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# Conformational Aspects of Segmented Poly(ester-urethanes)

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**Summary:** Segmented poly(ester-urethanes) containing hard and soft segments, were obtained from aromatic diisocyanates with thiodiglycol or diethylene glycol as chain extenders, and poly(ethylene glycol)adipate usig a multistep 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:** differential scanning calorimetry; polyurethanes; thermal properties; thermo-optical analysis; viscosity measurements

## Introduction

Polyurethanes are an unique class of polymers that offer the chance to obtain the properties by a proper selection of different materials in their composition.[1] The combination of polyols, diisocyanates and low molecular chain extenders gives rise to a multitude of forms suited for extremely different practical applications as fibers, paints, foams, resins, elastomers, and many others.[2-7] Also, they are utilized as coating materials in textile industry.[8,9]

The structural and compositional diversity of polyurethane elastomers represents an useful way to study the properties and the structure of these materials. The previous publications[10-15] presented the syntheses and some properties of new segmented and crosslinked polyurethane elastomers. The influence of polymer structure on the thermal stability, the behaviour in different organic solvents, the structure and morphology of these compounds were analyzed.

The purpose of the present study is to obtain information about the conformational behavior of segmented copolymers containing aromatic diisocyanates {4,4'-methylene diphenylene diisocyanate (MDI) or 2,4-tolylene diisocyanate (TDI)}, with thiodiglycol (TDG) or diethylene glycol (DEG) as chain extenders and poly(ethylene glycol)adipate (PEGA) as a function of the temperature, and to discuss the result in function of the soft and hard segments composition.

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The copolymers were characterized by thermo-optical and differential scanning calorimetry measurements. Also, the conformational modifications of the polyurethanes were analyzed in dilute solutions.

## Experimental

### Structure and Compositional Parameters of Poly(ester-urethanes)

The samples containing segmented block copolyurethanes were obtained from aromatic diisocyanates (4,4'-methylene diphenylene diisocyanate (MDI, Merck; distilled under reduced pressure) or 2,4-tolylene diisocyanate (TDI, Merck; distilled under reduced pressure), with thiodiglycol (TDG, Fluka) or diethylene glycol (DEG, Fibrex Savinesti) as chain extenders and poly(ethylene glycol)adipate (PEGA, Fibrex Savinesti, $M_n$ = 2000 g/mol) using a two steps polyaddition process in DMF.[16] In the first stage of reaction, the NCO-terminated prepolymer was formed. PEGA was dehydrated for 3 h at 120°C followed by adding the MDI or TDI. The reaction between diisocyanate and macrodiol was kept 1 h under nitrogen atmosphere at 90°C. The amount of diisocianate and PEGA was controlled at a NCO:OH molar ratio of 3:1. The second step is the reaction of free isocyanic group with chain extenders, i.e. diethylene glycol or thiodiglycol. The reaction temperature was allowed to cool at 60°C when the chain extender was added. The polymers were precipitated in water and dried under vacuum for several days.

The purity of segmented poly(ester-urethanes) was checked by IR and $^1$H-NMR (at 80°C in dymethyl sulfoxide – $d_6$) analyses.

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

Sample 1: $-(-O-R_3-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_q-$
Sample 2: $-(O-R_3-O-CO-NH-R_2-NH-CO-O-R_5-O-CO-NH-R_2-NH-CO-)_q-$
Sample 3: $-(O-R_4-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_q-$
Sample 4: $-(O-R_4-O-CO-NH-R_2-NH-CO-O-R_5-O-CO-NH-R_2-NH-CO-)_q-$

where:

| | |
|---|---|
| $R_1 = -C_6H_4-CH_2-C_6H_4-$ | derived from MDI |
| $R_2 = -C_6H_3(CH_3)-$ | derived from TDI |
| $R_3 = -(CH_2)_2-S-(CH_2)_2-$ | derived from TDG |
| $R_4 = -(CH_2)_2-O-CH_2)_2-)-$ | derived from DEG |
| $R_5 = [(CH_2)_2-O-CO-(CH_2)_4-CO-O]_n-(CH_2)_2-$ | derived from PEGA |

Scheme 1. Chemical structure of segmented poly(ester-urethanes).

Table 1 presents the compositional parameters obtained for studied samples of poly(ester-urethanes).[14]

Table 1. Characterization data of segmented poly(ester-urethanes).

| Sample | Soft segment | Hard segment | | Weight ratio %, $R_5$:($R_{1\text{ or }2}$:$R_{3\text{ or }4}$) |
|---|---|---|---|---|
| | $R_5$ | $R_{1\text{ or }2}$ | $R_{3\text{ or }4}$ | |
| MDITDG | PEGA | MDI | TDG | 74.98:(16.67:8.35) |
| MDIDEG | PEGA | MDI | DEG | 75.43:(16.36:8.21) |
| TDITDG | PEGA | TDI | TDG | 79.59:(13.59:6.82) |
| TDUDEG | PEGA | TDI | DEG | 80.11:(13.24:6.65) |

## Experimental Procedures

The differential scanning calorimetry (DSC) curves were determined in air atmosphere by a Mettler DSC 12E at a heating rate of 10°C/min, in temperature range from 10 to 100°C on samples of 10 mg, using the aluminum opened pans.

The thermo-optical measurements (TOA) were realized with the thermo-optical analyzer (TOA), which consists of an optical microscope equipped 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. All measurement was performed within one day after the samples were brought into solution in the interval of five hours; the concentration range was 0.5 to 3.5 g/dl. The kinetic energy corrections were found too negligible. The flow volume of the used viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ±0.035 % for different measurements of the same samples in DMF at a given temperature. Plots of $\eta_{sp}/c$ vs. c were extrapolated to zero concentration to obtain intrinsic viscosity $[\eta]$ according to Huggins equation.

## Results and Discussion

### Conformational Transition from DSC and TOA Investigations

DSC is one of the most suitable techniques used for the testing of polymer samples having complex structures such as polyurethane elastomers. Often, the endothermic and exothermic peaks could reveal special information on thermal behaviour. Nevertheless, the shape of the DSC curves can be associated with the morphology and the chemical composition of the tested samples.

The DSC diagrams from Figure 1 were drawn for samples 1-4 based on MDI or TDI with chain extenders TDG or DEG as hard segments and PEGA as soft segments in the temperature range of 10-100°C.

All samples exhibits a large endothermic peak at about 44-52°C, corresponding to the melting point of the soft segment ($T_{mss}$) and a small one, as it shows in previous paper[13] at about 230°C, the melting point of a hard segment ($T_{mhs}$). Thus, $T_{mss}$ is associated with the melting start of PEGA sequences (52°C) and $T_{mhs}$ with melting start of isocyanate/chain extenders.

A different thermal behaviour of soft segments having the same chemical structure (illustrated by $T_{mss}$) can also be seen from DSC plots due to isocyanate/chain extenders structures. Thus, the melting temperature of PEGA as soft sequences, revealed the following order:

TDIDEG < TDITDG < MDIDEG < MDITDG

These results indicate that MDI/chain extenders segments contributed to a higher $T_{mss}$ than TDI/chain extenders. So, it would be expected for 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. In addition, for MDITDG and MDIDEG or TDITDG and TDIDEG samples we can observe the contribution of S (from TDG structure) and O (from DEG structure) atoms to the $T_{mss}$. It can be seen that oxygen decreases, whereas sulfur increase the $T_{mss}$.

It can also be noticed from Figure 1 that the endothermic effects of soft segments ($\Delta H_{mss}$) for samples having asymmetrical isocyanate, TDI, into its structure are higher than those of samples with symmetrical isocyanate, MDI.

Literature[17] and previous our studies[13] indicate that at about 230°C the DSC heating curves of the segmented polyurethane materials exhibit an endotherm corresponding to the melting transition of the hard segments. The $T_{mhs}$ and $\Delta H_{mhs}$ values of segmented polyurethane materials with symmetrical hard segments, MDI, exhibit a considerably higher $\Delta H_{mhs}$, thus higher crystallinity, than the segmented polyurethane materials with asymmetrical hard segments, TDI.

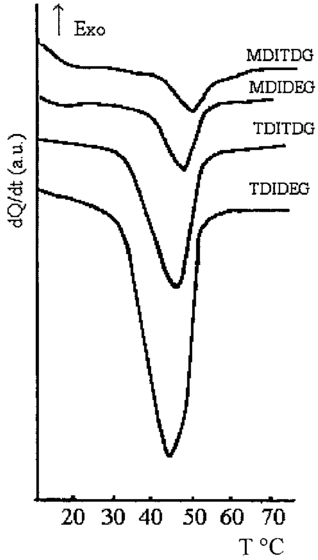

Fig. 1. DSC curves for segmented poly(ester-urethanes) in the temperature range 10-100°C:

Figure 2 presents TOA curves to detect a chain mobility transition temperature for MDIDEG, TDIDEG and TDITDG samples in the temperature range 20-100°C. The vertical scale represent transmitted light intensity by heating samples, although actually a voltage reading from the photoelectric circuit is arbitrary. It is obvious from Figure 2 that there is a close correlation between the chain mobility transition temperature observed in the temperature range studied for the specific heat increase and melting temperature of soft segments, $T_{mss}$ from DSC data. Thus, vertical lines from Figure 2 indicate that melting temperature of soft segments are placed in the same temperature range as in DSC measurement, and revered the same order: TDITDG < TDIDEG < MDIDEG. Also, the transition phenomenon is abrupt at more flexible samples and slower at more rigid samples.

Samples with MDI presents higher chain rigidity and, thus, the higher necessary energy for the melting process of soft segments than sample with TDI. Also, the samples with DEG as chain extender are higher flexibility and lower necessary energy for the melting process of soft segments, comparatively with sample with TDG.

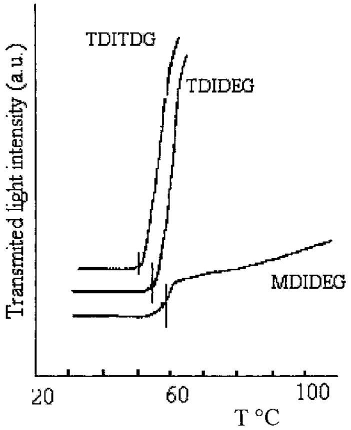

Fig. 2. TOA curves for segmented poly(ester-urethanes) in the temperature range 20-100°C. Vertical lines indicate the melting point of the soft segment, $T_{mss}$.

## Conformational Transition from Viscosity Measurements

Dondos et al.[18,19] present the results which demonstrate that the conformational transition in the viscosity curve is generally observed for all block copolymers. They assumed that in the low temperature range the conformation is quite "segregated", and that at temperature above the transition, the conformation tends to become closer to Gaussian.

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 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.

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.[20] 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.[10]

The variation of $[\eta]$ for poly(ester-urethanes) samples from Table 1 is shown in Figure 3.

All studied samples show inflexions in the viscosity in the range from 20 to 45°C. Generally, an inflexion in the $[\eta]$ 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, although the existence of this change is well established and reproducible. 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.

The thermo-optical and differential scanning calorimetry measurements analysis show that the diisocyanates with methyl 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.[17] 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.

Figure 3 shows also, that the conformation of the MDITDG polyurethane chain slightly changes to a more extended form, when goes from a lower to a higher temperature. At about 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, at lower temperature the solvent interacts especially with the soft segments not only because of the higher flexibility of the soft segments and the affinity between carbonyl groups from DMF and PEGA, but also because of a poor solvent penetration in the regions of the hard domains, that are physically crosslinked. At higher temperatures the physical crosslinks can be perturbed, thus that the modification of coil dimensions is a consequence of these phenomena.

In the MDIDEG sample (Figure 3) the transition is more evident and the transition range $\Delta T$ has a lower value.

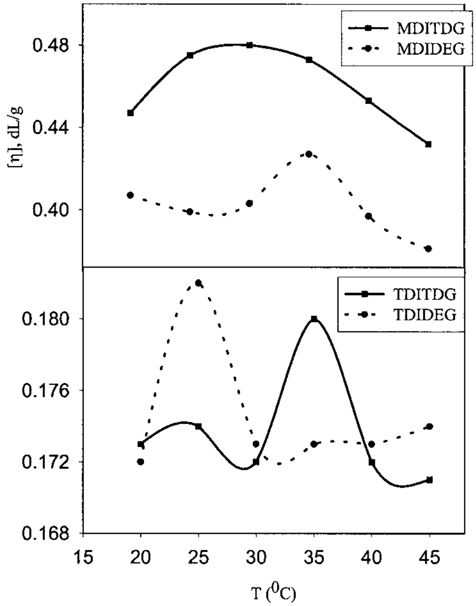

Fig. 3. Intrinsic viscosity versus temperature for segmented poly(ester-urethanes) in DMF.

Same conformational transitions occur in the polyurethanes with TDI in hard segments. The maximum of viscosity displaces from 25°C for more flexible TDIDEG sample, at 35°C for lesser flexible TDITDG sample.

It was demonstrated that the flexibility of polyurethane chains increases with the increase of the number of oxygen atoms in the backbone chain.[20] The possibility to occur the conformational transition in function of the temperature is more probable and evident in the samples with higher flexibility (e.g. MDIDEG sample with DEG in hard segments), comparatively with samples which have a lower flexibility (e.g. MDITDG sample with TDG in hard segments).

## Conclusions

The segmented poly(ester-urethanes) obtained from aromatic diisocyanates (4,4'-methylene diphenylene diisocyanate or 2,4-tolylene diisocyanate) with thiodiglycol or diethylene glycol, and poly(ethylene glycol)adipate using a multistep polyaddition process were studied by DSC, TOA and viscosity measurements in N,N-dimethyl-formamide at 20-45°C.

It can be noticed that the endothermic effects of soft segments for samples having asymmetrical isocyanate, TDI, into its structure are higher than of samples with symmetrical isocyanate, MDI. Thus, samples with MDI present higher chain rigidity and, thus, the higher necessary energy for the melting process of soft segments than sample with TDI. Also, for MDITDG and MDIDEG or TDITDG and TDIDEG samples we can observe the contribution of S (from TDG structure) and O (from DEG structure) atoms to the $T_{mss}$. It can be seen that oxygen decreases, whereas sulfur increases the $T_{mss}$.

Viscosity studies show discontinuities in the intrinsic viscosity $[\eta]$ as a function of temperature. This behavior is interpreted as a conformational transition of the copolymer generated to chain flexibility of soft and hard segments and modified of solvent quality versus temperature. It was demonstrated also, that the flexibility of polyurethane chains increases with the increase of the number of oxygen atoms in the backbone chain. Thus, the possibility to occur the conformational transition in function of the temperature is more evident in the samples with DEG sequences in hard segments which possess higher flexibility, comparatively with samples with TDG sequences in hard segments with lower flexibility.

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