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The Behavior of Poly(dimethylsiloxane-*co*-diphenylsiloxane)s in Good and Theta Solvents

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ABSTRACT: In this work, we investigated the behavior of poly(dimethylsiloxane-*co*-diphenylsiloxane)s under good and theta solvent conditions by using turbidimetry and viscosimetry. The evolution of the optical properties as a function of the solvent quality allowed the composition of the methylbenzene/methanol mixtures at the theta point to be determined. The intrinsic viscosity was determined in good (methylbenzene) and theta (methylbenzene/methanol) solvents at $T = 298$ K using different approaches. The unperturbed dimension parameters were calculated and are discussed as a function of copolymer composition. The introduction of the diphenylsiloxane units into a poly(dimethylsiloxane) chain results in an increase in the unperturbed dimensions as a consequence of the decrease in chain flexibility.

1. INTRODUCTION

Flexible polymers have attracted the interest of many investigators, whose intention has been to explain the various phenomena occurring when polymer molecules are dissolved in solvents of different qualities and their mixtures.[1] Poly(dimethylsiloxane) (PDMS), which consists of alternating Si and O atoms with two methyl groups attached to each Si atom, is the most representative for silicones and exhibits a variety of property combinations: highly flexible backbone, small dielectric constant, stability toward atomic oxygen, high permeability for different gases, hydrophobic and antiadhesive behavior, chemical and physiological inertness, etc. This polymer shows some peculiar features in chain construction[2] because its chain, $[-Si(CH_3)_2-O-]_x$, has a long Si−O bond length, a small van der Waals radius of the O atom, and a large angle at the O atom, which may reduce the steric repulsion. The siloxane chain is flexible in the sense that many configurations are accessible to it. The inherent rotational barrier around the Si−O bond at ordinary temperatures is of the order of RT (where R is the gas constant and T is the absolute temperature).[3] Because of their special properties, the polysiloxanes represent a group of quite unique polymers.

Silicone polymers containing organic groups other than methyl (i.e., long alkyl, phenyl, fluoro- or cyanoalkyl, vinyl, or hydrogen) have received considerable attention from the beginning of the silicones. Such substituents tend to modify the properties of the former PDMS, improving certain properties such as resistance to heat, oxidation, solvents, and/or radiation, adhesivity to particular substrates, lubricity, compressibility, shear resistance, and so forth.[4−6] As phenyl groups replace methyl groups in a polysiloxane chain, several changes occur. Some studies of the effect of the phenyl group content on the degradation behavior have recently been performed.[6−8] Generally, only a limited amount of poly(diphenylsiloxane) (PDPS) can be blended into a PDMS formulation to maintain the mechanical integrity. Copolymers of the two materials exhibit properties somewhere between those of the two pure materials.[6] The flexibility of the polysiloxane backbone decreases when methyl groups are replaced with bulky phenyl ones.[9] When substitution exceeds 0.75 mole fraction, the polymers are solid.[10] The solubility parameter of PDMS is increased by the presence of phenyl groups.[11] Thus, the solubility parameters of dimethyl-, methylphenyl-, and diphenyl-substituted polysiloxanes are (15350, 18410, and 19440) $J^{1/2}\cdot m^{-3/2}$, respectively. As a result, the miscibility of polyorganosiloxanes with organic polymers improves as the solubility parameter increases.[10] PDPS has a much higher glass transition temperature and viscosity than PDMS because of the limited mobility of the bulky phenyl groups. PDPS is a polymer with liquid-crystalline properties that can form a mesomorphic phase above its melting temperature.[5] It has been established that gelation occurs as a consequence of the crystallization of PDPS. Therefore, high-molecular-weight PDPS is soluble only in high-boiling solvents such as diphenyl ether, *o*-dichlorobenzene, and 1-chloronaphthalene at temperatures higher than $T = 423$ K.[12]

Solvent quality can have a great impact on the behavior of the macromolecular chains in solution as a function of the (co)polymer nature. Depending on the interactions between the macromolecular chain and the solvent molecules, the polymer may fully dissolve or the 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 compact globular conformation. If a second solvent is added to a polymer solution, the polymer coil is affected: the miscibility can be greatly enhanced or reduced, and the chain conformation, size, or shape changes as a function of the interactions established in the ternary system in accordance with the mixed-solvent composition.[13,14]

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In a poor solvent, polymer—solvent interactions are not favored. Therefore, attractive forces between the chains predominate, and consequently, the random coil adopts a contracted conformation. The situation when the polymer—solvent interactions vanish is known as the *theta state*, wherein the polymer chains behave ideally and the interactions of monomer units that are far from each other along the chain are neglected. The theta state of any polymer can be obtained, either by choosing an appropriate solvent (called a *theta solvent*) at constant temperature or by adjusting the temperature to an appropriate value (called the *theta temperature* or *Flory temperature*) in a given solvent. The unperturbed dimensions of PDMS chains appear to be affected by the solvent medium to a much greater degree than are polymethylene chains or chains of other nonpolar polymers. The polarity of the Si—O bond (and perhaps also of Si—C bonds) may render these chains more sensitive to the influence of the medium.[15] Earlier studies of the thermodynamic characteristics of poly(dimethylsiloxane-*co*-diphenylsiloxane) (PDMDPS) were performed using rather low molecular weight samples.[16]

In a previous study,[17] we investigated the effect of the solvent quality on the thermodynamic behavior of PDMDPS with the mole fraction of phenyl units (w_2) equal to 0.124 in methylbenzene/methanol mixtures. The conformational properties of a copolymer in solution are essentially dominated by the solvent quality, reflecting the balance of the interactions between the polymer chains and the solvent. The deterioration of the solvent quality produced a decrease in the hydrodynamic volume that was attributed to the repulsive interactions between PDMDPS and methanol, which produce a continuous contraction of the macromolecular coils until they reach the unperturbed dimensions at the theta point.

In this work, we investigated the properties of PDMDPS solutions under good and theta conditions by following the effect of copolymer composition on the thermodynamic parameters in perturbed and unperturbed states through viscometric and turbidimetric measurements.

2. EXPERIMENTAL SECTION

2.1. Materials. *2.1.1. Synthesis of the Polysiloxanes.* A 0.1 mL aliquot of a 25% aqueous solution of tetramethylammonium hydroxide (TMAH), $(CH_3)_4NOH$ (Aldrich), was introduced into a three-necked flask, and water was completely removed by azeotropic distillation with benzene. Next, 0.1 mL of dried dimethylformamide (DMF) was added, and 25 g of a mixture of octamethylcyclotetrasiloxane (D_4) and octaphenylcyclotetrasiloxane (Ph_4) (Fluka) (see Table 1) was loaded into the reactor under a nitrogen atmosphere. The mixture was stirred mechanically for 1.5 h at T = 353 K. TMAH was then deactivated by increasing the temperature to T = 423 K for 1 h, and the volatile compounds (catalyst decomposition products and low-molecular-weight siloxanes) were removed by vacuum distillation at T = 423 K and P = 10 mmHg. The composition and molecular masses of the resulted copolymers (see Table 2) were evaluated by ^{1}H NMR spectroscopy and gel-permeation chromatography (GPC), respectively.

2.1.2. Composition and Molecular Weight Measurements. The compositions of the resulting copolymers (Table 2) were estimated on the basis of the corresponding ^{1}H NMR spectra recorded on a BRUKER Avance DRX 400 spectrometer using $CDCl_3$ as the solvent. The peaks corresponding to the protons in the methyl (0.15 ppm) and phenyl [(7.0 to 7.6) ppm] groups, respectively, were taken into account for this.[17]

Table 1. Feed Molar Ratio of the Cyclosiloxanes Used in the Synthesis

sample	$(Ph_4/mol)/(D_4/mol)$
1	0.00/1.00
2	0.05/0.95
3	0.10/0.90
4	0.25/0.75
5	0.45/0.55

Table 2. Average Molecular Weights (M_n and M_w) and Polydispersity Indexes (M_w/M_n) of PDMDPS Samples with Different Molar Fractions of Diphenylsiloxane Units (w_2)

		M_n	M_w	
sample	w_2	$kg \cdot mol^{-1}$	$kg \cdot mol^{-1}$	M_w/M_n
1	0.0	186.0	289.2	1.55
2	0.056	243.3	870.1	3.57
3	0.124	144.2	316.9	2.19
4	0.280	105.5	181.1	1.71
5	0.465	95.4	162.0	1.69

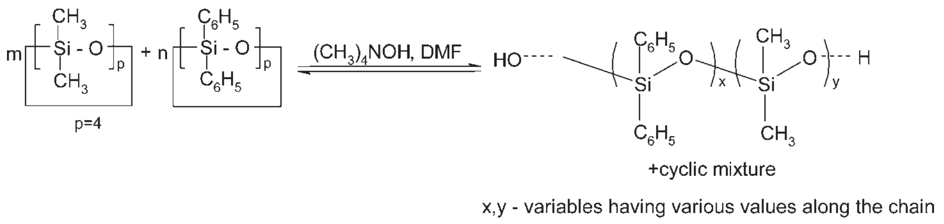
The molecular weights and polydispersity indexes of the samples (Table 2) were determined by GPC using a GPC PL-EMD 950 evaporative mass detector instrument. The system columns, which were based on styrene—divinyl benzene copolymer (PL gel, 5 μm C in series with PL gel, 5 μm D), were thermostatted at T = 298 K, and the samples were eluted with chloroform. The flow rate was 0.7 $mL \cdot min^{-1}$. 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 solvent mixture composition at the theta point. Polymer solutions in methylbenzene having different concentrations ($c < 2.9\ g \cdot dL^{-1}$) were titrated at T = 298 K with methanol until the first cloud point appeared. The volume fraction of methanol at the cloud point was plotted as a function of the logarithm of the polymer concentration at the cloud point and extrapolated to pure polymer. The volume fraction of methanol obtained by extrapolation corresponds to the theta composition. The turbidity and transmittance of PDMS and PDMDPS in methylbenzene and methylbenzene/methanol mixtures were monitored over the (400 to 600) nm wavelength range using a HACH 2100AN turbidimeter.

2.2.2. Refractive Index Increment Measurements. The refractive index increments of PDMDPS in methylbenzene at T = 293 K were determined. The refractive indices of the polymer solutions were determined using an Abbe refractometer (ATAGO NAR-1T LIQUID). The light source used in the unit was an LED with the D line at a wavelength of 589 nm.

2.2.3. Viscosity Measurements. Viscosity measurements were carried out in methylbenzene and in methylbenzene/methanol mixtures with volume fractions of methanol, φ_2^{θ}, corresponding to the theta conditions of the samples (as determined by the turbidimetric method) at T = (298 ± 0.01) K using an Ubbelohde suspended-level viscometer with a capillary diameter of 0.47 mm. All of the measurements were performed within

Scheme 1. Schematic Representation of PDMDPS Synthesis



1 day after the samples were brought into solution. The kinetic energy corrections were found to be negligible. The flow volume of the 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. Synthesis of Copolymers. PDMDPS samples were prepared by bulk anionic ring-opening copolymerization of D_4 and Ph_4 using TMAH as a catalyst and the Lewis base DMF as a promoter (Scheme 1). In the absence of Ph_4 in the reaction mixture, a PDMS sample was obtained as a reference sample. Basic catalysts are recommended for opening of the octaphenyltetrasiloxane cycle. The transient TMAH catalyst was chosen in this work because it could easily be removed at the end of the reaction by thermal decomposition to form volatile compounds (trimethylamine and methanol). DMF was added in order to increase the reaction rate by counterion complexation and hindrance of ion pair formation.[18,19] Four samples of copolymer with different compositions (Table 2) were prepared, investigated, and compared with a PDMS sample under the same thermodynamic conditions.

3.2. Viscometric Behavior under Good Solvent Conditions. The intrinsic viscosity, $[\eta]_H$, and Huggins constant, k_H, can be determined using the classical Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta]_H + k_H \cdot [\eta]_H^{\,2} \cdot c \qquad (1)$$

where η_{sp}/c is the reduced viscosity. The Huggins constant k_H offers information about the dimensions and shapes of polymer segments as well as hydrodynamic interactions between different segments of the same polymer chain. Figure 1 presents the plots of the reduced viscosity as a function of concentration for PDMDPS samples with different contents of diphenylsiloxane units in methylbenzene at $T = 298$ K.

The critical concentration, c', which separates the extremely dilute and dilute regimes, was determined for the studied systems by the Hernandez-Fuentes (HF) method.[20] 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 dilute concentrations, as a function of the last concentration introduced. From this representation, c' is determined by finding the cross point at which the fitted $[\eta]$ value suffers a change in trend. At c', the polymer chains first come into contact. An expansion of the macromolecular coil occurs below this concentration, and the crossover point c' depends on the chain length as well as on the chain flexibility (Table 3).

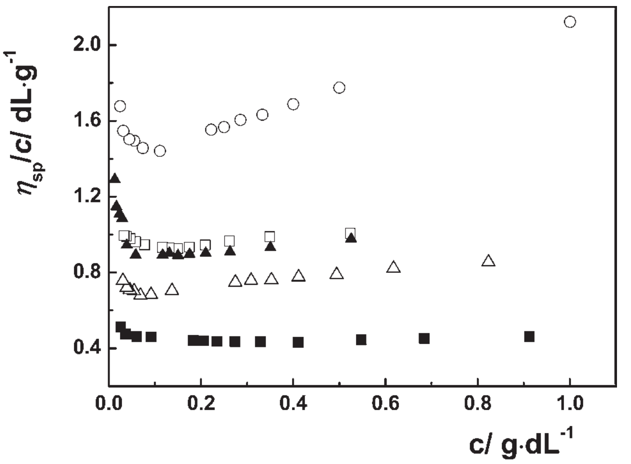


Figure 1. Plots of reduced viscosity, η_{sp}/c, as a function of concentration, c, for PDMDPS in methylbenzene at $T = 298$ K with different w_2: □, 0; ○, 0.056; ▲, 0.124; ■, 0.280; △, 0.465.

Table 3. Intrinsic Viscosities ($[\eta]_H$ and $[\eta]_w$), Huggins Constants (k_H), and Viscometric Interaction Parameters (B) in a Good Solvent (Methylbenzene) at T = 298 K

sample	$[\eta]_H$[a] dL·g^{-1}	k_H[a]	$[\eta]_w$[b] dL·g^{-1}	B[b]	k_H[c]	c' (HF) g·dL^{-1}	c^*[d] g·dL^{-1}
1	0.9324	0.1660	0.9162	0.2788	0.2212	0.1419	0.8258
2	1.3706	0.4267	1.4116	0.1703	0.3297	0.1004	0.5618
3	0.8534	0.3140	0.8579	0.2026	0.2974	0.0505	0.9023
4	0.4233	0.2322	0.4314	0.3278	0.1722	0.1806	1.8190
5	0.6945	0.4076	0.7099	0.1875	0.3125	0.0686	1.1087

[a] Calculated using eq 1. [b] Calculated using eq 3. [c] Calculated using eq 4. [d] Calculated using eq 2.

Another critical concentration, c^*, which separates the dilute and semidilute regimes, can be calculated according to the following equation:[21]

$$c^* = \frac{0.77}{[\eta]} \qquad (2)$$

The values of $[\eta]_H$ and k_H obtained in the dilute regime (for $c' < c < c^*$) are given in Table 3, which also includes the critical concentrations c' and c^*.

Figure 1 also illustrates very clearly the limitation of the Huggins equation in the data evaluation, especially in the region of very low concentrations, where the reduced viscosity deviates upward from linearity. Such positive deviations from linear behavior in the dependence of η_{sp}/c versus c in the region of very low concentrations have been reported previously for many

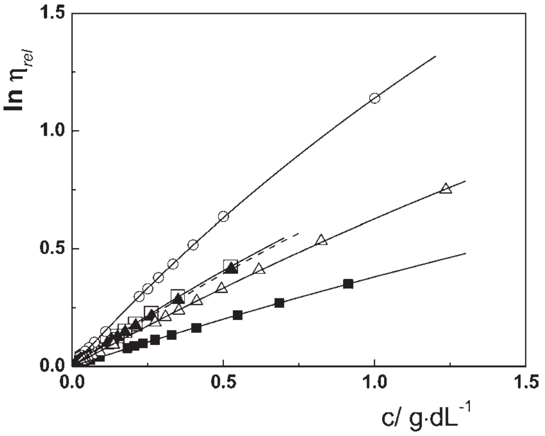


Figure 2. Plots of ln η_{rel} vs c for PDMDPS solutions in methylbenzene at T = 298 K with different w_2: □, 0; ○, 0.056; ▲, 0.124; ■, 0.280; △, 0.465. The lines correspond to best fits of the experimental data.

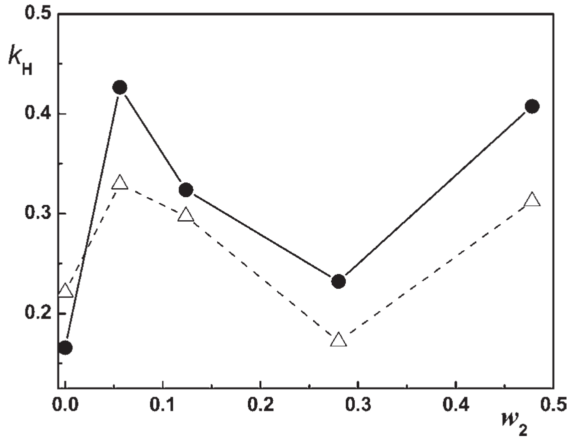


Figure 3. Dependence of k_H on w_2 of the copolymers in methylbenzene at T = 298 K, using k_H values calculated with: ●, eq 1; △, eq 4.

polymer solutions,[1,17,22,23] making the extrapolation of the experimental data to zero concentration more difficult.

Many efforts to obtain a linear dependence of the viscometric data for low polymer concentrations have been made. A new alternative method for the determination of $[\eta]$ of polyelectrolytes that was developed very recently[24] is based on the following equation:

$$\eta_{\text{rel}} = \frac{c[\eta]_{\text{w}} + Bc^2[\eta]_{\text{w}}[\eta]^{\bullet}}{1 + Bc[\eta]_{\text{w}}} \tag{3}$$

where B represents a system-specific constant and $[\eta]^{\bullet}$ is the characteristic specific hydrodynamic volume. Equation 3 was successfully verified for different polyelectrolyte solutions[24−28] and solutions of neutral polymers[22,23] and copolymers,[17] and thus, it can be applied for siloxane copolymers in solution.

The initial slopes of plots of ln η_{rel} as a function of c at sufficiently low shear rates and polymer concentrations (Figure 2) provide access to the intrinsic viscosities of PDMDPS copolymers. The $[\eta]_{\text{w}}$ values determined from the initial slopes obtained by fitting the experimental dependences of ln η_{rel} on c are given in Table 3. For all of the systems, we found that $[\eta]^{\bullet}$ is zero, as theoretically predicted for uncharged polymers.[25] The values of the intrinsic viscosity determined by applying eq 1 to the experimental data for $c > c'$ are in agreement with those determined from the initial slope according to eq 3).

Wolf and co-workers[27] compared the hydrodynamic interaction parameters k_{H} (from eq 1) with the B values obtained from eq 3 and obtained the following correlation:

$$k_{\text{H}} = \frac{1}{2} - B \tag{4}$$

which holds true only for the range of pair interactions within the macromolecular chain. For $B = 0$, which means no curvature in the plot of ln η_{rel} versus c, one obtains k_{H} = 0.5 (weak polymer−solvent interactions). B is positive for nearly uncharged polymers when the relative increase in viscosity slows down as the polymer concentration rises,[27] which is typical for thermodynamically good solvents. A comparison of the k_{H} values obtained from the linear part of the Huggins dependences for $c' < c < c^*$ (eq 1) with those calculated from the B values (eq 4) shows a reasonable agreement (Figure 3). The evolution of k_{H} as a function of w_2 is similar in the two cases, and k_{H} sensibly changes with changes in the content of diphenylsiloxane units. Usually, the values of k_{H} are in the range of 0.3 (good polymer−solvent interactions) to 0.5 (poor polymer−solvent interactions).

The dependence of k_{H} on the copolymer composition is complex, being influenced by the thermodynamic and hydrodynamic interactions among the copolymer chains. In our case, upon the introduction of a small content of diphenylsiloxane units, the repulsive interactions between the different copolymer units lead to an increase of the intrinsic viscosity and a large k_{H} value (greater than 0.4, indicating poor interactions between the polymer coils and the solvent). The balance between different types of interactions changes as the content of diphenylsiloxane units in the backbone increases, and the viscometric behavior is a result of the competition between the interactions of the macromolecular chains with the solvent and the intramolecular interactions between different segments along the chain.

3.3. Evaluation of Refractive Index Increments. The refractive index increment, dn/dc, is defined for a given wavelength, λ, and temperature by the following relationship:

$$\frac{\mathrm{d}n}{\mathrm{d}c} = \lim_{c \to 0} \left(\frac{\Delta n}{c}\right)_{\lambda, T} \tag{5}$$

where c is the concentration of the polymer solution (g·mL^{-1}) and $\Delta n = n_{\text{solution}} - n_{\text{o}}$, in which n_{solution} represents the refractive index of the polymer solution and n_{o} is the refractive index of the solvent (in our investigation, methylbenzene, for which n_{o} = 1.4965 at T = 293 K). The value of n_{solution} can be expressed in terms of n_{o} and c as follows:

$$n_{\text{solution}} = n_{\text{o}} + a \cdot c + b \cdot c^2 \tag{6}$$

where the a coefficient is equal to the refractive index increment dn/dc. For very low concentrations, the quadratic term can be neglected, and eq 6 becomes

$$n_{\text{solution}} = n_{\text{o}} + \frac{\mathrm{d}n}{\mathrm{d}c} \cdot c \tag{7}$$

The value of the refractive index of the pure polymer can be obtained by extrapoling to pure polymer the curve of the refractive index determined for solutions with different polymer concentrations.[29]

Table 4. Experimental Values of the Refractive Index (n) and the Refractive Index Increment ($\mathrm{d}n/\mathrm{d}c$) in Methylbenzene for the PDMDPS Samples

sample	n[a]	$\mathrm{d}n/\mathrm{d}c$ $\mathrm{mL \cdot g^{-1}}$
1	1.402	−0.095
2	1.480	−0.049
3	1.430	−0.074
4	1.511	−0.066
5	1.581	0.144

[a] Determined at 589 nm and T = 293 K.

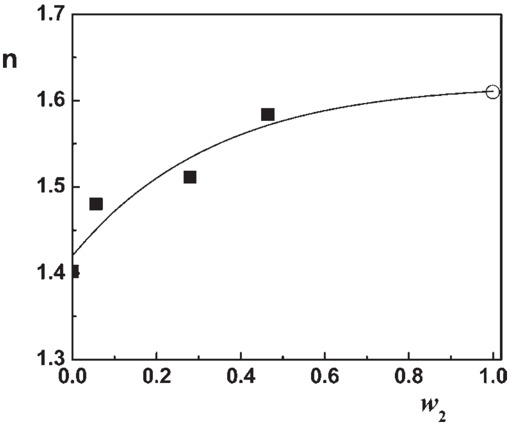


Figure 4. Effect of the content of diphenylsiloxane units on the refractive index of the PDMDPS copolymers: ■, present data; ○, literature data.[30]

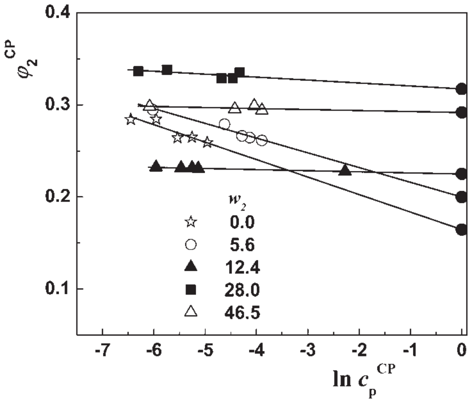


Figure 5. Turbidimetric titrations of the studied samples in toluene with different concentrations of methanol. The theta point (●) was determined for each sample by extrapoling the experimental curve to pure polymer.

Table 5. Theta Compositions of Methylbenzene/Methanol Mixtures (φ_2^{θ}) and Unperturbed Dimension Parameters of PDMDPS Samples with Different Contents of Diphenylsiloxane Units

sample	φ_2^{θ}	$[\eta]_{\theta}$[a] $\mathrm{dL \cdot g^{-1}}$	$10^3 \cdot K_{\theta}$ $\mathrm{dL \cdot g^{-1}}$	$10^4 \cdot (S_{\theta}^2/M)^{1/2}$ nm
1	0.1645	0.2628	0.4886	236.6092
2	0.1999	0.6421	0.6884	265.2413
3	0.2220	0.4177	0.7420	271.9574
4	0.3172	0.3474	0.8163	280.7492
5	0.2918	0.3248	0.8070	279.6744

[a] Calculated using eq 3.

According to the procedure proposed by Saveyn and coworkers,[29] the slope of the linear representation in eq 7 (when the polymer concentration expressed in $\mathrm{g \cdot mL^{-1}}$) gives the refractive index increment of the polymer in a given solvent. If this linearity is not verified, it is necessary to apply eq 6. The deviation from linearity occurs when there are strong interactions between the polymer chains and the solvent molecules. The values of the refractive indices of pure polymers, n, and of $\mathrm{d}n/\mathrm{d}c$ for the studied PDMDPS samples are presented in Table 4. Figure 4 illustrates the influence of the content of diphenylsiloxane units on the refractive index of the PDMDPS copolymers.

3.4. Theta Point Determination in Methylbenzene/Methanol Mixtures. The theta composition of a solvent mixture for a polymer can be determined from the turbidimetric titration of a dilute polymer solution with the nonsolvent at a constant temperature using the Elias method.[31] In this method, the volume fraction of the nonsolvent at the first cloud point (φ_2^{CP}) is plotted against the logarithm of the corresponding weight fraction of the polymer ($c_{\mathrm{p}}^{\mathrm{CP}}$) according to the following equation:[32,33]

$$\varphi_2^{\mathrm{CP}} = \varphi_2^{\theta} - B_{\theta} \ln c_{\mathrm{p}}^{\mathrm{CP}} \tag{8}$$

Extrapolation of the plot of φ_2^{CP} versus $\ln c_{\mathrm{p}}^{\mathrm{CP}}$ to pure polymer ($\ln c_{\mathrm{p}}^{\mathrm{CP}} = 0$) gives the theta composition of the nonsolvent (φ_2^{θ}).

The theta point was determined at T = 298 K by titration with methanol of five (co)polymer/methylbenzene solutions having the initial concentration in dilute regime until the first cloud point was observed. The results of the turbidimetric titrations and the theta compositions of the methylbenzene/methanol mixtures for all of the studied samples obtained using the Elias method are shown in Figure 5 and Table 5, respectively. The slopes of the curves in Figure 5 reflect the effect of the molecular weight, whereas the copolymer composition determines the value of the solvent composition at the theta point (Table 5), which is estimated by the extrapolation of the experimental curves to pure polymer.

Figure 6 illustrates the effect of the content of diphenylsiloxane units on the turbidimetric curves using plots of turbidity [expressed in nephelometric turbidity units (NTUs)] versus volume fraction of methanol. One can observe that the turbidity of the system abruptly increases above the theta point as a result of the weakening of the interactions between the polymer and solvent, the polymer−polymer interactions being favored. It can be observed that the turbidity and the theta composition of the PDMDPS copolymers are higher than those of PDMS.

It was also observed that the transmittance decreases faster at volume fractions of methanol above the theta composition (i.e., for $\varphi_2 < \varphi_2^{\theta}$) (Figure 7). One can observe that the theta composition is independent of the initial concentration of the polymer solution that is titrated.

From the dependence of φ_2^{θ} on w_2 (Figure 8), it can be observed that the composition of the methylbenzene/methanol

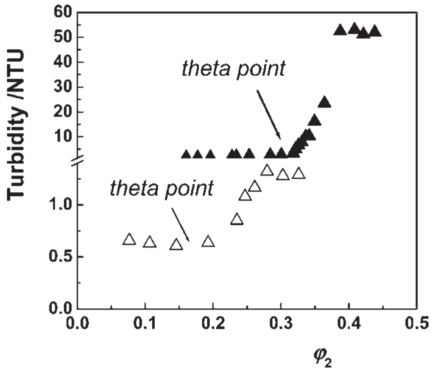


Figure 6. Turbidity of two samples with different w_2: △, 0.0 (c_{initial} = 0.533 g·dL^{-1}); ▲, 0.280 (c_{initial} = 0.483 g·dL^{-1}).

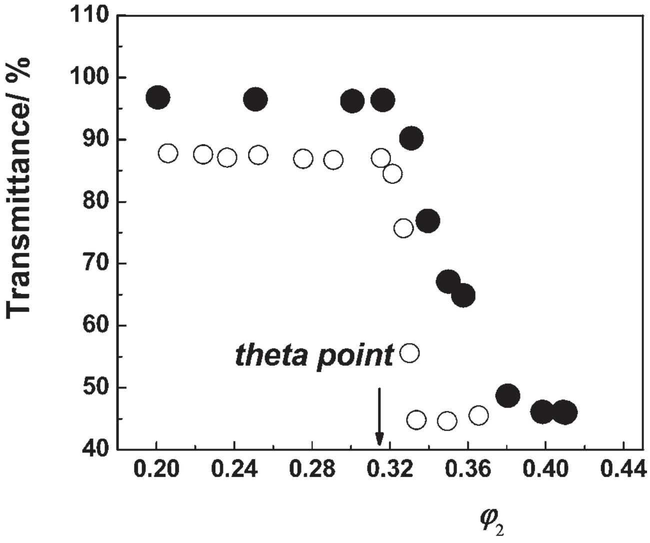


Figure 7. Transmittance as a function of the volume fraction of methanol for the copolymer with w_2 = 0.280: ○, c_{initial} = 1.980 g·dL^{-1}; ●, c_{initial} = 0.277 g·dL^{-1}.

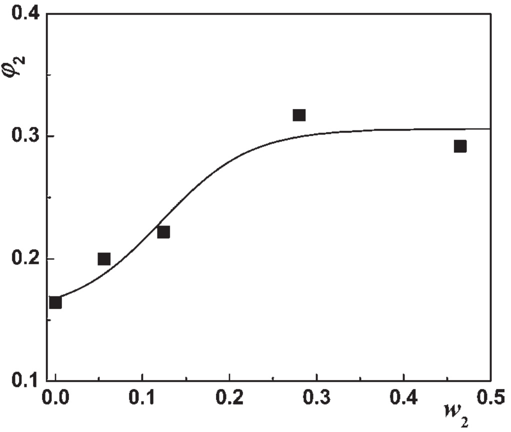


Figure 8. Effect of the content of diphenylsiloxane units on the theta composition for the PDMDPS samples.

mixture at the theta point becomes independent of the copolymer composition above w_2 = 0.3.

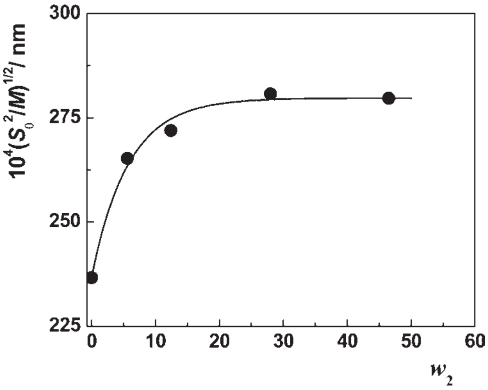


Figure 9. Dependence of $(S_\theta^2/M)^{1/2}$ as a function of PDMDPS composition.

3.5. Conformational Characteristics of the PDMDPS Copolymers in the Unperturbed State. The conformational characteristics of copolymers in solution depend on polymer—solvent interactions, which are essentially dominated by the solvent quality[17] as well as by the copolymer chemical composition,[34,35] which in our case is determined by the content of diphenylsiloxane units and their distribution along the polymer chain. The deterioration of the solvent quality produced a decrease in the hydrodynamic volume, which can be attributed to the repulsive interactions between PDMDPS and methanol, producing a contraction of the macromolecular coil.[17]

The intrinsic viscosity in the unperturbed state was determined for PDMDPS samples by means of the Wolf method (eq 3) at the methylbenzene/methanol composition corresponding to the theta condition (Table 4). The unperturbed parameter, K_θ, can be calculated from the viscosity—molecular weight relationship under theta conditions:

$$[\eta]_\theta = K_\theta M^{1/2} \tag{9}$$

The unperturbed dimensions can be then estimated from the relation

$$K_\theta = 6^{3/2}\phi_o \left(\frac{S_\theta^2}{M}\right)^{3/2} \tag{10}$$

where ϕ_o is Flory's constant ($\phi_o = 2.51 \times 10^{21}$ for $[\eta]$ expressed in dL·g^{-1}). Values of K_θ and $(S_\theta^2/M)^{1/2}$ for PDMS and PDMDPS are given in Table 5. Figure 9 shows the influence of the copolymer composition on the unperturbed dimensions of the macromolecular chain. It can be observed that the introduction of the diphenylsiloxane units into a PDMS chain results in a decrease in chain flexibility and thus an increase in the unperturbed dimensions. Above a particular content of diphenylsiloxane units (which approximately corresponds to a 3:1 molar ratio of methylsiloxane and phenylsiloxane units), the chain flexibility remains nearly constant (i.e., the chain stiffness has reached a maximum level).

4. CONCLUSION

The thermodinamic properties of poly(dimethylsiloxane-*co*-diphenylsiloxane)s under good (methylbenzene) and theta (methylbenzene/methanol) solvent conditions have been investigated. Turbidimetric titrations were performed at T = 298 K in order to establish the theta point for PDMDPS in solvent mixtures. From the dependence of the volume fraction of methanol as a function of the logarithm of polymer concentration corresponding to the cloud point, the theta composition of the solvent mixture was established by extrapolating the experimental curve to pure polymer. The turbidity and the transmittance curves undergo a sharp discontinuity below the theta point due to the alterations of the interactions between the polymer and the solvent, with the polymer—polymer interactions being favored.

The intrinsic viscosities and Huggins constant were determined using the classical Huggins equation, and the data were compared with those obtained by applying a new method proposed by Wolf.[24] The values of the intrinsic viscosity determined by the two methods are close, but the Wolf's new method more accurately provides the intrinsic viscosity values by modeling the viscometric data in the region of very low concentrations.

The unperturbed dimensions are influenced by the copolymer composition for a low content of diphenyl units in the copolymer chain, showing a decrease in the chain flexibility with increasing content of diphenylsiloxane bulk units in a flexible PDMS chain up to a maximum level of the chain stiffness, which was reached for a mole fraction of diphenylsiloxane units equal to approximately 0.3.

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