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Intermolecular association study of segmented polyurethane solutions by fluorescence spectroscopy and rheology

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Poly(ester urethane)s and poly(ether urethane)s containing different soft and hard segments were investigated by fluorescence spectra and rheology. Polarity dependence of the vibrational structure of the pyrene emission spectrum indicated the formation of aggregates at concentrations, significantly below the critical ones, which define the separation of dilute-semidilute domains. The results are discussed in correlation with rheological data, reporting the effects of steady shear flows on intermolecular association are reported. The rheological properties were measured experimentally on a rheometer with a cone plane measuring sistem. This study shows that the growth and strength of association structures are tuned by factors such as: synthesis process, composition of soft and hard segments, and polymer concentration.

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1. Introduction

Polyurethanes consititute of a large class of materials, characterized by the occurrence of the urethane group, resulting from the combination of polyols (hydrogen donor), diisocyanates (the hydrogen acceptor) and low molecular chain extenders. These materials have been used as adhesives [1], elastomers [2], foams [3], biomaterials [4], water-borne coatings [5], polymers for electronics [6], etc. The recent developments of medical technology, require polymer materials [7]. In the case of polymers used for medical applications, antithrombogenicity is one of the most important characteristics to be considered, as well as some suitable mechanical properties.

Polyurethanes are widely used materials, particularly for artificial hearts and blood vessels, for which elastic properties similar to those of the muscle are required, besides antithrombogenicity. Many applications of these polymers involve solutions used to obtain coating or adhesive films, for instance after drying. As a consequence, a good knowledge of the rheological properties of these solutions is important for their handling or formulation.

Previous studies of ours [8-14] presented the syntheses and some properties of a series of new segmented and crosslinked polyurethane elastomers. The influence of the polymer structure on thermal stability, the behaviuor in different organic solvents, the structure and morphology of these compounds were analyzed.

The present study provides information on the rheological properties of segmented copolymers obtained by the reaction of aromatic diisocyanates such as 4,4'-methylene diphenylene diisocyanate (MDI) or 2,4-tolylene diisocyanate (TDI), with poly(ethylene glycol)adipate (PEGA), poly(propylene glycol) (PPG), or polytetrahydrofurane (PTHF) and 4,4'-dihydroxydiethoxydiphenyl sulfone (DEDS) as chain extender, and discusses the results obtained in relation with the composition of the soft and hard segments.

2. Experimental

2.1. Structure and compositional parameters of polyurethanes

The samples containing segmented block copolyurethanes were previously prepared by the reaction of aromatic diisocyanates: such as MDI or TDI with PEGA, PPG or PTHF, with M_n=2000 g/mol, and DEDS as chain extender in a two step polyaddition process in N,N-dimethylformamide (DMF).

The general chemical structures of the studied segmented poly(ester urethane)s are as follows:

Sample PEGA/MDI-DEDS:
$-(O-R_3-O-CO-NH-R_1-NH-CO-O-R_4-O-CO-NH-R_1-NH-CO-)_{q1}-$
Sample PEGA/TDI-DEDS:
$-(O-R_3-O-CO-NH-R_2-NH-CO-O-R_4-O-CO-NH-R_2-NH-CO-)_{q2}-$
Sample PPG/MDI-DEDS:
$-(O-R_3-O-CO-NH-R_1-NH-CO-O-R_5-O-CO-NH-R_1-NH-CO-)_{q3}-$
Sample PPG/TDI-DEDS:
$-(O-R_3-O-CO-NH-R_2-NH-CO-O-R_5-O-CO-NH-R_2-NH-CO-)_{q4}-$
Sample PTHF/MDI-DEDS:
$-(O-R_3-O-CO-NH-R_1-NH-CO-O-R_6-O-CO-NH-R_1-NH-CO-)_{q5}-$
Sample PTHF/TDI-DEDS:
$-(O-R_3-O-CO-NH-R_2-NH-CO-O-R_6-O-CO-NH-R_2-NH-CO-)_{q6}-$

where:

$R_1 = -C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}$ is derived from MDI
$R_2 = -C_6H_3(CH_3)\text{-}$ is derived from TDI
$R_3 = -(CH_2)_2\text{-O-}C_6H_4\text{-}SO_2\text{-}C_6H_4\text{-O-}(CH_2)_2\text{-}$ is derived from DEDS
$R_4 = -[(CH_2)_2\text{-O-CO-}(CH_2)_4\text{-CO-O}]_n\text{-}(CH_2)_2\text{-}$ is derived from PEGA
$R_5 = -[(CH_2)_3\text{-O}]_k\text{-}$ is derived from PPG
$R_6 = -[(CH_2)_4\text{-O}]_p\text{-}$ is derived from PTHF

"q_1-q_6" and "n", "k", "p" subscripts represent the polymerization degrees.

Table 1 presents the compositional parameters obtained for the studied polyurethanes.

Table 1. Compositional parameters of soft and hard segments and number average molecular weights, M_n, of segmented polyurethanes in DMF at 25 °C.

Samples	Weight ratio (%) $R_{4,5,6}$:($R_{1\ or\ 2}$:R_3)	M_n
PEGA/MDI-DEDS	69.26:(18.33:12.41)	28 000
PEGA/TDI-DEDS	73.18:(13.57:13.25)	26 000
PPG/MDI-DEDS	69.26:(18.33:12.41)	29 300
PPG/TDI-DEDS	73.18:(13.57:13.25)	20 200
PTHF/MDI-DEDS	69.26:(18.33:12.41)	39 200
PTHF/TDI-DEDS	73.18:(13.57:13.25)	37 100

2.2. Fluorescence and viscoelastic measurements

Fluorescence measurements were carried out on a Perkin Elmer LS 55 spectrometer using 3.5 mL solution poured into a 1.0 cm square quartz cell. The excitation and emission bandwidths were 8 and 4 nm, respectively. All measurements were performed at room temperature, using air-equilibrated solutions.

The pyrene used as a marker for the hydrophobic domains was added at a concentration of $7.9 \cdot 10^{-6}$ M.

Polyurethane solutions with concentrations between 0.004-2.66 g/dL were prepared by dissolution of appropriate amounts of copolymer in 5 mL pyrene-DMF solution, and left for 24 h at room temperature, then heated for 20 minutes at 50^{o}C and left again to equilibrate, before measurements.

The studied parameter is the I_1/I_3 ratio of the intensities of the first and third peaks of the fluorescence spectrum of pyrene in polyurethane solutions.

For emission spectra, the excitation wavelength λ_{ex} was 335 nm, while for excitation spectra, the emission wavelength λ_{em} was 394 nm. The emission intensity was measured between 350 and 500 nm, and the excitation intensity was measured between 300 and 360 nm.

The viscometric experiments were carried out with a cone-plane measuring system, on a Bohlin Instrument, in DMF; the cone has of 4° angle and a diameter of 40 mm.

3. Results and discussion

3.1. Intermolecular association by fluorescence spectra

The existence of intra- and intermolecular associations in the solutions of polyurethanes listed in Table 1 is supported by steady-state fluorescence spectroscopy, employing pyrene as a hydrophobic probe. In the presence of micelles or similar supramolecular aggregates, pyrene is solubilized inside the hydrophobic part of such aggregates. As a result, significant changes in the spectroscopic properties are observed upon transferring of the probe from solvents environment to the non-polar environment of the polymer. Such changes are shown in Fig. 1, which presents typical excitation and emission spectra recorded for pyrene in DMF solutions of PPG/TDI-DEDS at various concentrations. The I_1 peak at $\lambda = 374\,\text{nm}$, which arises from the (0,0) transition from the lowest excited electronic state of pyrene, is a symmetry-forbidden transition that can be enhanced by the distortion of the π electron cloud. Thus, I_1 yields enhanced values of fluorescence intensity in the polar solvent DMF. On the other hand, peak I_3 (at approximately 385 nm), which shows maximum variation in intensity relative to the 0-0 band, is not forbidden, being thus relatively insensitive to DMF polarity.

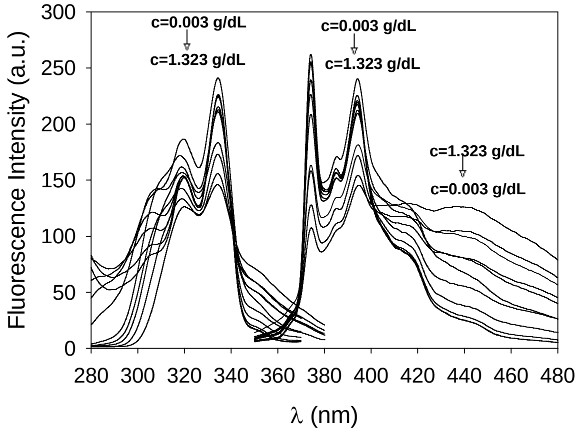

Fig. 1. Fluorescence excitation (monitored at $\lambda_{em} = 394\,\text{nm}$) and emission spectra (monitored at $\lambda_{ex} = 335\,\text{nm}$) of PPG/TDI-DEDS recorded at various concentrations in DMF, at room temperature.

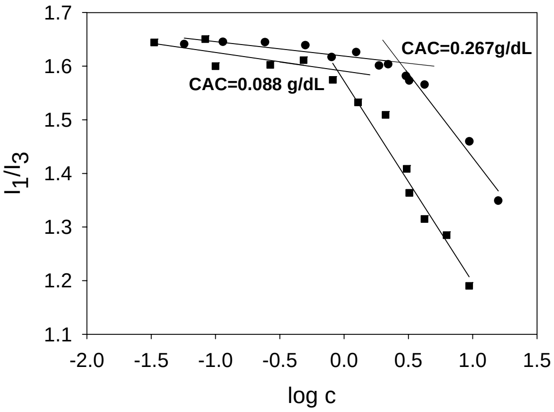

Fig. 2. Fluorescence intensity ratio I_1/I_3 (from pyrene emission spectra) as a function of concentration (g/L) for PEGA/MDI-DEDS (●) and PTHF/TDI-DEDS (■).

Fig. 2 exemplifies the variation of the I_1/I_3 ratio as a function of concentration for PEGA/MDI-DEDS and PTHF/TDI-DEDS samples. Above the 0.267 g/dL concentration for PEGA/MDI-DEDS or 0.088 g/dL for PTHF/TDI-DEDS, the slopes in Figure 2 sharply increase. The intersection between both slopes for each sample gives the critical aggregation concentration (CAC), which indicates that pyrene is present in the hydrophobic domains, due to the micellization process from the polymer solution above CAC. The CAC values are much smaller than the critical concentrations, c*, at which the polymer coils begin to overlap each other (the concentration which separates the dilute-semidilute domains), indicating that hydrophobic interactions exist even in dilute solutions. c* can be estimated from intrinsic viscosity ($c^* \cong [\eta]^{-1}$) [11]. Upon micellization, the I_1/I_3 ratio decreases rapidly over a rather narrow concentration range.

A critical aggregation concentration was observed for all studied samples, although at higher concentrations for poly(ester urethane)s, than for poly(ether urethane)s, as evidenced by the data presented in Table 2.

Table 2. Critical aggregation concentrations and critical concentrations between the dilute-semidilute domain for polyurethanes.

Samples	CAC, g/dL (from I_1/I_3)	c*, g/dL
PEGA/MDI-DEDS	0.267	2.110
PEGA/TDI-DEDS	0.242	4.762
PPG/MDI-DEDS	0.119	4.608
PPG/TDI-DEDS	0.097	5.464
PTHF/MDI-DEDS	0.143	2.326
PTHF/TDI-DEDS	0.088	2.958

3.2. Intermolecular interaction by rheological measurements

Figs. 3 and 4 plot the shear rate dependence of viscosity for PEGA/MDI-DEDS and PPG/MDI-DEDS, at different polymer concentrations.

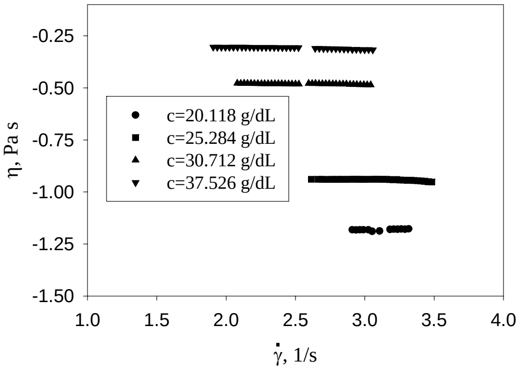

Fig. 3. Log-log plot of viscosity as a function of shear rate of PEGA/MDI-DEDS at room temperature and different concentrations.

The aggregation phenomena observed at lower concentration from the fluorescence spectra were disrupted at the studied shear rates, so that the behaviour of all studied solutions at room temperature and different concentrations was essentially Newtonian.

Polymer concentration dependencies of the viscosity at constant shear rate for the studied samples are shown in Fig. 5. It is evident that dependence of viscozity on concentration is higher for the sample with MDI in the hard segment.

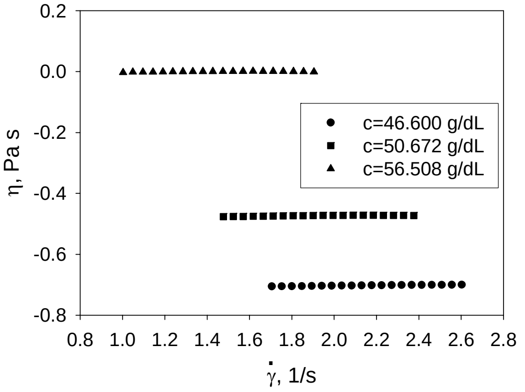

Fig. 4. Log-log plot of viscosity as a function of shear rate of PPG/MDI-DEDS at room temperature and different concentrations.

Such a behaviour, evidencing a higher rigidity of polyurethanes, may be attributed to a higher cohesive energy and bulkiness, because of the benzene rings present in the MDI segments. Moreover, the hydrogen bonding which generates crystalline structures increases the rigidity of the chain much more for poly(ester urethane)s than for poly(ether urethane)s. Also, dependence of viscosity on concentration for all samples from Fig. 5 is $\eta \propto c^{3.4}$. This dependence coincides with the theoretical prediction for concentrated polymer solutions in which entanglements between, macromolecules exist. [15]

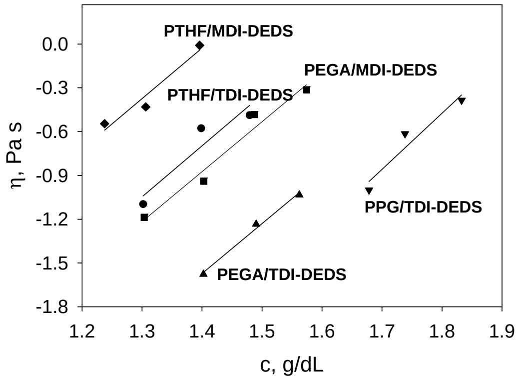

Fig. 5. Log-log plot of dependence of viscosity on concentration at constant shear rate for the studied polyurethanes, at room temperature.

From the values of η recorded at different temperatures (c.f. Fig. 6), the apparent energy of activation, E_A, and a pre-exponential constant, $\ln \eta_0$, were determined by linearization of equation (1) (Arrhenius-Frenkel-Eyring equation):

$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT} \tag{1}$$

where R is the universal gas constant and T is the absolute temperature.

Thus, for some samples from Table 1, the values of $\ln \eta_0$ and E_A are listed in Table 3.

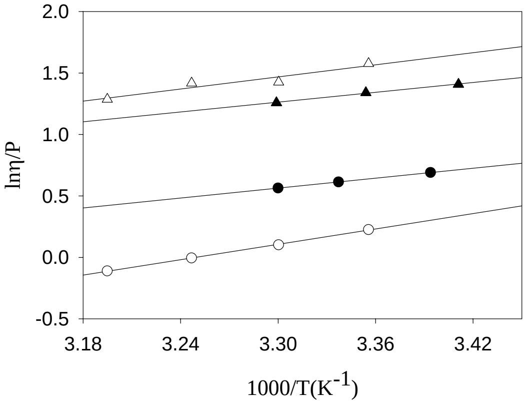

Fig. 6. Plot of $\ln \eta$ versus 1/T for: (Δ) PEGA/MDI-DEDS at c = 37.53 g/dL; (▲) PTHF/MDI-DEDS at c = 20.24 g/dL; (●) PPG/MDI-DEDS at c = 46.60 g/dL; (○) PEGA/TDI-DEDS at c = 36.50 g/dL

Table 3. Values of c (g/dL), $\ln \eta_0$, η_0 (P) and E_A (KJ/mole) for some of the studied polyurethanes.

Sample	c	$\ln \eta_0$	$\eta_0 \cdot 10^{-2}$	E_A
PEGA/MDI-DEDS	37.53	-3.94	1.939	13.64
PEGA/TDI-DEDS	36.50	-6.77	0.114	17.34
PPG/MDI-DEDS	46.60	-3.89	2.045	11.22
PTHF/MDI-DEDS	20.24	-3.14	4.328	11.09

According to the theory of Hirai and Eyring, [16] a lower value of η_0 is related to a lower value of flow activation entropy (in fact, it is proportional to $e^{-\Delta S^{+}/R}$, where ΔS^{+} is the flow activation entropy. [17]) A higher value of ΔS^{+} is related to a more rigid structure of the polymer chains, before the rheological test; a higher value of E_A means a higher energy barrier for the movement of an element of the fluid. In the case of the polymer solutions under study, this barrier can be related to the interaction between chain segments (these interactions being, in their turn, related to polymer entanglements or being specific, such as hydrogen bonding). As the samples have closed molecular weights in concentrated regimes, any speculation on different forms of entanglement seems to be fruitless. However, analysis of the possible forms of hydrogen bonding, which increase rigidity and the apparent energy of activation, may represent an interesting view in these cases. Basically, one can distinguish four types of hydrogen bonding solvent - hard segment, solvent - soft segment, hard segment - soft segment, and hard segment - hard segment for poly(ester urethane)s in DMF. For poly(ether-urethane)s in DMF, hydrogen bonding appears between hard - hard segments and solvent - hard segments. Thus, a higher apparent energy of activation for poly(ester urethane)s, comparatively with poly(ether urethane)s, is possible.

4. Conclusions

Fluorescence and rheological measurements have been performed to study the aggregate/micelle formation in polyurethanes with different soft and hard segments.

Fluorescence spectra in the DMF solutions of the studied polyurethanes show the existence of hydrophobic aggregates even in dilute solutions, so that the critical aggregation concentrations observed for all studied samples are much smaller than the overlap concentration, c*, estimated from intrinsic viscosity. Also, the critical aggregation concentrations values are higher for poly(ester urethane)s than for poly(ether urethane)s.

The rheological behaviour of some poly(ester urethane)s and poly(ether urethane)s was investigated in DMF at different temperatures. Influence of structure, concentration and temperature is reflected by viscometric data. The Newtonian behaviour indicates that the aggregation phenomena observed at low concentration from fluorescence spectra were disrupted for the studied shear rates range at high concentration.

The influence of hydrogen bonding reveals the higher apparent energy of activation, and thus the higher rigidity of the chain, for poly(ester urethane)s than for poly(ether urethane)s.

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