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INFLUENCE OF CHAIN EXTENDER ON THE UNPERTURBED DIMENSIONS OF POLY(ESTER-URETHANE)S

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The dilute solution property of segmented poly(ester urethane)s obtained by the reaction of aromatic diisocyanates with poly(ethylene glycol)adipate and different chain extender, using a multistep polyaddition process was studied by viscometry. A new method proposed by Qian et al. was utilized for determination of unperturbed dimensions of poly(ester urethane)s having different chain extender by the measurement of the intrinsic viscosity at non-theta conditions only. The influence of the chain extender on the unperturbed dimensions and on the flexibility of these polymers was revealed.

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1. Introduction

Polyurethanes are an important class of polymers that offer the chance to obtain the designed properties by a proper selection of different segments in their composition [1]. The combination of polyols, diisocyanates and low molecular chain extenders gives rise to a multitude of forms suitable 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 experimental parameters obtained in the study of polyurethanes in solution are influenced by the multicomponent systems with soft and hard segments, introducing multiple errors. The absolute molecular weight measurements of segmented polyurethanes by different methods are complicated by the fact that, in addition to molecular weight distribution, copolymers usually exhibit a distribution of composition [10,11,12]. The use of multiple monomers instead of two for polymerization, the possibility of side reactions yielding to allophonate cross-linking for example, and the generally poor solubility in common solvents are additional complication factors. Thus, the most common results presented in the literature are weight-average molecular weight data based on gel permeation chromatography (GPC) curves.

The unperturbed dimensions expressed by intrinsic viscosity in unperturbed state, $[\eta]_\theta$, are conventionally determined by solution-viscosity method at theta conditions. The direct measurement is not possible if the theta solvent is not available or unknown, as for segmented poly(ester urethane)s having multiple components. Also, another procedure based on the non-theta solvent measurements on several fraction samples introduces multiple errors for these polymers.

The previous publications [11-14] presented the syntheses and some properties of a series of new segmented and crosslinked polyurethane elastomers. The influence of polymer structure on the thermal stability, the behavior 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 and unperturbed dimension parameters, $[\eta]_\theta$ and K_θ, of segmented copolymers prepared by the

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reaction of 4,4'-methylene diphenylene diisocyanate (MDI) with poly(ethylene glycol)adipate (PEGA) and 4,4'-dihidroxydiethoxydiphenyl sulphone (DEDS), thiodiglycol (TDG) or diethylene glycol (DEG) as chain extender as a function of temperature, and to discuss the result in connection with the chain extender. A new method based on the Einstein viscosity equation [15] modified by Guth-Simha-Gold and the model based on concentration dependence of polymer chain dimensions proposed by Qian et al. [16] was utilized for determination of unperturbed dimensions.

2. Experimental

The samples containing segmented block copolyurethanes were obtained from aromatic diisocyanates MDI, with PEGA and TDG, diethylene DEG, or DEDS as chain extenders using a two step polyaddition process [8,9].

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

Table 1. Characterization data of segmented poly(ester urethane)s

Sample	Soft segments (SS)	Hard segments (HS1)	(HS2)	Weight ratio, % SS:(HS1+HS2)
MDITDG	PEGA	MDI	TDG	74.98:25.02
MDIDEG	PEGA	MDI	DEG	75.43:24.57
MDIDEDS	PEGA	MDI	DEDS	69.26:30.74

Sample MDITDG: $-(-O-R_2-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_{q1}-$
Sample MDIDEG: $-(-O-R_3-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_{q2}-$
Sample MDIDEDS: $-(-O-R_4-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_{q3}-$
Where:

$R_1 = -C_6H_4-CH_2-C_6H_4-$	derived from MDI
$R_2 = -(CH_2)_2-S-(CH_2)_2-$	derived from TDG
$R_3 = -(CH_2)_2-O-(CH_2)_2-$	derived from DEG
$R_4 = -(CH_2)_2-O-C_6H_4-SO_2-C_6H_4-O-(CH_2)_2-$	derived from DEDS
$R_5 = [(CH_2)_2-O-CO-(CH_2)_4-CO-O]_n-(CH_2)_2-$	derived from PEGA

Subscripts q1-q3 and n are the polymerization degrees.

Scheme 1

The number-average molecular weight, M_n, and polydispersity of the studied samples (Table 2) were determined by GPC by using a GPC PL-EMD 950 evaporative mass detector instrument. The system columns were thermostated at 25°C. Calibration was performed with narrow polydispersity polystyrene standards (Polymers Laboratories Ltd.). The samples were eluted with DMF and the flow rate was 0.7 ml/min. The analysis of the elution data was performed by a computer program based on the normalization of the chromatograms. GPC curves of studied samples did not evidence the presence of low molecular weight fractions, which might affect this study [17].

The viscosity measurements were carried out in DMF in the 17 - 45 °C temperature range (±0.01 °C), using 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:

$$\eta_{sp}/c = [\eta] + k_1 \cdot [\eta]^2_{Huggins} \cdot c \tag{1}$$

in which η_{sp} is the specific viscosity and k_1 is the Huggins constant, respectively.

Table 2 shows the intrinsic viscosity determined by Huggins equation in DMF at 25 °C .

Table 2. Average molecular weights, polydispersities and intrinsic viscosities [η] of segmented poly(ester urethane)s in DMF at 25 °C.

Sample	M_n	M_w	M_w/M_n	[η], DMF (dL/g)
MDITDG	22347	40966	1.83	0.360
MDIDEG	20765	36836	1.77	0.319
MDIDEDS	27993	43669	1.56	0.474

3. Results and discussion

Fig. 1 shows the typical concentration dependence of reduced viscosity, η_{sp}/c, of MDIDEDS in DMF at 17 °C. All the curves of η_{sp}/c vs c in the studied concentration regions and in temperature range are straight lines.

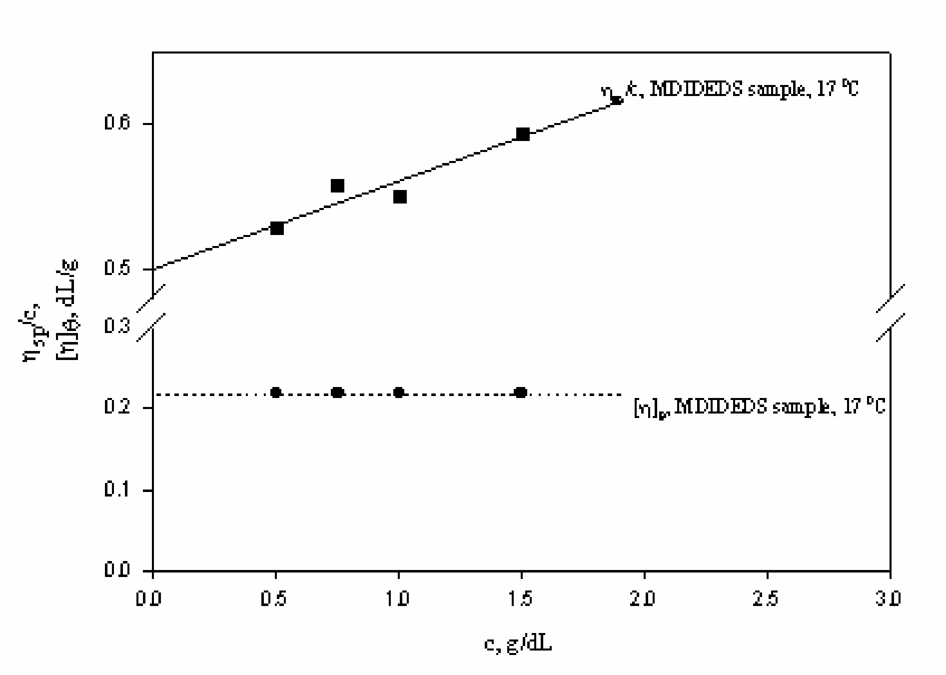

Fig. 1. Plot of η_{sp}/c (—) and $[\eta]_\theta$ (.....) vs c for MDIDEDS at 17 °C.

The variations of intrinsic viscosity, [η], calculated by Huggins equation, of segmented poly(ester urethane)s versus temperature are shown in Fig. 2

In a previous paper [17] we discussed the appearance of conformational transition at 25 °C and 35 °C from reduced viscosity in semidilute, dilute and extremely diluted concentration domain, and from intrinsic viscosity at different temperatures. The results were interpreted in relation to the conformational transition observed at 35 °C for PEGA in the same solvent and as a function of the hard segment compositions.

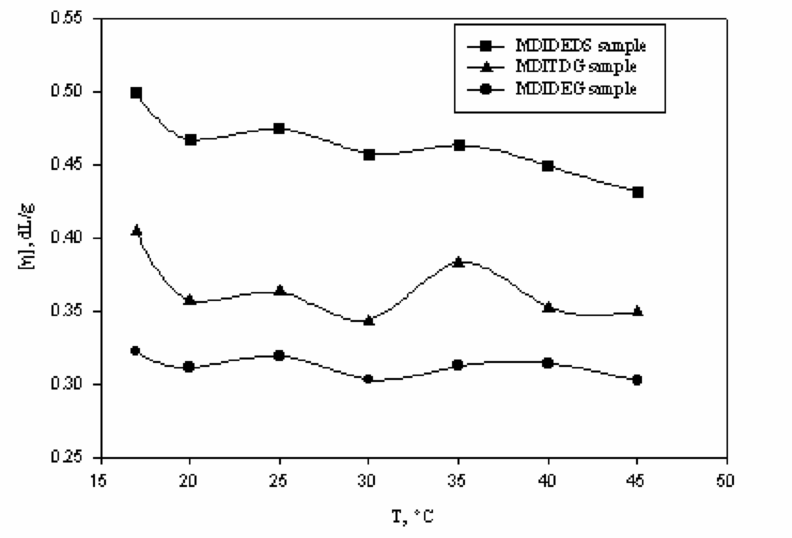

Fig. 2. Variation of intrinsic viscosity with temperature for poly(ester-urethane)s samples in DMF.

In order to know the unperturbed dimensions and to observe if the behavior shown by viscometric measurements is reflected in the unperturbed dimensions of the poly(ester urethane) chains, we used a method proposed by Qian et al. [16] for the determination of intrinsic viscosity in unperturbed state. They establish a novel approach to determine the $[\eta]_\theta$ of a polymer sample by means of its dilute-solution viscosity measurement at non-theta conditions (equation (2)).

$$[\eta]_\theta = \frac{[\eta]\left[1-\exp\left(-\frac{c}{c^*}\right)\right]}{\frac{0.77^3\rho}{c^*}-\exp\left(-\frac{c}{c^*}\right)} \tag{2}$$

c* from equation (2) is a critical concentration at which the polymer coils begin to overlap each other, defined by equation (3), and ρ is the coil density, approximated by equation (4).

$$c^* = \frac{3M}{4\pi N_A R_G^3} = \frac{3\phi'}{4\pi N_A[\eta]} \tag{3}$$

where R_G is the radius of gyration of polymer molecule in solution and $\phi' = 3.1\text{x}10^{24}$ [18].

$$\rho = \frac{c}{\eta_{sp}}\left(1.25 + 0.5\sqrt{56.4\eta_{sp} + 6.25}\right) \tag{4}$$

The [η] of a polymer sample can be obtained using equation (1).

The unperturbed values obtained for polystyrene, poly(oxyethylene), poly(methyl methacrylate), poly(vinyl chloride) and poly(isobutene) are consistent with experimental values at theta conditions or with values calculated according to Mark-Houwink-Sakurada equation at theta conditions [16].

In the present study, using the data of η_{sp}/c and [η] from Figs. 1 and 2, the $[\eta]_\theta$ was calculated according to equations (2-4). The results are shown in Fig. 1 for 17 °C at different concentrations and in Fig. 3 at different concentrations and different temperatures.

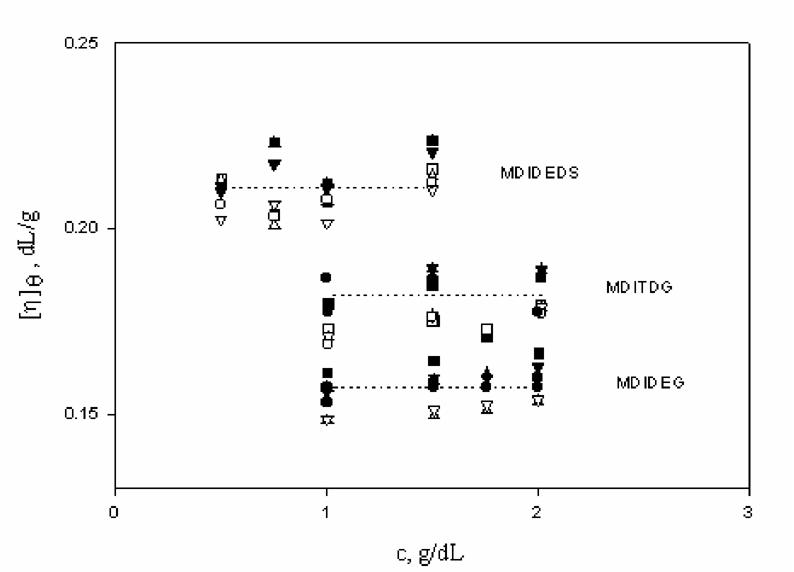

Fig. 3. Plot of $[\eta]_\theta$ *vs* c for MDIDEDS, MDITDG and MDIDEG samples at different temperatures: (■) – 17 °C; (▲) – 20 °C; (▼) – 25 °C; (•)-30 °C; ( )-35 °C; (Δ)-40 °C; (∇)-45 °C.

It is observed that $[\eta]_\theta$ values are constant for different concentrations, but are slightly different in function of temperature.

The unperturbed dimensions, K_θ were calculated with equation (5). The obtained values are comparable with the literature data for different polyurethanes [10,19].

$$[\eta]_\theta = K_\theta M^{1/2} \qquad (5)$$

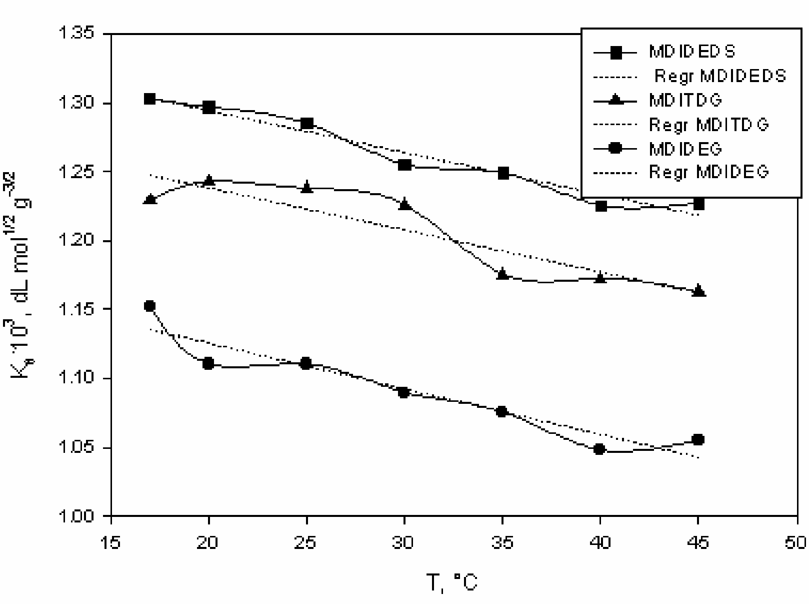

Fig. 4. Values of the unperturbed parameters K_θ, for MDIDEDS, MDIDTDG and MDIDEG samples at different temperatures.

The transition phenomena observed in Figs. 2 and 3 for $[\eta]$ and $[\eta]_\theta$ are also accompanied by discontinuity in the temperature variation of the unperturbed dimension parameters (Fig. 4). These results seem to indicate that the conformational transition can be due to intermolecular interactions, but do not exclude the influence of intramolecular interactions [19,20].

The obtained values for unperturbed dimensions indicate also, that DEDS chain extender contributed to higher unperturbed dimensions than TDG and DEG chain extenders. Thus, the flexibility of the poly(ester-urethane)s increase in the following order:
MDIDEDS<MDITDG<MDIDEG

4. Conclusions

The segmented poly(ester urethane)s obtained by the reaction of aromatic diisocyanates (4,4'-methylene diphenylene diisocyanate or 2,4-tolylene diisocyanate) with poly(ethylene glycol)adipate and 4,4'-dihidroxydiethoxydiphenyl sulphone, thiodiglycol or diethylene glycol as chain extenders, using a multistep polyaddition process, were studied by viscosity measurements in N,N-dimethyl formamide at 17 – 45 °C.

Viscosity studies show discontinuities in the intrinsic viscosity $[\eta]$ as a function of temperature. This behavior was interpreted in a previous paper as a conformational transition of the copolymer chain. Here, the results are discussed in function of the hard segment compositions.

The method based on the Einstein viscosity equation modified by Guth-Simha-Gold and the model based on concentration dependence of polymer chain dimensions proposed by Qian et al. was utilized for determination of intrinsic viscosity in unperturbed state, $[\eta]_\theta$, at different solution concentrations and temperatures. The $[\eta]_\theta$ values obtained for MDIDEDS, MDITDG and MDIDEG samples are almost independent on concentration, but depend on temperatures. The transition phenomena observed for $[\eta]$ and $[\eta]_\theta$ are accompanied by discontinuity in the temperature variation of the unperturbed dimension parameters. Also, it is observed that the unperturbed dimensions for the sample having MDI/DEDS in hard segment are higher than those of the sample having MDI/ TDG or MDI/DEG in hard segment. Thus, the flexibility of the studied poly(ester-urethane)s increase in the order: MDIDEDS<MDITDG<MDIDEG.

References

[1] E. Yamazaki, H. Hanahata, J. Hiwabari, Y. Kitahama, Polym. J. **29,** 811 (1997).
[2] T. Speckhard, S. L. Cooper, Rubber. Chem. Technol. **59**, 405 (1986).
[3] J. T. Koberstein, T. P. Russel, Macromolecules **19**, 149 (1986).
[4] H. S. Lee, Y. K. Wang, S. L. Hsu, Macromolecules **20**, 2089 (1987).
[5] C. W. Heuse, X. Yang, D. Yang, S. L. Hsu, Macromolecules **25**, 925 (1992).
[6] M. D. Lelah, S. L. Cooper, Polyurethanes in Medicine, CRC Press, Boca Raton, Fl. (1996).
[7] T. L. Wang, T. H. Hsiech, Polym. J. **28**, 839 (1996).
[8] A. Grigoriu, D. Macocinschi, D. Filip, S. Vlad, Bul. Inst. Polit. Iasi, **VIII 1-2**, 109 (2001).
[9] A. Grigoriu, D. Macocinschi, D. Filip, S. Vlad, Rev. Rom. Text. **1-2**, 325 (2001).
[10] Z. S. Petrovic, J. Ferguson, Prog. Polym. Sci., **16**, 695 (1991).
[11] S. Ioan, G. Grigorescu, A. Stanciu, J. Optoelectron. Adv. Mater. **2**, 397 (2000).
[12] S. Ioan, C. Aberle, G. Grigorescu, A. Stanciu, T. Aberle, Int. J. Polym. Analysis and Characterization, **7**, 221 (2002).
[13] S. Ioan, G. Grigorescu, A. Stanciu, Polymer **42**, 3633 (2000).
[14] S. Ioan, G. Grigorescu, A. Stanciu, Eur. Polym. J. **38**, 2295 (2002).
[15] A. Einstein, Ann. Phys. **34**, 519 (1911).
[16] J. W. Qian, M. Wang, D. L. Han, R. S. Cheng, Eur Polym J. **37**, 1403 (2001).
[17] S. Ioan, A. Taranu, D. Macocinschi, Polym International, in press.
[18] J. W. Qian, A. Rudin, Eur. Polym. J. **28**, 773 (1992).
[19] C. Tsitsilianis, G .Staikos, A. Dondos, Makromol. Chem. **191**, 2309 (1990).
[20] A. Dondos, D. Papanagopoulos, J. Polym. Sci., Polym. Phys. **32**, 1281 (1996).