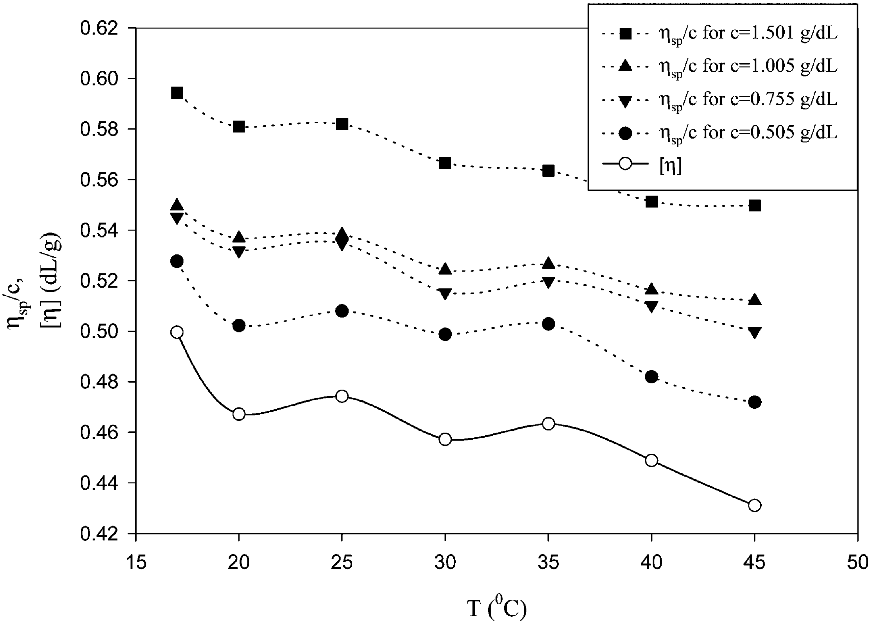

FIGURE 3 Variation of reduced viscosity η_{sp}/c and intrinsic viscosity $[\eta]$ with temperature for MDIDEDS sample in DMF.

substituents in hard segment, such as TDI, have a higher flexibility comparatively with the samples containing MDI, which are believed to possess significant chain rigidity because of the high cohesive energy and bulkiness of the benzene ring [10]. Thus, the intrinsic viscosity of samples from Table 1 with MDI is higher than that of samples with TDI not only because of the differences of molecular weights but also, because of the different flexibility.

All studied samples show inflexions of the viscosity in the range from 17 to 45°C. This behavior has been interpreted as a conformational transition of the polymer chain. Figures 2 and 3 show that the conformation of the MDIDEDS and TDIDEDS polyurethane chains changes to a more extended form, when goes from a lower to a higher temperature. At about 20°C and 30°C this phenomenon is inverted. The increase in viscosity, caused by an increase of the hydrodynamic volume of the polymer coils, may be the result of improved solvent power for the copolymer as a whole. The improved solubility of the copolymer could be caused by one segment or by both segments. In this context, the solvent interacts with the soft segments because of the higher flexibility of the soft segments and the affinity between carbonyl groups from DMF and PEGA, and also because of a solvent penetration in the regions of the hard domains that are physically crosslinked, with increase of temperature; the physical crosslinks can be perturbed, thus the modification of coil dimensions is a consequence of these phenomena.

Furthermore, from our investigation of the segmented polyurethane it appears that the conformational transitions are transmitted also, by PEGA segments. Thus, a discontinuity in the variation of the intrinsic viscosity of PEGA with $M_n = 2000$ versus temperature, characterized by an increase of the dimensions in 27–35°C domain, has also been observed [6].

It is difficult to explain the conformational modification of the poly(ester urethane) chain when temperature increases. In a first step, we can suppose the existence of PEGA-solvent and hard block-solvent contacts. When the temperature is increasing, solvent penetrates easier in physical crosslinks of hard blocks, increasing thus the hard segment-solvent contacts. Hard block solubility also depends on their composition. Thus, we suppose that the 4,4'-dihidroxydiethoxydiphenyl sulphone chain extender from the hard segments influenced these conformational transitions beside the PEGA from the soft segments; because the conformational transitions and their amplitudes are identical in MDIDEDS and TDIDEDS samples we supposed that aromatic diisocyanates did not influence this modification.

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