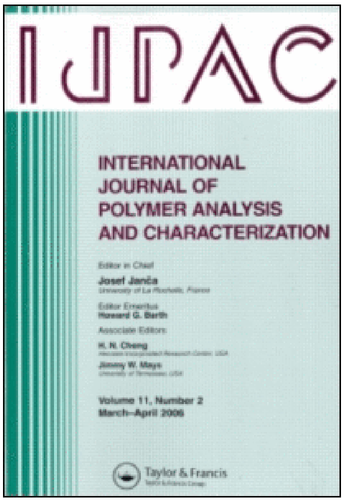

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Compositional Parameters of Segmented Poly(ester-siloxane)-Urethanes and Limitations in the Study of Dilute Solution Properties

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Compositional Parameters of Segmented Poly(ester-siloxane)-Urethanes and Limitations in the Study of Dilute Solution Properties

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This article discusses the syntheses, compositional parameters, and behavior of poly(ester-siloxane)-urethanes in dilute solution by GPC, refractometry, light scattering, and viscosity, as induced by chemical structure. From the theoretical point of view and experimental data, modified composition of the soft and hard segments yields different chain dimensions. Specific refractive index increments of these segmented copolymers in N,N-dimethylformamide and dimethylsulfoxide have been determined by the Lorenz-Lorentz equation and the corresponding group contributions to the molar refraction and to the molar volume. The results are in good agreement with the experimental values. It was observed that the light scattering studies are affected by the existence of the multicomponent systems, the compositional heterogeneity, and the possibility of structural formation of chains in solution, which cannot be destroyed by filtration.

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Keywords: Poly(ester-siloxane)-urethanes; Compositional parameters; GPC; Light scattering; Refractometry; Viscometry

The equilibrium flexibility of a polymer-chain backbone, that is, the ability of the backbone to rotate, has always been of great interest to polymer scientists. Siloxane-containing polymers present opportunities for the investigation of configurational properties that are not present in more common carbon-backbone polymers. The siloxanic elastomers present very important physical and chemical properties, previously discussed. They are considered to have high flexibility[1–4], very good resistance to temperature, oxidizing agents and ultraviolet radiation, very low glass-transition temperature and good gas permeability and biocompatibility, but they exhibit rather poor mechanical properties[5,6]. However, the polyurethanes show superior mechanical properties but reduced thermostability[7–14]. These disadvantages of siloxanic elastomers and polyurethanes can be overcome by preparing block copolymers with hard segments based on polyurethanes, polyamides and polycarbonate-polyurethanes and soft segments based on polybutadiene, polyisobutylene and polydimethylsiloxane[15–18]. Increasing interest in multiphase copolymers based on polydimethylsiloxane is mainly due to their unique combination of properties, which is related to their chemical structure and macromolecular architecture[7,8,19–21]. These compounds are a very important group of products that open a range of new applications.

Recent progress in medical technology makes it desirable to develop polymeric materials for medical purposes having a wide variety of functions[7,22]. In the case of polymers used for medical design, antithrombogeneity is one of the most important factors to be taken into account, as well as suitable mechanical properties. Segmented polyurethane and segmented poly(urethaneurea) are widely used materials for these purposes, particularly for artificial hearts, and blood vessels, where elastic properties similar to those of muscle are required, as well as antithrombogeneity[23,24].

The structural and compositional diversity of polyurethane elastomers represents a useful way to study the properties and the structure of these materials. Previous papers[25–31] presented the syntheses of new polyurethane elastomers containing very flexible chains; their structure and morphology was investigated through different methods. Also, the influence of polymer structure on the thermal stability and on their behavior in different organic solvents was analyzed. In the present article, the compositional parameters and molecular weight of segmented poly(ester-siloxane)-urethanes, as well as their properties in dilute solution, are presented.

EXPERIMENTAL

Materials

Benzyltrimethylammonium siloxane (BTMAS) was prepared according to Stockmayer et al.[32]. Octamethylcyclotetrasiloxane (D_4, Fluka) was distilled and dried over molecular sieves. 4,4′-Methylenediphenylene diisocyanate (MDI, Suprasec ICI), 2,4-tolylene diisocyanate (TDI, Riedel) and hexamethylene diisocyanate (HDI, Aldrich) were vacuum-distilled and stored at 10°C in the dark. 1,4-Butanediol (BD, Aldrich) and dibutyltin laurate (Bu_2SnL_2, Aldrich) were used as received. Poly(ethylene glycol) adipate (PEGA) was supplied by FIBREX Savinesti. α,ω-Dimethyl polydimethyl (3-hydroxypropyl) methylsiloxane (PDMS-500) was supplied by Rhone Poulenc under the trade name Rhodia Lub 500.

Polymer Synthesis

Poly(dimethylsiloxane)diol was obtained by ring opening polymerization of octamethylcyclotetrasiloxane in tetrahydrofuran solution in the presence of BTMAS and water, at 35°C for 18 h[33]. Linear polyurethane-polysiloxane elastomers were prepared by melt polyaddition using a multistep procedure[26,28,34]. Thus, in a reactor equipped with a mechanical stirrer, a nitrogen inlet tube and a vacuum line, 64.74 g of PEGA were placed and heated under stirring at 125°C and 2–3 mm Hg residual pressure for 4 h in order to remove traces of water. After that, the temperature was reduced to 80°C and 16.20 g of MDI and 0.001 g of Bu_2SnL_2 were added under nitrogen flow. In another reactor, 12.00 g of PDMS and 0.6 g of MDI were reacted in the same way. Then, the MDI/PEGA/MDI and MDI/PDMS/MDI prepolymers were mixed for about 30 min. Subsequently, 2.52 g of MDI and 3.932 g of BD were introduced in the reaction mixture. After 30 min, all the content of the reactor was poured in a mold and maintained at 80°C for 8 h to complete the reaction. Finally, $300 \times 200 \times 1$ mm plates were obtained, and thermally treated at 65°C for 6 h. Using this procedure, the samples 2, 3, 5, and 7 (Tables I and II) were obtained. Because the PDMS-500 is a monofunctional compound, it was introduced in the reaction mixture after PEGA, diisocyanate and BD were reacted (sample 4 and 6 in Tables I and II). The chemical composition of the samples is shown in Tables I and II.

Measurements

Gel permeation chromatography (GPC) in *N*,*N*-dimethylformamide (DMF) was conducted with an evaporative light scattering detector

TABLE I Chemical composition of the soft segments of polyurethane samples.

Sample	Mass	PEGA	PDMS 10000	PDMS 2000	PDMS 500
PUS1	g	77.20	–	–	–
	$mol{\cdot}10^2$	3.86			
	$mol\ OH{\cdot}10^2$	7.72			
PUS2	g	64.74	12.00	–	–
	$mol{\cdot}10^2$	3.237	0.12		
	$mol\ OH{\cdot}10^2$	6.474	0.24		
PUS3	g	65.20	–	12.00	–
	$mol{\cdot}10^2$	3.26		0.6	
	$mol\ OH{\cdot}10^2$	6.52		1.2	
PUS4	g	65.76	–	–	12.00
	$mol{\cdot}10^2$	3.288			2.4
	$mol\ OH{\cdot}10^2$	6.576			2.4
PUS5	g	70.92	12.00	–	–
	$mol{\cdot}10^2$	3.546	0.12		
	$mol\ OH{\cdot}10^2$	7.092	0.24		
PUS6	g	71.92	–	–	12.00
	$mol\ 10^2$	3.596			2.4
	$mol\ OH{\cdot}10^2$	7.192			2.4
PUS7	g	71.39	12.00	–	–
	$mol{\cdot}10^2$	3.570	0.12		
	$mol\ OH{\cdot}10^2$	7.140	0.24		

(PL EMD-950) equipped with two PL gel 5 µm MIXED-C 300 × 7.5 mm columns (Polymer Laboratories, U.K.). The system column was 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 volume of the injected polymer solutions was 20 µL. The analysis of the elution data was performed by a computer program based on the normalization of the chromatograms.

Static light scattering measurements were performed with fully computerized and modified SOFICA photogoniometers (G. Baur, Instrumentenbau, Hausen, Germany), equipped with a He-Ne laser ($\lambda_0 = 632.8$ nm). The measurements were performed at 25°C in an angular region from 35 to 145°, in steps of 5°. Two different solvents were used: DMF and dimethylsulfoxide (DMSO). The concentration in all cases was between 0.2 and 2%. Generally, light scattering experiments in such a polar solvent are very difficult to carry out because of particulates.

TABLE II Chemical composition of the hard segments of polyurethane samples.

Sample	Mass	BD	MDI	TDI	HDI
PUS1	g	3.479	19.32	–	–
	mol·10^2	3.86	7.72		
PUS2	g	3.932	19.32	–	–
	mol·10^2	4.363	7.72		
PUS3	g	3.479	19.32	–	–
	mol·10^2	3.86	7.72		
PUS4	g	2.913	19.32	–	–
	mol·10^2	3.232	7.72		
PUS5	g	3.653	–	13.445	–
	mol·10^2	4.054		7.72	
PUS6	g	2.635	–	13.445	–
	mol·10^2	2.924		7.72	
PUS7	g	3.632	–	–	12.985
	mol·10^2	4.03			7.72

For this reason, to obtain pure samples, the raw materials were filtrated several times through a G5 glass filter.

The specific refractive index increments of solutions (ν) were measured with a Zeiss interferometer and a Brice-Phoenix differential refractometer at 25°C for different concentrations of polymers. Also, ν values of these segmented copolymers in DMF and DMSO were determined by the Lorenz-Lorentz equation and the corresponding group contributions to the molar refraction and to the molar volume.

The viscometric measurements were carried out in DMF at 25°C using an Ubbelohde suspended-level viscometer. The kinetic energy corrections were found to be negligible. The flow time for the reagent-grade DMF was 150.7 s. The flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ±0.035%.

RESULTS AND DISCUSSION

Compositional Parameters of Segmented Poly(ester-siloxane)-Urethanes

A significant alternation of the flexible and hard segments in polyurethane was obtained using the multistep melt polyaddition technique. In the polymerization reactions the molar ratio of NCO/OH was approximately 1:1. Also, the same concentration of diisocianates (0.0772 mol) for all samples was used. The presence of 1,4-butanediol as a chain extender leads to segmented polyurethanes of high crystallinity and strength. The polysiloxane compounds were monofunctional (PDMS-500) or difunctional type with $M_n = 2000$ and 10000, respectively.

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

Sample 1

$-[-O-R_1-O-CO-NH-R_4-NH-CO-O-R_5-O-]_q-$

Sample 2, 3, 5, 7

$-[-O-R_1-O-CO-NH-R_4-NH-CO-O-R_5-O-]_q-CO-NH-$

$-R_4-NH-CO-[-O-R_2-O-CO-NH-R_4-NH-CO-O-R_5-O-]_r-$

Sample 4, 6

$-[-O-R_1-O-CO-NH-R_4-NH-CO-O-R_5-O-]_q-CO-NH-$

$-R_4-NH-CO-O-R_3$

where:

$R_1 = [(CH_2)_2\text{-}O\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}O]_n\text{-}(CH_2)_2\text{-}$	PEGA
$R_2 = \text{-}(CH_3)_2Si[O\text{-}(CH_3)_2Si]_m$	PDMS-2 000, PDMS-10 000
$R_3 = \text{-}(CH_2)_3\,[Si(CH_3)_2\text{-}O]_r\,\text{-}Si\,(CH_3)_3$	PDMS-500
$R_4 = \text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}$	MDI
$\text{-}C_6H_3(CH_3)\text{-}$	TDI
$\text{-}(CH_2)_6\text{-}$	HDI
$R_5 = \text{-}(CH_2)_4\text{-}$	BD

SCHEME 1

In order to discuss the behavior of segmented poly(ester-siloxane)-urethanes in dilute solution, the compositional parameters were calculated from Equations (1) to (5):

Soft segment concentration (SSC)

The 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:

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

The molecular weight of the repeating unit M_o

$$M_o = M_{\text{pol}} + M_{\text{izo}} + r(M_{\text{ce}} + M_{\text{izo}}) \tag{2}$$

where $r = N_{\text{ce}}/N_{\text{pol}}$ is the molar ratio, N_{ce} is the number of moles of the chain extender and N_{pol} is that of polyol.

The molecular weight of the hard segment (M_{nhs})

$$M_{\text{nhs}} = \text{HSC}(M_{\text{pol}} - 34)/\text{SSC} = \text{HSC} \cdot M_{\text{nss}}/\text{SSC} \tag{3}$$

where the hard-segment concentration (HSC) is

$$\text{HSC} = 100 - \text{SSC} \tag{4}$$

The molecular weight of the soft segment (M_{nss})

$$M_{\text{nss}} = M_{\text{pol}} - 34 \tag{5}$$

Table III presents the obtained results for the compositional parameters.

As can be observed from the values of the molecular weight of the repeating unit consisting of one soft segment and one hard segment M_o, the siloxane component in the soft segments increases the elastomer molecular weight in the following order: PDMS-500 < PDMS-2000 < PDMS-10000, while the diisocyanate component from hard segments determines the increase of the molecular weight of the elastomer chain in the following order: HDI < TDI < MDI.

Segmented Poly(ester-siloxane)-Urethanes in Dilute Solution

A relatively limited amount of data has been published on the solution properties of segmented polyurethanes. The study of polyurethanes in solution is important because their behavior in solution is influenced by the content of the soft and hard segments, as well as for interpretation of

TABLE III Compositional parameter of segmented poly(ester-siloxane)-urethanes.

	SSC, %								
Sample	PEGA	PDMS-10,000	PDMS-2000	PDMS-500	M_{nss}	HSC, %	M_{nhs}	r	M_o
PUS1	76.00	–	–	–	1,966	24	621	1.000	2,591
PUS2	63.64	11.96	–	–	3,232	24	1,02	1.300	3,941
PUS3	64.09	–	11.80	–	1,966	24	621	1.000	2,591
PUS4	64.64	–	–	11.59	1,740	24	550	0.720	2,264
PUS5	69.71	11.96	–	–	3,138	18	689	1.106	3,624
PUS6	70.70	–	–	11.59	1,757	18	386	0.610	2,121
PUS7	70.18	11.96	–	–	3,131	18	687	1.092	3,602

the obtained parameters. Due to the crystallinity of the hard segment, its rigidity and strong hydrogen bonding, segmented polyurethanes are soluble in a limited number of very polar solvents, such as dimethylformamide, dimethylacetamide and dimethylsulfoxide. Their solubility also depends on the nature of the soft segment. Specific properties of polyurethane solutions may arise from possible structure formation due to the association of macromolecules and due to rigid hard blocks that may form some kind of liquid crystalline-like structure. 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. The use of three monomers for the polymerization instead of two, the possibility of side reactions yielding allophonate cross-linking, for example, and the generally poor solubility in common solvents are additional complicating factors. Thus, the most common results presented in the literature are weight molecular weight data based on GPC[35].

GPC Investigation

The number-average molecular weights M_n, the weight-average-molecular weights M_w and the polidispersity M_w/M_n of the segmented poly(ester-siloxane)-urethanes determined by GPC are listed in Table IV. The narrow polydispersity index could be due to the synthesis conditions and to the thermal treatment to which these samples were subjected after preparation. Also, the values of the average molecular weight of the samples are of the same order of the molecular weights of the repeating unit M_o.

TABLE IV Number-average molecular weights and polydispersities determined by GPC measurements, intrinsic viscosities $[\eta]$ and Huggins constants of poly(ester-siloxane)-urethanes in dimethylformamide at 25°C.

Code	$M_n \cdot 10^{-4}$	M_w/M_n	$[\eta]$ (mL/g)	k_1
PUS1	6.7	1.37	45.6	0.33
PUS2	8.4	1.34	51.1	0.39
PUS3	5.6	1.49	39.4	0.42
PUS4	6.6	1.36	35.7	0.43
PUS5	11.1	1.34	54.7	0.37
PUS6	4.6	1.36	33.4	0.42
PUS7	6.2	1.27	37.0	0.39

Theoretical and Experimental Values of Specific Refractive Index Increments

Accurate values of the specific refractive index increment v of these copolymer solutions are needed to obtain the weight-average molecular weight by light scattering or for the estimation of the molecular weight distribution by size exclusion chromatography[29]. For copolymers, the specific refractive index increments of solutions depend on the refractivity and content of components. These dependences become complicated for copolymers containing three or more components largely differing in refractivity.

The theoretical values of specific refractive index increments of segmented polyurethanes were calculated with Equation (6) applied for a multiblock copolymer containing hard and soft segments[36]:

$$v = w_s \cdot v_s + w_h \cdot v_h \tag{6}$$

where v_s is the specific refractive index increment of the soft segment and v_h is the specific refractive index increment of the hard segment; w_s and w_h are the weight fraction of the soft and hard segment, respectively. The weight fraction of the hard segment is defined by the ratio of the hard-segment molecular weight to the overall molecular weight ($w_h = \frac{M_h}{M_g+M_h}$, where M_h and M_s are the molecular weights of the hard and soft segments, respectively).

As mentioned in the literature[37–39] the theoretical values of specific refractive index increments in DMF and DMSO were calculated based on the assumption that the molar volume V_u and the molar refraction R_u of the chain repeating unit are additive functions of composition (equations (7) and (8)):

$$V_u = \sum_i a_i \cdot V_i \tag{7}$$

$$R_u = \sum_i a_i \cdot R_i \tag{8}$$

where V_i and R_i are the contributions of groups, and a_i is the number of groups i in the repeating unit.

Huglin[40] presents the Lorenz-Lorentz equation relating the specific refractive index increment to the refractive index of polymer n_2 and solvent n_1:

$$v = \bar{v}[(n_2^2 - 1)/(n_2^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2)] \cdot (n_1^2 + 2)^2/6 \cdot n_1 \tag{9}$$

where the molar refraction is related to the refractive index n_2 by[43,44]:

$$R_u = V_u \cdot (n_2^2 - 1)/(n_2^2 + 2) \tag{10}$$

The precise definitions of the hard and soft segments vary in the literature; in this investigation the soft segment is defined as that portion of the polymer chain originating from the PEGA and PDMS while the hard segments are reaction products of the diisocyanate and chain-extender monomer (MDI + BD, HDI + BD, TDI + BD) (Table I).

The results of calculations for MDI units cannot be checked against the experimental data. For this reason, ν value was calculated for Equation (9) where the refractive index of polymers, n_2, was determined from Equation (10) and the refractive index of solvents was $n_1 = 1.427$ for DMF and $n_1 = 1.476$ for DMSO.

The molar refraction R_u and the molar volume V_u were calculated with Equations (7) and (8), where the increments of various substructures R_i and V_i are taken from literature[38,39,43,44] (Table V).

The partial specific volume $\bar{v}_2$ has been approximated by the specific volume v_2 of polymer in solid state. Literature shows that this approximation is justified for polyurethanes with low MDI concentrations[45] . The same procedures were utilized for determination of the specific refractive index increments for HDI, TDI, and BD.

The specific refractive index increments of hard segments MDI + BD, HDI + BD, and TDI + BD presented in Table VI were calculated considering that ν values of the mixed components are an additive function of the composition expressed in terms of weight fraction, w.

The ν values for soft segments PEGA and PEGA + PDMS were evaluated with the same method (table V). Also, specific refractive index increments of poly(ester-siloxane)-urethanes in DMSO and DMF calculated from Equation (6) with ν_s and ν_h from Table VI are presented in Table VII. From Table VII one can conclude that there is a good agreement between the experimental and theoretical values of specific refractive index increments.

TABLE V Increments of various polymer structures.

Increment	R_i (cm^3/g)	V_i (cm^3)	R_i/V_i
–O–	1.625	9.052	0.180
–CN	6.477	24.445	0.265
$-CH_2-$	4.504	15.528	0.290
$-CH_3$	5.901	25.798	0.229
C_6H_3 (arom)	24.785	53.710	0.462
p-C_6H_4 (arom)	38.119	97.054	0.393
–OH	8.290	32.491	0.255
$\rangle C{=}O$	4.590	13.170	0.349

TABLE VI Molecular weight, molar refraction, molar volume, refractive index, and specific refractive index increments in DMSO and DMF at 25°C of the soft and hard segments.

Sample	m	R*	V*	n_2	v (from eq. (4)) (cm^3/g))	
		(cm^3/g)	(cm^3)	(from eq. (5))	DMSO	DMF
MDI	250.26	96.946 90.46	276.63 248.49	1.618	0.149	0.196
HDI	168.20	43.228	160.162	1.452	−0.023	0.024
TDI	174.16	46.89	146.502	1.553	0.063	0.101
BD	90.12	34.596	127.094	1.457	−0.027	0.040
MDI + BD 79.333/20.667	–	–	–	–	0.113[a]	0.164[a]
HDI + BD 73.05/26.95	–	–	–	–	− 0.024[a]	0.028[a]
TDI + BD 73.75/26.25	–	–	–	–	−0.039[a]	0.085[a]
PEGA	172.18	39.454	137.612	1.485	0.007	0.0398
PDMS	74.15	–	–	–	0.076[b]	0.027[b]
PEGA + PDMS 84.2/15.8	–	–	–	–	0.018	0.038

* Calculated from Table IV, which presents the increments of various polymer substructures.

[a] Calculated from additive contributions of components at the refractive index increments.

[b] Calculated from the variation of the refractive index increment with the refractive index of different solvents [39].

Light Scattering Data

Figure 1 shows the Berry plots from the PUS1 in DMSO. The Berry plot differs from the more familiar Zimm plot by the fact that the root of Kc/R_θ is now plotted. The K parameter contains the refractive index increments experimentally determined (Table VII). From the intercept, the apparent weight-average molecular weight M_{ap} is obtained. From the slopes of the angular dependence, the apparent radii of gyration R_{ap} are found, and from the concentration dependence, the second virial coefficients are derived. The Berry plot has the advantage, among others, that it also takes into account the influence of the third virial coefficient. The results obtained for the samples PUS1–PUS7 are given in Table VIII.

TABLE VII Experimental (ν_{exp}) and theoretic (ν_{th}) specific refractive index increments in DMSO and DMF at 25°C of segmented polyurethanes.

	ν_{exp}		ν_{th}	
Sample	DMSO	DMF	DMSO	DMF
PUS1	0.033	0.065	0.032	0.070
PUS2	0.042	0.062	0.041	0.068
PUS3	0.040	0.062	0.041	0.068
PUS4	0.040	0.060	0.041	0.068
PUS5	0.004	0.042	0.004	0.047
PUS6	0.004	0.041	0.004	0.047
PUS7	0.008	0.033	0.008	0.036

From Figure 1 can be observed that the errors in the determination of weight-average molecular weights, radii of gyration, and second virial coefficients are quite high, due to the difficulty of extrpolation to zero angle and concentration. Thus, the characteristics of Berry plots are indicative of the presence of strong supplementary interactions.

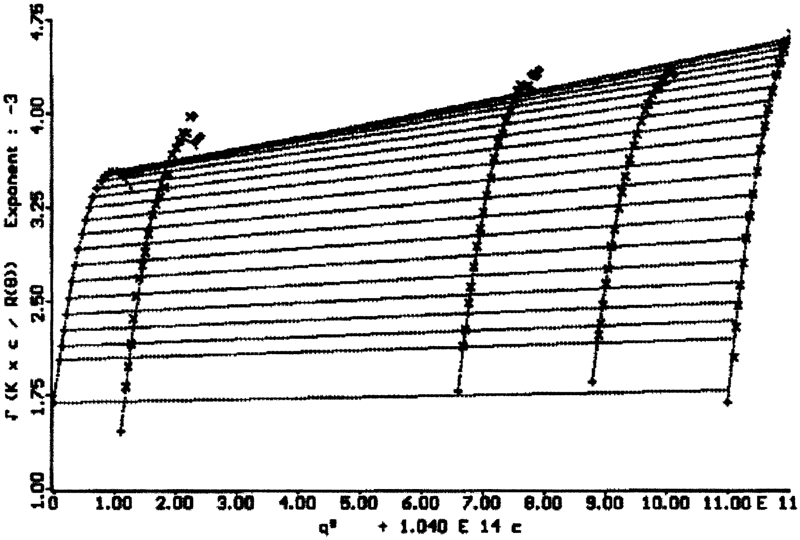

FIGURE 1 Berry plot of static light scattering intensities for PUS1 in DMSO at 25°C: $M_{ap} = 350,000$, $R_{ap} = 115\,\text{nm}$, $A_2 = 0.166 \cdot 10^{-4}\,\text{mol mL/g}^2$.

TABLE VIII Light scattering data for poly(ester-siloxane)-urethanes in DMF and DMSO at 25°C.

Sample/solvent	M_{ap}	R_{ap}, nm	$A_2 \cdot 10^4$, mL·mol/g^2
PUS1/DMSO	350,000	115	0.166
PUS1/DMF	445,000	112	4.210
PUS2/DMSO	420,000	121	0.121
PUS3/DMSO	334,000	119	0.159
PUS4/DMSO	292,000	99	0.129
PUS5/DMSO	447,000	127	0.115
PUS7/DMSO	317,000	110	0.104

In the literature, the absolute weight-average molecular weights and absolute radius of gyration for binary copolymers were determined from apparent molecular weights and apparent radii of gyration in different solvents, respectively. If the copolymers are heterogeneous by composition then the molecular weight will depend on the refractive index of the

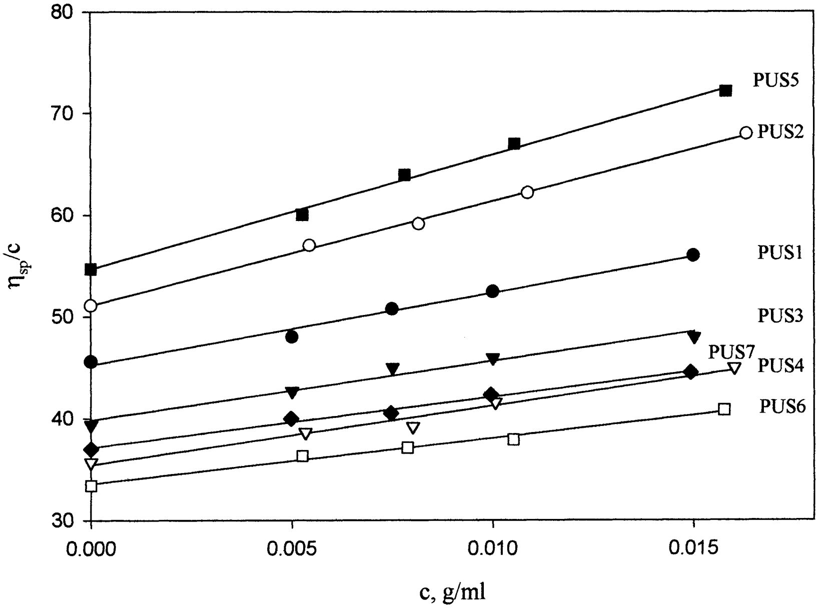

FIGURE 2 Reduced viscosity vs. concentration for poly(ester-siloxane)-urethanes in DMF at 25°C.

solvent. For multicomponent copolymers, the determination of the structural parameters by the light scattering method is more difficult.

For the studied samples, the GPC investigation reveals a narrow polydispersity index. If we consider that the studied copolymers have two components—soft and hard segments—the differences between the weight-average molecular weights determined in DMF and DMSO show that the samples possess very high compositional heterogeneity. However, the poly(ester-siloxane)-urethanes are multicomponent copolymers and the larges differences from light scattering and GPC data are caused by compositional heterogeneity and the influences of the components, so that possible structure formations are due to the association of macromolecules in the polar solvent and some kind of liquid crystalline-like structure. As evidenced from Figure 1, these structural formations cannot be avoided by filtration.

The values of apparent radii of gyration R_{ap}, even when they are quite high, show that the presence of the PDMS-10,000 in the soft segment results in higher chain dimensions, followed by the PDMS-2000 and PDMS-500. Also, the diisocyanate component from the hard segments increases the dimensions of the elastomer chain in the order HDI < TDI < MDI. These results are in agreement with the molecular weight of the repeating unit M_o, calculated from the studied samples (Table III).

The values of the second virial coefficients for sample PUS1 in DMSO are lower than those in DMF.

These investigations of poly(ester-siloxane)-urethanes in dilute solution show that the absolute values of the weight-average molecular weights, radii of gyration, and second virial coefficients are difficult to obtain in general. The reasons for this difficulty, in addition to compositional heterogeneity, is that copolymers in solution exhibit poor solubility in common solvents; association of macromolecules and rigid hard blocks may form some kind of liquid crystalline-like structures.

Viscosity

The intrinsic viscosity $[\eta]$ and the slope constant k_1 were calculated by means of the Huggins equation. The results are given in Figure 2 and Table IV.

In all cases the Huggins constants k_1 are relatively high, indicating the existence of hydrodynamic interactions. Thus, the differences between weight-average molecular weight determined by light scattering and GPC methods are due to the compositional heterogeneity and possibly liquid crystalline-like structure.

Also, the intrinsic viscosities values of different samples lead approximately to the same conclusions as those obtained from the modification of the dimensions determined by light scattering, namely, the siloxane component in soft segments increases the elastomer chain length in the following order: PDMS-500 < PDMS-2000 < PDMS-10000, while the diisocyanate component from hard segments increases the dimensions of the elastomer chain in the order HDI < TDI < MDI.

CONCLUSIONS

The present article is concerned with the syntheses and evaluation of poly(ester-siloxane)-urethanes properties in dilute solution by GPC, refractometry, light scattering, and viscosity in DMF and DMSO at 25°C. From the light scattering determinations, viscosity data, and the molecular weight of the repeating unit M_o the siloxane component from the soft segments causes dimensions of the elastomer chain to increase in the order of PDMS-500 < PDMS-2000 < PDMS-10000 and the diisocyanate component from the hard segments causes an increase of the dimensions of the elastomer chain in the order of HDI < TDI < MDI. However, the light scattering studies are affected by errors introduced by the presence of multicomponent systems, the compositional heterogeneity, and the possibility of associated macromolecular structures in solution.

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