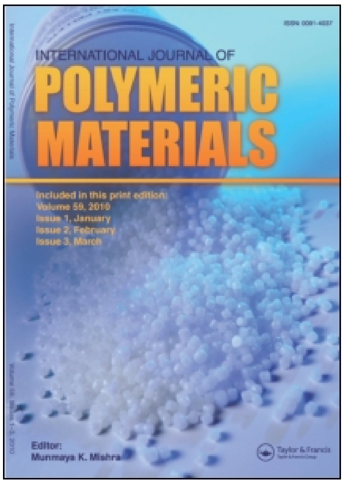

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Viscometric Study of Segmented Poly(ester-urethane) Solutions in Dilute and Extremely Dilute Concentration Domains

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Viscometric Study of Segmented Poly(ester-urethane) Solutions in Dilute and Extremely Dilute Concentration Domains

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Synthesis and viscometric behavior of segmented poly(ester-urethane)s in N,N-dimethyl-formamide solution ranged from semidilute to extremely dilute concentration were investigated. The data reflected the conformation changes in the 17–45°C range, and the results are discussed in relation to the behavior of the poly(ethylene glycol)adipate in the same solvent. The intrinsic viscosities and critical concentration that separate the dilute–extremely dilute regimes are also studied. A scanning law between the reduced viscosity η_{sp}/c *and the concentration for the extremely dilute regime is found and the deviations from Huggins dependence at different temperatures are discussed.*

Keywords: segmented poly(ester urethane), conformational transition, dilute solution, extremely dilute solution

INTRODUCTION

Polyurethanes are an important class of polymers that offer the chance to obtain certain 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 suited for extremely varied practical applications as fibers, paints, foams, resins, elastomers, and many others [2–7]. Also, they are utilized as coating materials in the textile industry [8–9].

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For these reasons the understanding of the solution behavior of polyurethanes is important for their characterization in solution as well as for the interpretation of their conformational characteristics. Due to the crystallinity of the hard segment, its rigidity and strong hydrogen bonding, the segmented polyurethanes are soluble in a limited number of very polar solvents, such as *N,N*-dimethyl-formamide (DMF). Their solubility depends especially on the hard block length, composition and concentration, and to a lesser extent on the soft segment nature. Specific properties of polyurethane solutions may arise from their composition and the transition phenomenon in solution affects the efficiency in their practical application.

A relatively limited amount of data has been published on the solution properties of segmented polyurethanes [10]. The absolute molecular weight measurements of segmented polyurethanes by different methods are complicated by the fact that, in addition to the molecular weight distribution, copolymers usually exhibit a distribution of composition [11–12]. The use of multiple monomers instead of two for the polymerization, the possible side reactions yielding to allophanate crosslinking 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 GPC curves.

The authors' previous publications [11–14] present 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 behavior in different organic solvents, and the structure and morphology of these compounds were analyzed. Also, the segmented poly(ester urethane)s obtained from aromatic diisocyanates 4,4′-methylene diphenylene diisocyanate (MDI) or 2,4-tolylene diisocyanate (TDI) with poly(ethylene glycol)adipate (PEGA) and thiodiglycol (TDG) or diethyleneglycol (DEG) as chain extender, using a multistep polyaddition process, were studied by viscosity measurements in N,N-dimethyl formamide at 20°C–45°C. The studies show discontinuities in the intrinsic viscosity $[\eta]$ as a function of temperature. This behavior is interpreted as a conformational transition of the copolymer chain. The results are discussed in relation to the behavior of PEGA in the same solvent and as a function of the hard segment composition [15,16]. The influence of the hard segments MDI and TDI on the unperturbed dimensions of the segmented poly(ester urethane)s was also observed [17].

The purpose of the present study is to obtain information about the conformational behavior by viscometry of segmented copolymers, made by the reaction of aromatic diisocyanates such as MDI or TDI, with PEGA and 4,4′-dihidroxydiethoxydiphenyl sulphone (DEDS) as chain extender, as a function of temperature. The viscosity of copolymers in the extremely dilute concentrations domain was also determined and the abnormal viscosity behavior in extremely dilute concentrations was observed and interpreted.

EXPERIMENTAL

Structure and Compositional Parameters of Poly(ester urethane)s

The samples containing segmented block copolyurethanes were prepared by the reaction of aromatic diisocyanates such as MDI or TDI, both from Merck and distilled under reduced pressure, with PEGA from Fibrex Savinesti ($M_n = 2000$ g/mol) and 4,4′-dihidroxydiethoxydiphenyl sulphone as chain extender (DEDS) [18–19] using a two steps polyaddition process in DMF [20]. The 4,4′-dihidroxydiethoxydiphenyl sulphone chain extender utilized in this work introduces high performance having excellent chemical and thermal stability, because of the strong resonant aryl-sulphone groups, and because of the hexavalent sulfur [19]. In the first stage of reaction, the NCO-terminated prepolymer was formed: PEGA was dehydrated for 3 h at 120°C followed by the addition of MDI or TDI. This reaction between diisocyanate and hydroxy-terminated polyester prepolymer (PEGA) was performed for 1 h at 90°C under nitrogen atmosphere. The amounts of diisocianate and PEGA were controlled at a NCO:OH molar ratio of 3:1. The second step is the reaction of the free isocyanate group with the chain extender: the reaction mixture 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 urethane)s was checked by IR and ^{1}H-NMR (at 80°C in dimethyl sulfoxide—d_6) analyses.

The general chemical structures of the segmented poly(ester urethane)s studied in this work are:

$$\text{Sample MDIDEDS}: -(\mathrm{O{-}R_3{-}O{-}CO{-}NH{-}R_1{-}NH{-}CO{-}O} \\ -\mathrm{R_4{-}O{-}CO{-}NH{-}R_1{-}NH{-}CO{-}})_{q1}-$$

$$\text{Sample TDIDEDS}: -(\mathrm{O{-}R_3{-}O{-}CO{-}NH{-}R_2{-}NH{-}CO{-}O} \\ -\mathrm{R_4{-}O{-}CO{-}NH{-}R_2{-}NH{-}CO{-}})_{q2}-$$

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

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

In order to discuss the behavior of segmented poly(ester urethanes) in dilute solution, the compositional parameters were calculated from Eqs. 1 and 2 as follows [11]:

(i) Soft segment-concentration

The soft segment-concentration (SSC) is defined as the mass of the polyol (m_{pol}) without hydroxyl groups (m_{OH}) divided by the total mass of the polymer, expressed as a percentage:

$$SSC = (m_{pol} - m_{OH}) \cdot 100/m_{total} \tag{1}$$

(ii) Hard segment concentration

The hard-segment concentration (HSC) is:

$$HSC = 100 - SSC \tag{2}$$

Table 1 presents the compositional parameters obtained for the studied samples of poly(ester urethnane)s.

Molecular Weight Characterization

The number-average molecular weight, M_n, and polydispersity of the studied samples (Table 1) were determined by gel permeation chromatography (GPC) by using a GPC PL-EMD 950 evaporative mass detector instrument. The system columns were thermostated at 25°C. Calibration was performed with polystyrene standards having narrow polydispersity (Polymers Laboratories Ltd.). The samples were eluted with DMF and the flow rate was 0.7 mL min^{-1}. The analysis of the

TABLE 1 Compositional 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

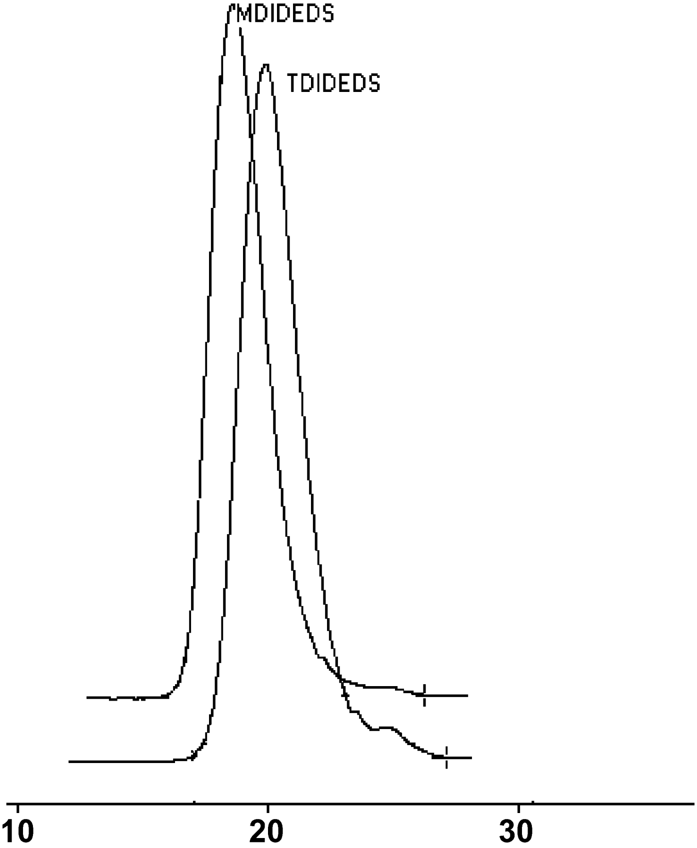

FIGURE 1 GPC curves of MDIDEDS and TDIDEDS samples.

elution data was performed by a computer program based on the normalization of the chromatograms. GPC curves of the studied samples from Figure 1 did not evidence the presence of low molecular weight fractions, which might affect this study.

Table 1 shows the differences between compositional parameters and molecular weights of MDIDEDS samples and TDIDEDS samples, due to different activity and different molecular weights of the corresponding diisocyanates MDI or TDI in the synthesis process.

Viscosity Measurements

The viscosity measurements were carried out in DMF in the 17°C–45°C temperature range (±0.01°C), using an Ubbelohde suspended-level viscometer. All the measurements were performed within one day after the samples were brought into solution within 5 h. The concentration range was 0.25–5 g/dL for poly(ester urethane)s and 1.5–4.8 g/dL for PEGA. The kinetic energy corrections were found to be 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 samples in DMF at a given temperature. Plots of η_{sp}/c vs. c in the dilute domain were extrapolated to zero concentration to obtain intrinsic viscosity $[\eta]$ according to Huggins and Mead and Fuoss equations:

$$\eta_{sp}/c = [\eta] + k_1 \cdot [\eta]^2_{\text{Huggins}} \cdot c \tag{3}$$

$$\frac{\ln(\eta_{rel})}{c} = [\eta] - k_2 \cdot [\eta]^2_{\text{Mead-Fuoss}} \cdot c \tag{4}$$

where η_{rel} is the relative viscosity, η_{sp} is the specific viscosity and k_1 and k_2 are the Huggins and the Mead–Fuoss constants, respectively. Intrinsic viscosities were determined by simultaneous extrapolation of η_{sp}/c vs. c and $\ln \eta_{rel}/c$ vs. c plots to zero concentration with accuracy of the order of ±1.3% for relative viscosity of the solution $1.2 < \eta_{rel} < 1.85$. For TDIDEDS sample the relative viscosity was also measured in the extremely dilute and the semidilute domains.

To verify the reproducibility of the results, repeated measurements were carried out with new solutions. No change over a period of a few days could be found with the studied samples at the studied temperatures. After six days the flow times of solutions increased with approximately 0.6% and after one month with 2.2%.

Table 1 shows the intrinsic viscosity determined by the Huggins equation for the studied samples in DMF at 25°C.

Refractometric Measurements

Specific refractive index increments (dn/dc) of PEGA solutions in DMF at five concentrations were measured with the Zeiss interferometer in the 20–45°C temperature range using 436 nm wavelength in a standard way [21].

RESULTS AND DISCUSSION

Conformational Transitions of Poly(ester urethane)s

Dondos et al. [22–23] present the results that demonstrate that the conformational transition in the viscosity curve is generally observed for all block copolymers.

Different properties of polyurethanes show the existence of highly flexible chains, that is a low degree of intermolecular interaction, and the presence of crosslinks, which can be of a chemical or physical nature. Thus, the studied poly(ester urethane)s are block copolymers, consisting of two phases designated as soft segments, which are flexible blocks, and hard segments, which are rigid blocks [11]. Hard blocks are also associated with hydrogen bonding and physical crosslinks.

The polyurethane–solvent interaction parameter can be analyzed by a simplistic, so-called two-parameters theory, where the 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 that take into consideration more interaction parameters [11,24]. In the present work the studied polyurethanes are multicomponent compounds and the determination of the interactions that may occur is very complicated. Thus, the method of investigation of conformational transition in solution was limited to intrinsic viscosity measurements [12].

The variations of η_{sp}/c and $[\eta]$ for poly(ester urethane) samples in Table 1 are shown in Figures 2 and 3. The accuracy of the viscometric

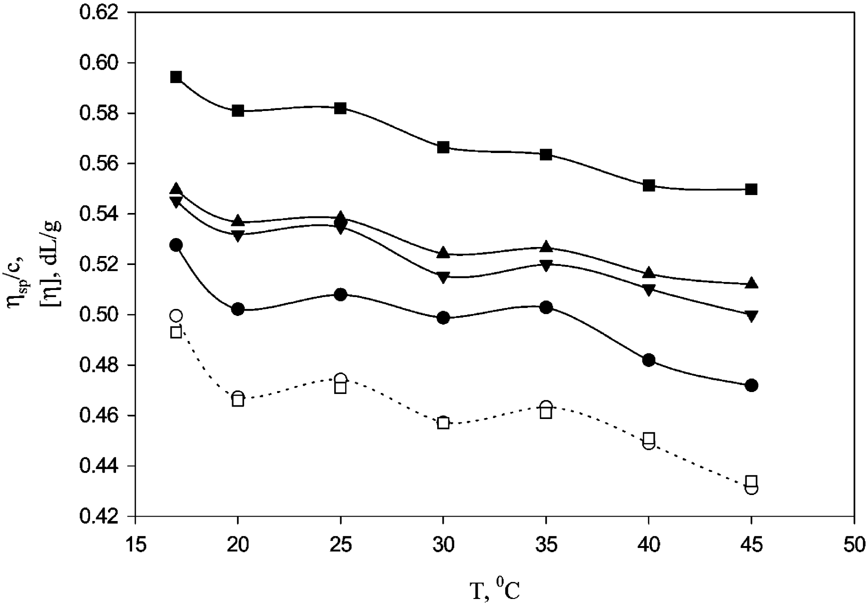

FIGURE 2 Variation of reduced viscosity η_{sp}/c and intrinsic viscosity $[\eta]$ with temperature for MDIDEDS sample in DMF.

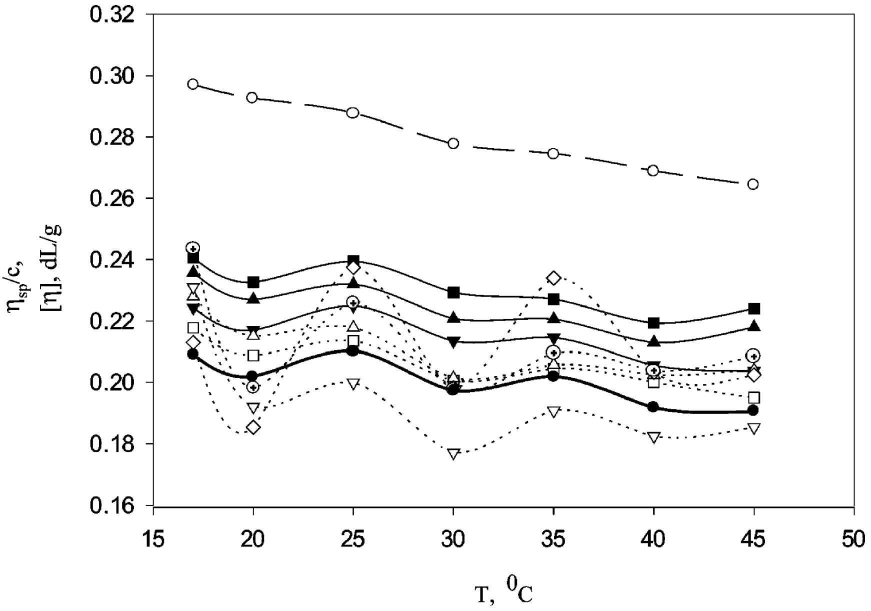

FIGURE 3 Variation of reduced viscosity η_{sp}/c and intrinsic viscosity $[\eta]$ with temperature for TDIDEDS sample in DMF: $c = 5.015\,g/dL$—semidilute domain; $1.0047\,g/dL \le c \le 2.0033\,g/dL$—dilute domain; $0.2525\,g/dL \le c \le 0.6340\,g/dL$—extremely dilute domain.

results is observed from Figure 2 where small differences between intrinsic viscosity values determined by Huggins and Mead–Fuoss methods are observed.

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.

In the present work the explanation of the conformational transition is not easy, although the existence of this change is well established and reproducible. A tentative interpretation of these phenomena considers the differences of interaction of solvent with soft (more flexible) and hard (with physical crosslinks) segments depending on the temperature, which modifies the conformation of the chain in solution. Moreover, there are preferential interactions between DMF and soft segment, due to the carbonyl groups.

Depending on the chemical composition, the polyurethanes possess different global flexibilities. It is known that in the case of polyurethanes based on diisocyanates with methyl substituents in the hard segment, those based on TDI have a higher flexibility compared with the related samples based on MDI, which are believed to possess significant chain rigidity because of the high cohesive energy and bulkiness of the benzene ring [25]. Thus, the intrinsic viscosity of samples based on MDI in Table 1 is higher than that of samples based on TDI not only because of the differences of molecular weights but also because of the different flexibility.

All samples show inflexions in the viscosity at 25°C and 35°C. These modifications of viscosity with temperature were also observed in the study of segmented copolymers based on the aromatic diisocyanates, such as MDI or TDI, with PEGA and with thiodiglycol (TDG) or diethylene glycol (DEG) as chain extenders [16]. This behavior has been interpreted as a probable conformational transition of the polymer chain. The increase of viscosity, caused by an increase of the hydrodynamic volume of the polymer coils, may be the result of the 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 of DMF and PEGA, but also because of the poor solvent penetration in the regions of the hard domains that are physically crosslinked. At higher temperatures the physical crosslinks can be perturbed, and thus the modification of coil dimensions is a consequence of these phenomena.

From Figure 3 it is also observed that the conformational transitions are more evident in extremely dilute solutions, for the relative viscosity below 1.2 and are unobservable in the semidilute domain, for a relative viscosity above 1.85. Thus, the curves corresponding to variation of η_{sp}/c with temperature in the extremely dilute domain, for $0.6340\,g/dL \leq c \leq 0.3370\,g\,dL^{-1}$, exhibit discontinuities with maximum amplitudes, whereas the curves corresponding to these variations in the dilute domain, for $2.0033\,g/dL \leq c \leq 1.0047\,g/dL$ exhibit discontinuities with smaller amplitudes. Also, in the semidilute domain, for $c = 5.0105\,g/dL$, the conformational transitions are unobservable. This behavior was found also by Dondos and Papanagopoulos [26].

Furthermore, from the authors' investigation of the segmented polyurethane it appears that the conformational transitions are also transmitted by PEGA segments. Thus, a discontinuity has been observed in the variation of the intrinsic viscosity of PEGA with $M_n = 2000$ versus temperature, characterized by an increase of the dimensions in the 27–35°C interval (Figure 4).

It has been demonstrated that, when the transition takes place, this conformational change of the polymer chain should influence the

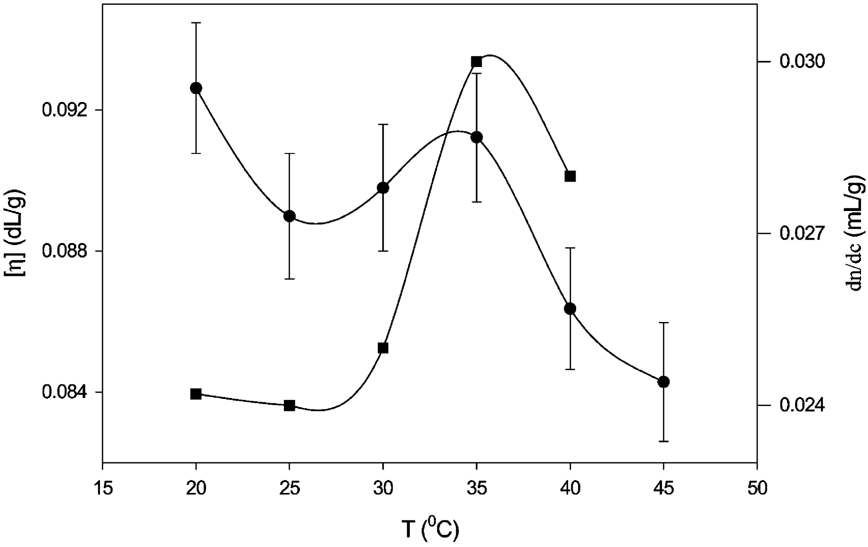

FIGURE 4 Variation with temperature of intrinsic viscosity [η] and refractive index increments, dn/dc, of PEGA sample in DMF. The vertical lines represent the errors for $[\eta]_{\mathrm{Huggins}}$ measurements (±2%).

partial specific volume ($\bar{v}$) of the chain in solution. Because $\bar{v}$ is directly related to the refractive index increment, dn/dc, the refractive index increment in DMF was measured as a function of temperature between 20°C and 40°C for PEGA (Figure 4). The change in conformation should influence the partial specific volume of the polymer ($\bar{v}$), and, depending on that, the refractive index increment, dn/dc. The relation between $\bar{v}$ and dn/dc can be expressed by the semiempirical Gladstone–Dale equation [27]:

$$dn/dc = \bar{R} - (n_0 - 1)\bar{v} \tag{5}$$

where $\bar{R}$ is the molar specific refractivity of the polymer and n_0 is the refractive index of the solvent.

As the chain conformation changes in solution from a less extended form to a more extended one, the partial specific volume of the polymer should increase. This is reflected by a decrease in dn/dc, as seen in Figure 4. On further increase of temperature, the chain flexibility in solution again decreases from about 27°C to about 35°C where chain dimension reaches the same value as before the transition. It is necessary to take into account that dn/dc should be considered only as a gross approximation to visualize what happens with the partial specific volume of the chain in this temperature region, because all the parameters in Eq. 5, that is the refractive index of the solvent, the molar refractivity, and the specific volume, are interdependent and change with temperature. The results show that a conformational transition occurs, but it is difficult to give an explanation for the phenomenon. Also, the decrease of the intrinsic viscosity and of the refractive index increment in Figure 4 above 35°C is supposed to be due to the structural modification of PEGA sample in the bulk state below its melting temperature. For PEGA with $M_{\mathrm{n}} = 2000$ differential scanning calorimetry shows that the melting temperature is about 48°C.

It is difficult to explain the conformational modification of the poly(ester urethane) chain when the temperature increases, but it is evident that the conformational transition of PEGA is reflected in the conformational transition of the studied poly(ester urethane)s. As a first step, one can suppose the existence of PEGA-solvent preferential adsorption. When the temperature increases, the solvent penetrates in the physical crosslinks of hard blocks, thus increasing the hard segment-solvent contacts. Hard block solubility also depends on the composition. However, it is difficult to propose a certain mechanism of the macromolecular chain behavior as function of temperature.

Viscometric Study from Dilute to Extremely Dilute Concentration

The thermodynamic properties of linear polymer solutions are usually discussed from the viewpoint of their dependence on concentration (c) and molecular weight (M). Experimental and theoretical papers have established the existence of different concentration domains: dilute, semidilute, and concentrated [28–29]. Each concentration regime has its own distinctive features, that is, measured quantities display different patterns of behavior depending on the considered regime. When the concentration increases, the interactions progressively become predominant and at a certain concentration c^* the domains of the polymer molecules begin to overlap and eventual entanglements may develop. This concentration separates the dilute and the semidilute regimes. Many papers also deal with viscometric anomalies observed in very dilute solutions [26–34] and define another critical concentration, c^{**}. In the present study, the experimental investigation was carried out over a large change of concentrations, including the extremely dilute domain, for TDIDEDS sample. The dependencies of reduced viscosity (η_{sp}/c, dL/g) versus concentration (c, g/dL) are presented in Figures 5 and 6 for different temperatures. The critical

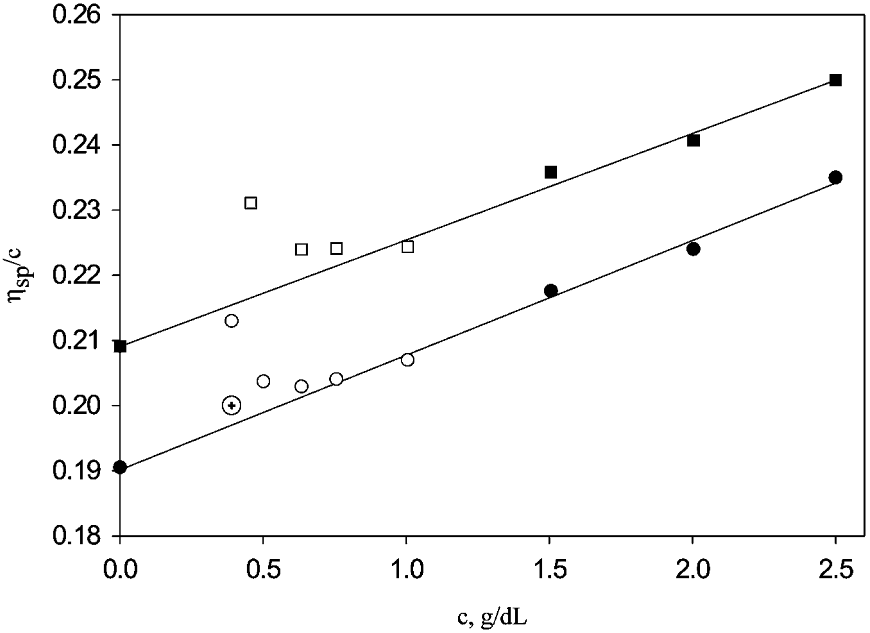

FIGURE 5 Variation of η_{sp}/c vs. concentration in the dilute and extremely dilute domains, at 17°C and 45°C for TDIDEDS sample.

concentration that separates dilute to semidilute domains, c^*, was determined with Eq. 6 [35]:

$$c^* = \frac{0.77}{[\eta]} \tag{6}$$

Below the critical concentration c^{**}, the change in the slope of the straight lines representing the variation of the reduced viscosity as a function of concentration was observed for all temperatures. Figures 5 and 6 show the dependence on temperature of these slopes. Thus, Figure 5 illustrates the upward change of the slope at 17°C and 45°C, and Figure 6 illustrates the downward change of the slope at the transition temperatures 25°C and 35°C, in the extremely dilute domain.

From the experimental data in the extremely dilute domain, the following equation was established for TDIDEDS sample:

$$\eta_{sp}/c \cong A \cdot c^a, \text{ for } c < c^{**} \tag{7}$$

Eq. 7 was obtained according to Figure 7, where $\ln(\eta_{sp}/c) = f(\ln(c))$ for TDIDEDS sample at different temperature is represented. The

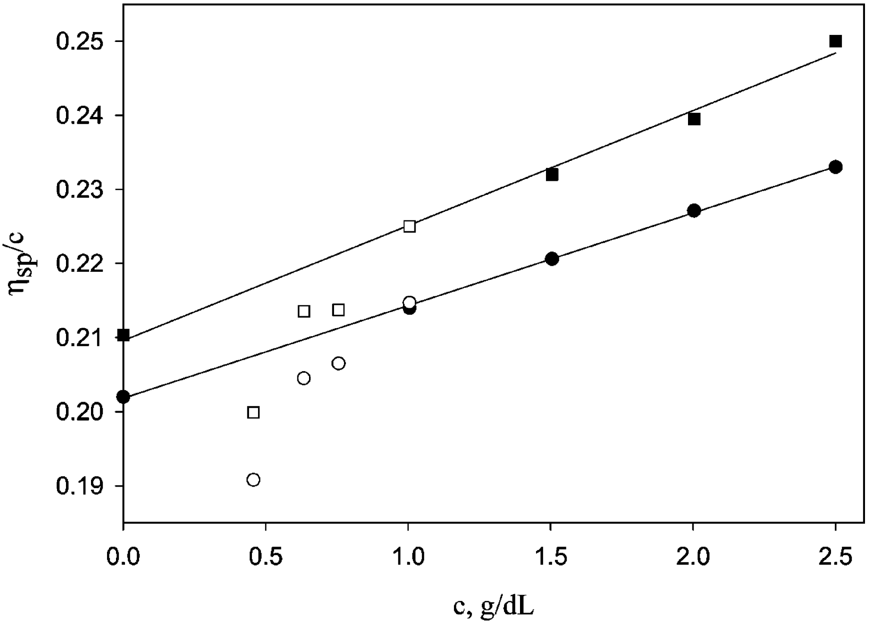

FIGURE 6 Variation of η_{sp}/c vs. concentration in the dilute and extremely dilute domains, at 25°C and 35°C for TDIDEDS sample.

values of "A" and "a" were determined from the obtained linear dependencies.

The results are presented in Figure 8, together with the variation of intrinsic viscosity. It is observed that "A" coefficient is comparable with the intrinsic viscosity and the maximum values of "A" and "a" are identical with the maximum values obtained for intrinsic viscosity.

Many papers deal with viscometric anomalies observed in very dilute solutions [36–37]. These anomalies have been attributed to adsorption phenomena [38–40], to possible conformational changes of the macromolecules [41] or to the real change in the size-shape of the polymer molecules below the critical concentration c^{**} [42]. The anomalies consist in the upward or downward change of the slope of η_{sp}/c versus c dependence below the critical concentration and are affected by the presence of the branching of the polymer chain as well as by viscometer capillary size [43]. Dondos et al. [26,34,44] showed that above c^{**} a decrease of the hydrodynamic dimensions of the polymer occurs.

Yang et al. [45] shows that these anomalies are due to the influence of the polymer adsorbed on the wall of viscometer capillary in the study of polyvinyl alcohol in NaCl/water solutions ranging from dilute

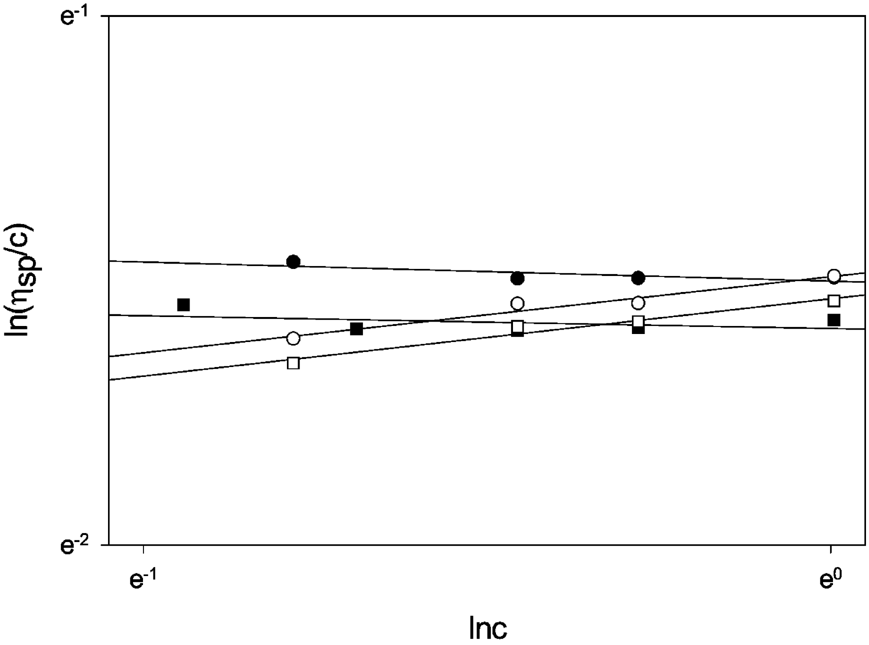

FIGURE 7 Plot of $\ln(\eta_{sp}/c)$ as a function of ln(c) for solutions of TDIDEDS sample in DMF at different temperatures, for $c < c^{**}$.

to extremely dilute concentration. In general, in order to determine the viscosity of polymer solution, a thoroughly cleaned viscometer was used first to measure the flow time of the pure solvent, namely t_0. After drying it, the flow time of the polymer solution with different concentrations, namely t, was measured. Thus, the relative viscosity of polymer solution can be determined by the t/t_0 ratio. Yang et al. consider that this procedure is incorrect because in measuring the flow time of polymer solution the viscometer capillary state is not the same as in measuring the flow time of the pure solvent. If the viscometer was thoroughly washed by the pure solvent for 3–5 times immediately after the flow time of polymer solution has been measured, the residual of polymer solution should have been washed away except for the adsorbed polymer on the walls of the viscometer capillary. Accordingly, to measure the flow time of the pure solvent, namely t_0', by now, the capillary state of the viscometer is the same as in measuring the flow time of polymer solution. As a result, the relative viscosity of polymer solution should be determined by t/t_0'. The abnormal viscosity behavior of polymer solution in extremely dilute concentrations due

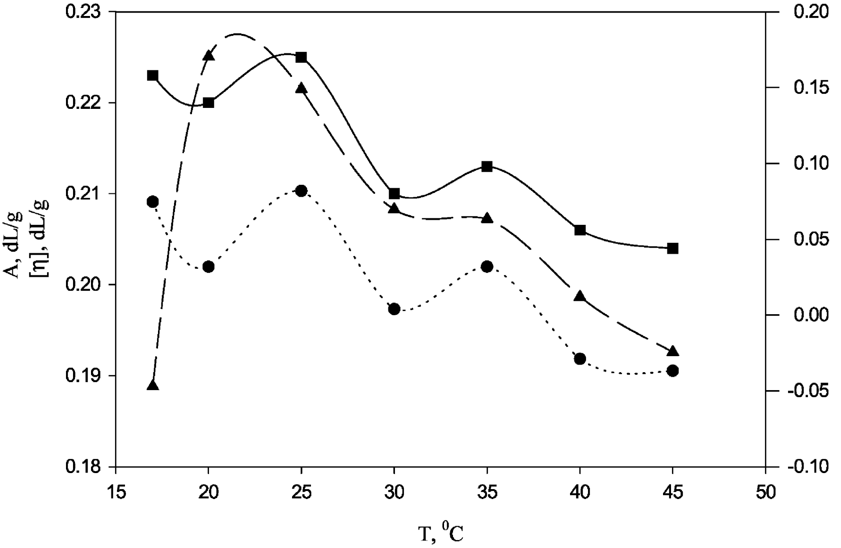

FIGURE 8 Dependences of "A" coefficients and "a" exponents from Eq. 7 and intrinsic viscosities in function of temperature for TDIDEDS samples.

to the influence of adsorbed polymer on the viscosity of polymer solution was removed by using improved viscosity measurement procedure (t/t_0') to determine the viscosity of polymer solution. Thus, Yang et al. obtained a linear relationship between η_{sp}/c vs. c in all concentrations, from the dilute to the extremely dilute domains, and discussed that the improved viscosity measurement procedure can eliminate the influence of the adsorbed polymer on the walls of the viscometer capillary. Yang et al. showed that a poor solvent will encourage the polymer to adsorb on the walls of viscometer capillary and the parameter $\Delta t = t_0' - t_0$ increases when the solvent becomes poorer.

In the present data, Figure 5 includes also the η'_{sp}/c values calculated with this correction for $c = 0.39\,g/dL$. The flow time of the pure solvent, measured after the flow time of polymer solution has been measured and the viscometer was washed, becomes longer ($t'_0 > t_0$) and thus, $\eta'_{sp}/c = ((t/t'_0) - 1)/c$ becomes smaller, but not sufficiently to obtain a linear relationship vs. c corresponding to the Huggins equation in all domains of concentration from the dilute to the extremely dilute range. Clearly, this method introduces errors because of the washing of the viscometer by the pure solvent for 3, 4, or 5 times giving different values of t'_0. The authors' studies confirm the possibility of the existence of the adsorption phenomenon, but do not exclude the appearance of some supplementary polymer-solvent interactions attributed to the polarity of copolymer chains and solvent [46] with possible conformational changes of the macromolecular chains [41] or to real changes in the size-shape of the polymer molecules below critical concentration c^{**} [43].

In this context, Wu et al. [46] observed this characteristic behavior by viscosity and low angle light scattering measurements for polystyrene-based telechelic ionomers containing ionic groups only at chain ends, when dissolved in a polar solvent. This behavior is specific to salt-free random ionomers in polar organic solvents and for salt-free polyelectrolytes in water. The authors show an important role of intermolecular electrostatic interactions and a lack of intramolecular electrostatic interactions that can be responsible for the upturn in the reduced viscosity below the critical concentration c^{**}.

Also, according to the conclusions of Dondos et al. [32,33], the viscometer capillary size, reflected in the change of the flow times of the solvent, can modify the slope of the η_{sp}/c versus c dependence in the extremely dilute concentration domain.

CONCLUSIONS

The segmented poly(ester-urethanes) 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 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 is interpreted as conformational transitions of the copolymer chain. The results reflect the influence of the soft component, PEGA, in the same solvent.

The authors observe also, that the conformational transitions are more evident in the extremely dilute domain and are insignificant in the semidilute domain.

The deviation from the Huggins dependence was discussed. Thus, the authors consider that the deviations from the Huggins law in the extremely dilute domain of concentration are due to the adsorption phenomenon on the wall of the viscometer capillary and to the possibility of the appearance of some supplementary polymer-solvent interactions attributable to the polarity of the copolymer chains and solvent. The anomalies consist in the upward or downward change of the slope of η_{sp}/c versus c dependence below the critical concentration and are affected by the temperature.

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