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Influence of the Solvent Quality on the Thermodynamic Behavior of Polymethylphenylsiloxane Solutions

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In this work we investigate the effect of the solvent quality on the thermodynamic behavior of the polydimethyldiphenylsiloxane copolymer by using turbidimetry and viscosimetry. The turbidimetric method was used for the determination of the composition of the solvent mixture at the theta point. The experimental data obtained by using the capillary viscometry both in good and theta solvent conditions have been processed by using classical Huggins equation and new Wolf model (2007), which allows the calculation of intrinsic viscosities and other hydrodynamic parameters. The results obtained by using the two approaches were discussed comparatively. The conformational properties of copolymer in solution depend on their molecular structure, which is essentially dominated by the solvent quality, reflecting the balance of the interactions between the polymer chains and each solvent and that between solvent molecules.

1. Introduction

Solvent quality can have a great impact on the behavior of the macromolecular chains in solution as a function of the polymer nature. Depending on the interaction between the polymer and solvent molecules, the polymer may fully dissolve or solution can split into a polymer-rich phase and a polymer-depleted phase. In a “good solvent”, polymer coils swell and adopt an expanded conformation, whereas in a “poor solvent” the polymer chain collapses, producing a globular compact conformation. The conformational transition phenomenon directly alters the solution behavior and also strongly affects the efficiency of polymer additives in their practical application such as polymeric drag reducer, polymeric flocculent, and so forth.^{1–4} For this reason the selection of appropriate solvents for a given polymer can pose a challenge and various approaches have been proposed to estimate the solvent power or polymer solubility, that is, solubility parameter. With addition of a second solvent to a polymer solution, the conformation of the polymer coil can be strongly affected because of the new interactions established in the ternary system, in accordance with the mixed solvent composition.⁵

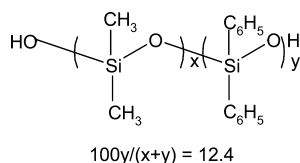
Compared with the polymer/solvent interactions in the binary solutions, the interactions undoubtedly become more complicated in the ternary solutions. Owing to the complex effects induced by the nature of conformation transition and coil dimension change, different conclusions were reported in the literature. For example, the composition of mixed solvent plays a significant role in changing the degree of the affinity between polymer and solvent mixture. One characteristic feature of a polymer/mixed solvents ternary system is the phenomenon of the cosolvency.^{6–10} A cosolvent system represents a mixture of two liquids, which are poor solvents or nonsolvents for the polymer, where the expansion of the coil may take place in spite of the negative excluded volume of the polymer in the individual components.¹¹ Another characteristic feature of a ternary system is the preferential adsorption of one of the liquids in the mixed solvents by the polymer, and this is not always the good solvent.^{6–12} This can occur in some particular mixtures, called “synergistic solvents”, where the addition of a precipitant causes an increase of the dissolving power of the mixture.

Synergism as a phenomenon is associated with the signoidal form of the preferential adsorption, when an inversion of the preferential adsorption as a function of the solvent mixture is observed, and for a certain range of solvent composition, the solvent, less adequate from a thermodynamic point of view, is preferentially adsorbed.^{6,7} Prolongo et al.¹¹ suggested that the action of mixed solvent partly changes the chain dimensions because of the interaction between the liquids. Wunderlich¹³ also found that the hydrodynamic volume of the polymer depended on the enthalpy of mixing of the two solvent components. Dondos et al.^{14,15} attributed the increase of the intrinsic viscosity in mixed solvents to the existence of unfavorable interactions between the two liquids. In the opinion of Pingping et al.,⁸ the change in the dimensions of the polymer chain in a solvent mixture might be ultimately interpreted in terms of the molecular characteristics of the system.

Flexible polymers have attracted the interest of many investigators which intend to explain the various phenomena occurring when polymer molecules are dissolved in solvents of different qualities and their mixtures. Polydimethylsiloxane (PDMS) is one of the most thoroughly flexible polymers studied, there being a relative abundance of data for various PDMS/solvent systems.¹⁶ With introduction of diphenylsiloxane units into PDMS backbone, an important derivative of PDMS, namely, dimethylsiloxane-*co*-diphenylsiloxane (PDM DPS), can be obtained. Phenyl groups attached to the silicon atoms from the polysiloxane backbone lead to a decrease of flexibility¹⁷ but to an improvement of certain properties such as resistance to heat, oxidation, solvents, and/or radiation, adhesivity to certain substrates, lubricity, compressibility, shear resistance, increase of glass transition temperature and viscosity, and so forth.^{18–20} The presence of the diphenylsiloxane units also determines the improvement of the optical properties of the silicones. As the content in diphenylsiloxane units rise, the refractive index increases. Silicone polymers containing diphenylsiloxane groups and a refractive index of 1.43–1.46 are useful in bio-optic applications in obtaining a thin lens (e.g., intraocular lenses). The diphenylsiloxane units have a marked anisotropy of polarizability increasing the optical sensitivity of siloxane polymers.^{21,22}

Motivated by the fundamental and practical considerations outlined above, in this work we investigate the effect of the

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Scheme 1. Simplified Representation of Polydimethyldiphenylsiloxane Chemical Structure

solvent quality on the thermodynamic behavior of the polydimethyldiphenylsiloxane copolymer by using turbidimetry and viscosimetry.

2. Material and Methods

2.1. Materials. 2.1.1. Synthesis of the PDMDPS Copolymer. PDMDPS was prepared by bulk anionic ring-opening copolymerization of octamethylcyclotetrasiloxane (D_4) and octaphenylcyclotetrasiloxane (Ph_4), using tetramethylammonium hydroxide (TMAH) as a catalyst and a Lewis base, dimethylformamide (DMF), as promoter. The basic catalysts are preferred to open octaphenyltetrasiloxane cycle. The transient TMAH catalyst was chosen in this paper because, at the reaction end, it can be easily removed by thermal decomposition when volatile compounds (trimethylamine and methanol) are formed. DMF was added to increase the reaction rate by counterion complexation and hindrance of the ion pair's formation.²³

TMAH (0.1 mL) as 25 wt% aqueous solution was introduced into a three-necked flask and water was completely removed by azeotropic distillation with benzene. Then a drop of dried DMF, 19.3 g of D_4 , and 5.7 g of Ph_4 were loaded into a reactor under a nitrogen atmosphere. The mixture was stirred mechanically for 1.5 h at 80 °C. Then TMAH was deactivated by temperature rising at 150 °C for 1 h, and the volatile compounds (catalyst decomposition products and low molecular weight siloxanes) were removed by vacuum distillation at 150 °C/10 mmHg.

The composition of the resulted copolymer (Scheme 1) was estimated based on the 1H NMR spectrum recorded on a Bruker AVANCE DRX 400 spectrometer, using $CDCl_3$ as a solvent. The peaks corresponding to the protons in the methyl (0.15 ppm) and phenyl (7.0–7.6 ppm) groups, respectively, were taken into account for this. A diphenylsiloxane units content of 12.4% was found in the copolymer.²³

2.1.2. Molecular Weight and Polydispersity. The number average molecular weight and the polydispersity index of this copolymer is $14.41 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ and 2.2, respectively. These values were determined by gel permeation chromatography by using a GPC PL-EMD 950 evaporative mass detector instrument. The system columns were thermostated at 25 °C. The PDMDPS sample was eluted with chloroform. The flow rate was $0.7 \text{ mL} \cdot \text{min}^{-1}$. A computer program based on the normalization of chromatograms performed the analysis of the elution data.

2.2. Methods. 2.2.1. Turbidity Measurements. The turbidimetric method was used for the determination of the composition of the solvent mixture at the θ point. The polymer solutions in toluene having different concentrations ($0.3 < c < 0.8 \text{ g} \cdot \text{dL}^{-1}$) were titrated at 25 °C with methanol until the first cloud point appears. The volume fraction of methanol at the cloud point was plotted as a function of logarithm of polymer concentration at the cloud point and extrapolated to pure polymer (100% polymer). The volume fraction of methanol obtained by extrapolation corresponds to the θ composition. The turbidity and transmittance of PDMDPS in toluene and toluene/methanol

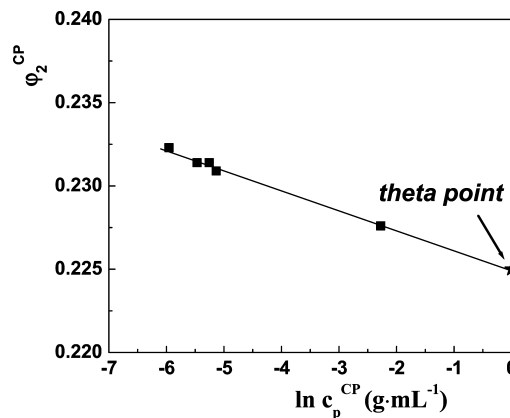


Figure 1. Turbidimetric titration of PDMDPS solutions in toluene of different concentrations with methanol.

mixtures were monitored in the range of 400–600 nm wavelengths by using a HACH 2100AN turbidimeter.

2.2.2. Viscosity Measurements. Viscosity measurements were carried out in toluene and toluene/methanol mixtures for different volume fractions of methanol, ϕ_2 (0, 0.10, 0.15, and 0.20, respectively), at 25 °C (± 0.01 °C), using an Ubbelohde suspended-level viscometer with 0.47 mm capillary diameter. All measurements were performed within 1 day after the samples were brought into solution. The kinetic energy corrections were found negligible. The flow volume of the used viscometer exceeded 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ± 0.01 s.

3. Results and Discussion

3.1. θ Point Determination. The dependence of the solvent mixture composition and the polymer concentration at the first cloud point can be shown by the following equation:^{24,25}

$$\phi_2^{CP} = \phi_2^\theta - B_\theta \ln c_p^{CP} \quad (1)$$

where ϕ_2^{CP} and c_p^{CP} represent the solvent mixture composition and the polymer concentration, respectively, at the first cloud point.

The θ point was determined at 25 °C by the titration with methanol of five copolymer/toluene solutions having the initial concentration in a dilute regime until the first cloud point was observed. The θ composition of the toluene/methanol mixture was established at $\phi_2^\theta = 0.225$ from the dependence of ϕ_2^{CP} as a function of $\ln c_p^{CP}$ by extrapolation to pure polymer ($\ln c_p^{CP} = 0$) (Figure 1).

In Figure 2 is illustrated the turbidimetric curve for a polymer solution in toluene ($0.337 \text{ g} \cdot \text{dL}^{-1}$) in terms of NTU (Nephelometric Turbidity Unit) versus volume fraction of methanol. One can observe that the turbidity of the system abruptly increases above θ point due to the decrease of the interactions between polymer and solvent, the polymer/polymer interactions being favored.

It was also observed that the transmittance decreases faster at a volume fraction of methanol above 0.225 (Figure 3).

3.2. Interactions between the Solvents. The conformation of polymer chains in the presence of two solvents of different qualities is changed as compared to those adopted in each polymer/solvent binary system and the solvent power depends on the mixture composition.

Usually, the mixing process of two liquids is nonideal and the influence of the nonideality and the interactions between

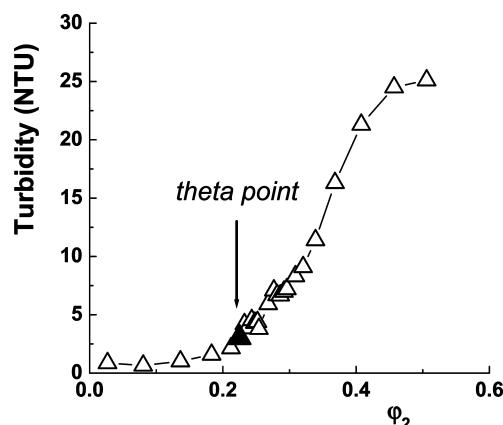


Figure 2. Variation of turbidity of PDMDPS solution as a function of volume fraction of methanol.

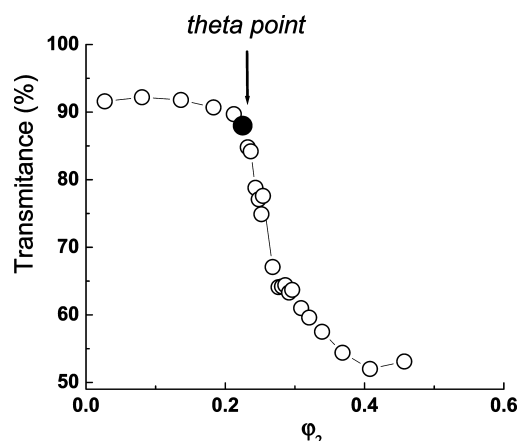


Figure 3. Variation of transmittance as a function of volume fraction of methanol.

the two liquids on the power of mixture and the dimensions of polymer chain should be taken into account in one way or another.

For a better understanding of the relationship between the conformation of copolymer chains and the molecular characteristics of solvents, the dependence of the viscosity of toluene/methanol mixtures as a function of the volume fraction of methanol is analyzed. To discuss the interactions between two liquids, Grunberg and Nissan²⁶ proposed a parameter d , calculated from the following equation,

$$\log \eta_0 = x_1 \log \eta_1 + x_2 \log \eta_2 + x_1 x_2 d \quad (2)$$

where η_0 is the viscosity of the toluene-methanol mixture, x_1 and η_1 are the mole fraction and viscosity of toluene, and x_2 and η_2 are the mole fraction and viscosity of methanol, respectively.

In Figure 4 is shown the variation of the parameter d as a function of the volume fraction of methanol for the toluene/methanol mixture.

The values of the parameter d are negative in the studied composition range ($\varphi_2 < 0.225$), indicating that no specific interactions exist between the liquid components. Thus, in the whole range of the studied composition, the thermodynamic parameters will be discussed considering only the polymer/solvent/solvent ternary interactions or polymer/polymer, polymer/solvent binary interactions. Above $\varphi_2 = 0.225$, some interactions between toluene and methanol molecules appear because of the changes in free volume in the mixture of electron donor/acceptor

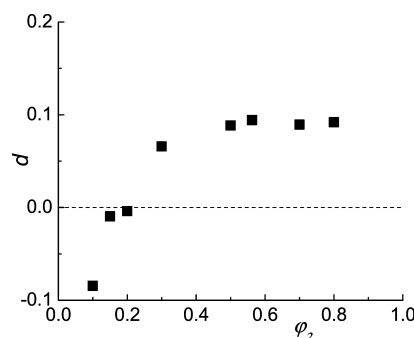


Figure 4. Variation of the parameter d as a function of volume fraction of methanol.

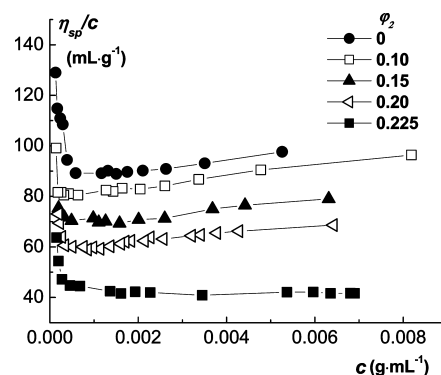


Figure 5. Plot of reduced viscosity, η_{sp}/c , as a function of concentration, c , for PDMDPS in toluene and toluene/methanol mixture at 25 °C.

type interactions between methanol and toluene (toluene being a π -electron donor).²⁷

3.3. Viscosity of the Copolymer Solutions in the Toluene/Methanol Mixture. The intrinsic viscosities, $[\eta]_H$, and Huggins constant, k_H , can be determined by using the classic Huggins equation,

$$\eta_{sp}/c = [\eta]_H + k_H [\eta]_H^2 c \quad (3)$$

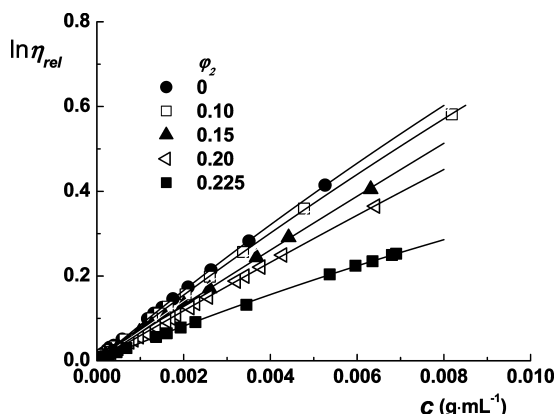
where η_{sp}/c is reduced viscosity and k_H is the Huggins constant, which offers information about the dimension and shape of polymer segments, as well as hydrodynamic interactions between different segments of the same polymer chain.

Figure 5 presents the plots of the reduced viscosity as a function of concentration for PDMDPS in toluene and toluene/methanol mixture for different volume fractions of methanol, φ_2 . The critical concentration, c' , which separates the dilute and extremely dilute regimes, for the studied systems were determined by Hernandez-Fuentes method.²⁸ According to this method, c' is determined from the representation of $[\eta]$ obtained by the successive introduction of a concentration in the Huggins plot, starting initially from the values obtained in the first three most diluted concentrations, as a function of the last concentration introduced. From this representation, c' is determined by finding the crosspoint at which the fitted $[\eta]$ value suffers a change in trend. The c' values decrease by increasing the methanol content in the solvent mixture (Table 1). At the critical concentration c' , the polymer chains first come into contact. An expansion of the macromolecular coil occurs below this concentration and the crossover point c' moves to lower concentrations as the methanol content increases.

The values of $[\eta]_H$ and k_H obtained in the dilute regime (for $c > c'$) are given in Table 1. It can be observed that $[\eta]_H$ values decrease with decreasing the solvent quality (with increasing

Table 1. Intrinsic Viscosity Values ($[\eta]_H, [\eta]_w$), Huggins Constants (k_H), and Viscometric Interaction Parameter, B , of PDMDPS in Toluene and Toluene/Methanol Mixtures for Different Volume Fractions of Methanol, φ_2 , at 25 °C

φ_2	$[\eta]_H$, eq 3 (mL·g ⁻¹)	k_H , eq 3	$[\eta]_w$, eq 4 (mL·g ⁻¹)	B , eq 4	k_H , eq 4	$c' \times 10^3$ (g·mL ⁻¹)
0	85.34	0.3140	85.79	0.2026	0.2974	0.505
0.10	79.51	0.3298	79.73	0.1835	0.3165	0.479
0.15	66.43	0.4777	67.97	0.1330	0.3670	0.399
0.20	59.84	0.3943	59.81	0.1260	0.3740	0.353
0.225	41.77	-0.00229	42.44	0.5558	-0.05581	0.281

**Figure 6.** Plot of $\ln(\eta_{rel})$ versus c for PDMDPS solutions in toluene and toluene/methanol mixtures at 25 °C. The lines correspond to the best fitting of the experimental data.

the φ_2 values), whereas the k_H values are slowly modified by changing the methanol content in the mixture. Also, in the region of low polymer concentrations, the reduced viscosity deviates upward from linearity. Such positive deviations from the linear behavior in the dependencies η_{sp}/c versus concentration c in the region of very low concentrations were previously reported for many polymer solutions,^{16,29,30} making more difficult the extrapolation of the experimental data to zero concentration.

To obtain some reliable data on the intrinsic viscosity, a new alternative equation was developed very recently for polyelectrolytes:³¹

$$\eta_{rel} = \frac{c[\eta]_w + Bc^2[\eta]_w[\eta]^*}{1 + Bc[\eta]_w} \quad (4)$$

where B represents a system specific constant $B = 0.5 - k_H$, which holds true for the range of pair interactions between the solute molecules,^{32–34} and $[\eta]^*$ is the characteristic specific hydrodynamic volume.

Equation 4 was successfully verified for different polyelectrolyte solutions^{32–35} as well as for neutral polymers.^{16,30} For uncharged polymers we found that $[\eta]^*$ is zero, as theoretically predicted.³² We apply this equation to PDMDPS in toluene and toluene/methanol mixtures (Figure 6).

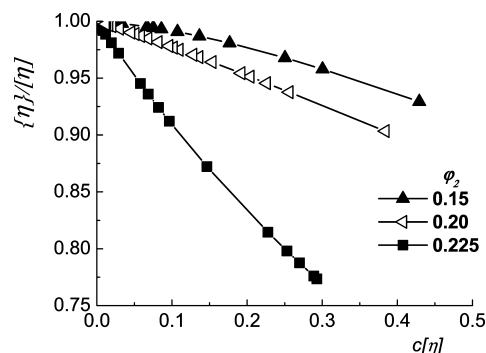
The $[\eta]_w$ values determined from the initial slope obtained by fitting the experimental dependencies of $\ln \eta_{rel}$ versus c are given in Table 1. For all systems $[\eta]^* = 0$.

The values of the intrinsic viscosity determined by applying eq 3 to the experimental data for $c > c'$ are close to those determined from the initial slope (eq 4).

Wolf and co-workers³⁴ compared the hydrodynamic interaction parameters k_H (from eq 3) with the B values resulting from eq 4 and obtained the following correlation,

$$k_H = \frac{1}{2} - B \quad (5)$$

which holds true only for the range of pair interactions between the macromolecular chain. For $B = 0$, which means no curvature

**Figure 7.** Reduced specific hydrodynamic volume ($\{\eta\}/[\eta]$) as a function of the reduced copolymer concentration ($c[\eta]$) for PDMDPS solutions near the θ point, for different volume fractions of methanol, φ_2 .

in the plot of $\ln \eta_{rel}$ versus c , one obtains $k_H = 0.5$ (weak polymer/solvent interactions). B is positive for almost uncharged polymers when the relative increase in viscosity slows down as the polymer concentration rises,³⁴ typical for thermodynamically good solvents.

A comparison of the k_H values resulting from the linear part of the Huggins dependencies (Figure 5) with those calculated from B values (eq 4) shows reasonable agreement.

Equation 4 also provides easy access to the specific hydrodynamic volume $\{\eta\}$ at a given polymer concentration, c : $\{\eta\} = (\partial \ln \eta / \partial c)_{T,p,\dot{\gamma}}$. The intrinsic viscosity represents the specific hydrodynamic volume of isolated polymer coils:

$$\lim_{\substack{c \rightarrow 0 \\ \dot{\gamma} \rightarrow 0}} \{\eta\} = [\eta]$$

The ratio $\{\eta\}/[\eta]$ provides information on the changes in the hydrodynamic volume of individual macromolecules induced by the presence of other polymers.³² By considering $[\eta]^* = 0$, this ratio can be calculated from the following equation:

$$\frac{\{\eta\}}{[\eta]} = \frac{1}{1 + 2B(c[\eta]) + B^2(c[\eta])^2} \quad (6)$$

where $c[\eta]$ is a dimensionless reduced concentration.

Figure 7 shows curves calculated by means of eq 6 and the parameters of Table 1 for the PDMDPS in toluene and toluene/methanol mixtures near the θ point. All curves commence from $\{\eta\}/[\eta] = 1$ at $c[\eta] = 0$ when the specific hydrodynamic volume $\{\eta\}$ becomes equal to $[\eta]$. The decrease of the $\{\eta\}/[\eta]$ ratio with increasing $c[\eta]$ is smaller for the uncharged polymer (our systems) as compared with polyelectrolytes.^{32–35} The slope of the curves reflects the thermodynamic quality of the solvent; that is, a higher slope corresponds to a better solvent. For the best solvent (toluene), the macromolecular coils at infinite dilution present a higher extension as compared with their unperturbed dimensions. As the thermodynamic quality of the solvent becomes worse, $\{\eta\}$ decreases to a greater degree with increasing polymer concentration. For uncharged polymers, the reduction of the solvent quality leads to higher k_H values and linear dependencies as in Figure 7.

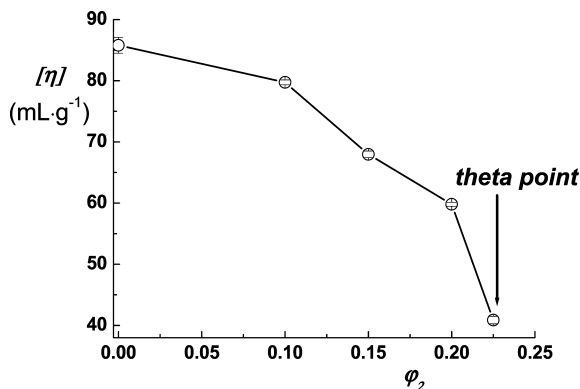


Figure 8. Plot of $[\eta]$ against binary mixture composition, ϕ_2 , for PDMDPS solutions at 25 °C.

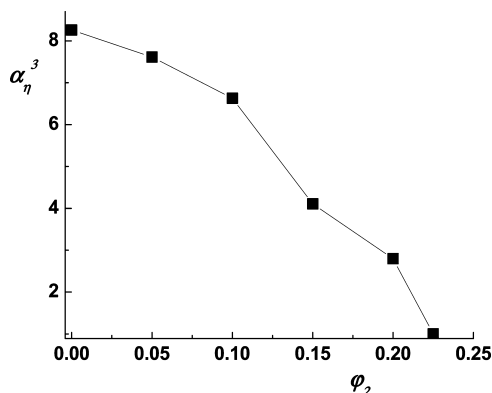


Figure 9. Influence of the volume fraction of methanol on the viscometric expansion factor for PDMDPS solutions at 25 °C.

3.4. Conformational Properties of PDMDPS in Toluene/Methanol Mixture. It is well-known that $[\eta]$ is a measure of the conformational chain of polymer in the limit of infinite dilution and in the absence of shear, which is influenced by the nature of the polymer, the quality of the solvent, and any changes in temperature. On the basis of the results shown in Table 1, Figure 8 shows the influence of the solvent quality of the intrinsic viscosity of PDMDPS solutions. The viscosity decreases approximately two times at the θ point as compared with the good solvent conditions (toluene solution).

A better image can be obtained from a dimensionless parameter, that is, the viscometric expansion factor, α_η^3 (Figure 9),

$$\alpha_\eta^3 = \frac{[\eta]}{[\eta]_\theta} \quad (7)$$

where the subscript “ θ ” refers to the unperturbed chain.

From the viscosity–molecular weight relationship in θ condition,

$$[\eta]_\theta = K_\theta M^{0.5} \quad (8)$$

the unperturbed parameter, K_θ , was determined as being $1.108 \times 10^{-3} \text{ dL} \cdot \text{mol}^{1/2} \cdot \text{g}^{3/2}$. The unperturbed dimensions can be estimated from the relation,

$$K_\theta = 6^{3/2} \phi_0 (S_\theta^2/M)^{3/2} \quad (9)$$

where ϕ_0 is Flory’s constant, $\phi_0 = 2.51 \times 10^{21}$ (for $[\eta]$ expressed in $\text{dL} \cdot \text{g}^{-1}$).

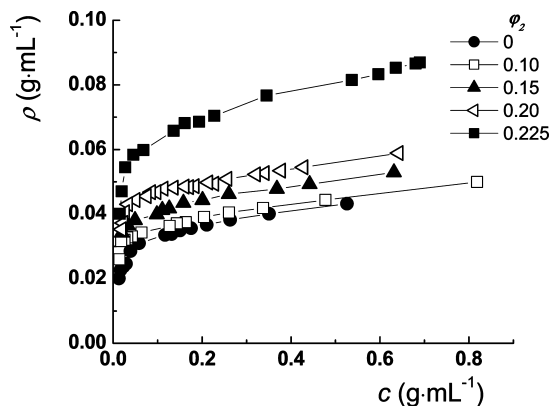


Figure 10. Variation of coil density with concentration for PDMDPS in toluene and toluene/methanol mixture at 25 °C.

Thus, for PDMDPS one obtains $S_\theta^2/M = 2.57 \times 10^{-18} \text{ cm}^2$, which shows that the introduction of the diphenylsiloxane sequences into a polydimethylsiloxane (PDMS) chain determines the stiffness of the chain (for PDMS it was found that $5.4 \times 10^{-18} \text{ cm}^2 < S_\theta^2/M < 8.66 \times 10^{-18} \text{ cm}^2$).¹⁶

The nature of interaction between liquids governs the solubility of a polymer in binary liquid mixtures. The changes in molecular dimension of the polymer in these systems are manifested in the varied molecular extension parameters and the unperturbed dimension due to the interaction with two component liquid mixtures.¹⁵ The influence of solvent mixtures on the conformational properties of PDMDPS in dilute solutions can be discussed by using the Qian and Rudin method.^{36–38} According to this method, the coil density of the polymer chains in solution, ρ , can be determined from the viscosity data, as follows:

$$\rho = \frac{c}{\eta_{sp}} (1.25 + 0.5 \sqrt{56.4 \eta_{sp} + 6.25}) \quad (10)$$

Figure 10 shows the variation of the coil density as a function of concentration for PDMDPS in toluene and toluene/methanol mixture at 25 °C. The polymer coil density increases by increasing the polymer concentration and the nonsolvent volume fraction due to the increase of the polymer/polymer interactions. The increase of the polymer density is more significant at low polymer concentrations because of the changes in conformation of polymer coils by adding a small quantity of nonsolvent.

Modification of coil density is reflected in the variation of the hydrodynamic volume that can be calculated with the following relationship:

$$V_H = \frac{M}{\rho N_A} \quad (11)$$

The hydrodynamic volume decreases by increasing the polymer concentration because of the changes in conformation of polymer chain (Figure 11).

The conformational properties of copolymers in solution depend on its molecular structure,^{16,39} which is essentially dominated in our case by the content of Ph_2SiO units and their distribution along the polymer chain and the solvent quality. The deterioration of the solvent quality produced a decrease of the hydrodynamic volume, which can be attributed to the repulsive interactions between PDMDPS and methanol producing a contraction of the macromolecular coil.

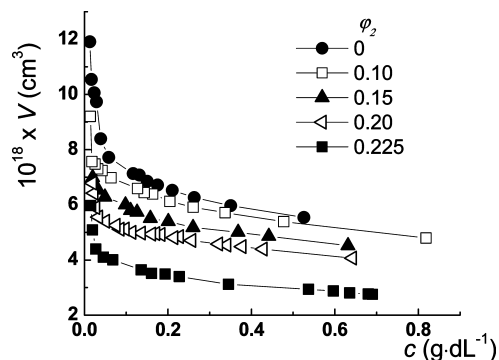


Figure 11. Variation of hydrodynamic volume with coil density at different concentrations of PDMDPS in toluene and toluene/methanol mixture at 25 °C.

4. Conclusion

The thermodynamic properties of a polydimethyldiphenylsiloxane copolymer containing 12.4% diphenyl units in toluene and different toluene/methanol mixtures were investigated to establish the effect of the solvent quality on the conformational changes of the macromolecular coil.

Turbidimetric titrations were performed at 25 °C to establish the θ point for PDMDPS in a solvent mixture. From the dependence of the volume fraction of methanol (φ_2) as a function of logarithm of polymer concentration corresponding to the cloud point, the θ composition of the solvent mixture was established at $\varphi_2 = 0.225$ (the extrapolation of the experimental curve to pure polymer). The turbidity and the transmittance curves undergo a sharp discontinuity below θ point because of the alterations of the interactions between polymer and solvent, the polymer/polymer interactions being favored.

The intrinsic viscosities and Huggins constant were determined by using the classic Huggins equation and the data were compared with those obtained by applying a new method proposed by Wolf.³¹ The values of the intrinsic viscosity determined by both methods are closed, but the new Wolf method provides more accurately the intrinsic viscosity values by modeling the viscometric data in the region of very low concentrations. The hydrodynamic interaction parameter (which gives the indications concerning the polymer/polymer interactions) and the reduced specific hydrodynamic volume (which provides information on the changes in the hydrodynamic volume of individual macromolecules) were also determined and discussed. The macromolecular coils at infinite dilution present a higher extension in toluene as compared with their unperturbed dimensions achieved for the volume fraction of methanol of 0.225. The enhancement of the polymer/polymer interactions by increasing the polymer concentration and the methanol volume fraction induces the increase of the polymer coil density.

Acknowledgment

The authors are grateful to Prof. Bernhard A. Wolf from Johannes Gutenberg Universität Mainz for the useful discussions and comments. This work was supported by CNCS-UEFISCU project PNII-IDEI, contract no. 516/2009, code ID-980 (additional contract no. 1/2010).

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Received for review July 16, 2010

Revised manuscript received September 29, 2010

Accepted October 12, 2010

IE1015238