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Second virial coefficient of a series of polysiloxanes: the effect of side groups and molecular weight

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This study reports the results of analyzing the second virial coefficient (A_2) in a good solvent for a series of polysiloxane chains in which the pairs of substituents connected to the silicon are CH_3, CH_3; C_2H_5, C_2H_5; CH_3, C_6H_{13}; CH_3, $C_{16}H_{33}$; and CH_3, C_6H_5. The effect of the side group and molecular weight on A_2 was investigated using the Helical Wormlike (HW) chain model. A theoretical analysis of the interpenetration function (ψ) was carried out using a Two-Parameter (TP) scheme. The theoretical-experimental behaviour of A_2in a series of polysiloxanes was investigated considering the effects of the type of substituent on the main chain, molecular conformation, and molecular weight. The results obtained were strongly dependent on the flexibility of the side groups and the molecular weight of the polymer. Within the HW model and TP scheme, the A_2 value for poly(dimethylsiloxane) (PDMS1 and PDMS2), poly(diethylsiloxane) and poly(methylhexylsiloxane) agrees with the experimental results obtained through the coupled system (Gel Permeation Chromatography/Light Scattering: GPC/LS). However, the A_2 calculated for PDMS3, poly(methylhexadecylsiloxane) (PMHDS) and poly(methylphenylsiloxane) (PMPS) showed a significant difference from the experimental value. On the basis of the theory for the HW model, the deviation in PDMS3 may be due to the effect of the end chains. For PMHDS and PMPS, the model used is outside of the coil limit (validity of TP model). In PMHDS the determination of the (*RMSradius)*^{2} value from the GPC/LS system is strongly influenced by the interaction between the bulky side group and the main chain, which affects the calculation of A_2.

Keywords: Polysiloxane; second virial coefficient; gyration-radius expansion factor; interpenetration function; molecular conformation.

Este estudio reporta los resultados del análisis del segundo coeficiente del virial A_2 para una serie de cadenas de polisiloxano en las cuales los pares de grupos laterales unidos al silicio son: CH_3, CH_3; C_2H_5, C_2H_5; CH_3, C_6H_{13}; CH_3, $C_{16}H_{33}$; CH_3 y C_6H_5. El efecto del grupo lateral y peso molecular en el valor del A_2 es analizado a través del modelo de cadena Helicoidal tipo Gusano (HW). El análisis teórico de la función de interpenetración (ψ) fue llevada a cabo utilizando el esquema de los Dos Parámetros (TP). El comportamiento teórico-experimental del A_2 para la serie de polisiloxanos fue investigado considerando los efectos del tipo de grupo lateral unido a la cadena principal de la conformación molecular y del peso molecular del polímero. Los resultados obtenidos muestran una fuerte influencia de la flexibilidad de los grupos laterales y del peso molecular del polímero. Dentro del modelo HW y el esquema TP, el valor del A_2 para el poli(dimetilsiloxano) (PDMS1 y PDMS2), poli(dietilsiloxano) y poli(metilhexilsiloxano) se encuentra en buena aproximación con el obtenido a través del sistema acoplado de Cromatografía de Permeación en Gel/Dispersión de Luz (GPC/LS). Sin embargo, el cálculo del A_2 para el PDMS3, poli(metilhexadecilsiloxano) y poli(fenilmetilsiloxano) presenta una significativa diferencia con el valor obtenido experimentalmente. Con base en la teoría del modelo HW, la desviación en el PDMS3 puede provenir de los efectos de los grupos terminales de la cadena de siloxano. Para el PDMHDS y PMPS se utilizó un modelo que se encuentra fuera del límite de ovillo (validez del modelo TP). En PDMHDS, la determinación del tamaño molecular (*RMSradius)*^{2} a través del sistema acoplado GPC/LS está fuertemente influenciada por la interacción entre el grupo lateral alquilo más largo y la cadena principal, lo cual afecta el cálculo del A_2.

Descriptores: Polisiloxano; segundo coeficiente del virial; factor de expansión del radio de giro; función de interpenetración; conformación molecular.

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1. Introduction

Silicon-containing polymers, such as the polysiloxanes and polysilanes, have practical importance for the applications of a precursor of silicon carbides, pervaporation membranes, photo-and electroactive polymers, but they have been insufficiently studied with regard to the correlation between their physical-chemical properties and molecular conformation [1]. In particular, the polysiloxanes are important industrial materials owing to their special properties such as high chemical and thermal stability, and the flexibility of their backbones arising from the low rotational barrier energy around the silicon-oxygen bond. Their low toxicity can be used to advantage in designing a selectively oxygen-permeable membrane material and new side-chain liquid crystalline polymers [1,2]. Of these silicon-containing polymers, the most important is the poly(dimethylsiloxane) (PDMS). PDMS has been utilized in rubbers, resins, water repellents, release agents, dielectric fluids, anti-foams, polishes, lubricants, and devices for both prosthetic and cosmetic purposes [3-5]. Other polysiloxanes, such as poly(diethylsiloxane) (PDES), poly(methylhexyl-siloxane) (PMHS), poly(methyl-hexadecylsiloxane) (PMHDS), and poly(methylphenylsiloxane) (PMPS), have been produced in laboratories but do not yet have a broad commercial application.

Some features of the siloxane bond have a great impact on the physical chemistry of polysiloxanes. The Si-O bond distance, 1.64 Å, is shorter than the sum of the covalent radii, which is 1.76 Å, implying a partial double Si-O bond. Nonetheless, the barrier of linearisation of the Si-O, ≈2.5 KJ mol^{-1} in $(Me_3Si)_2O$, as well as the barrier of linearisation of the SiOSi angle, ≈1.3 KJ mol^{-1}, are very low [6]. Thus, the polysiloxane chain is so unusually flexible that the SiOSi angle, 140-180° is much wider than a tetrahedral angle. The silicon atom is relatively large and the substituents appear only at every other atom in the chain. In addition, as is well known, the physical properties of flexible linear polymers can be modified through the introduction of side groups. Thus, in the case of the polysiloxanes, the entropy gain on polymerization decreases with the increase in size and polarity of the organic substituent connected to the silicon. Consequently, the yield of the polymer at equilibrium can be strongly reduced when a bulky or polar monomer is used as a substitute [7]. The expected effect of the introduction of side groups would be to cause the polymer backbone to kink. However it has also been suggested that the addition of large side groups will result in a loss of flexibility. For example, the poly(di-n-alkylsiloxane)s form a liquid crystalline mesophase whose stability increases with the length of the alkyl side chains [2]. The conformation analysis of polysiloxanes is complicated, and the majority of the studies are based on calculations obtained using some simulation techniques for oligosilanes. Molecular dynamic simulations and other methods, for example, are still being developed [1,8-10].

In polymer solutions, the contribution to the excluded volume is known to depend not only on the actual volume of the chain unit, but also on its interaction with the solvent molecules and the observable physical properties dependent on the chain length, concentration, side and end groups, and basic interaction parameters. The values of these interaction parameters are contained in A_2, and before evaluating the polymer A_2, it is necessary to compare the properties of chains in an unperturbed state, *i.e.* at θ-conditions with those corresponding to a good solvent. In θ-conditions, A_2 vanishes because of the high molecular weight and also because the ratio *RMSradius/M$_W$* becomes a constant, independent of the molecular weight [11]. With respect to the A_2 model, the theory of A_2, based on the helical wormlike (HW) chain model, semi-quantitatively explains the behaviour of the interpenetration function (ψ) between polymers as a function of the values of the HW model parameters determined from an analysis of the unperturbed mean square radius of gyration $(\langle s^2\rangle o)$ and the gyration-radius expansion factor (α_s^2) [12]. The HW chain may be described essentially in terms of three parameters: the constant curvature κ_0, torsion τ_0 of its characteristic helix taken at the minimum zero of its elastic energy, and the static stiffness parameter λ^{-1}. In the case of ψ, which is not a universal function of α_s^2, change with α_s^2 depends not only on the molecular weight of the polymer but also on the excluded-volume strength (or solvent Power = **B**) [13]. Thus, in the Two Parameter (TP) scheme, ψ is a function only of α_s^3 and the excluded-volume parameter (z), and **B** is proportional to the binary cluster integral β between beads and a parameter is unnecessary [12-14]. This is an essential characteristic of the TP scheme. Subsequently, our main objective is to develop a theoretical analysis and discussion of ψ in order to show explicitly the individual contributions of ψ on the effects of the chain stiffness of $\langle s^2\rangle o$ (effect of side groups on the molecular conformation) and the intra- and intermolecular excluded-volume interactions (α_s^2 in good solvent) to obtain thus the A_2 value of the polymer. Yamakawa *et al.* proposed a procedure for examining the agreement between theory and experiments involving the interactions in a polymer solution, based on the correlation between the expansion factor and ψ [15]. Although various basic theories of α_s^2 and ψ have been developed in polymer solution thermodynamics, if we insist on consistency in intramolecular and intermolecular theories of interaction, there exist few expressions for ψ which can be chosen for a given theory of α_s^2. Basically, there are only three such consistent combinations: (1) the original Flory-Krigbaun-Orofino theory of ψ (FKO,o) [Eq. (1)] and the original Flory theory of α_s^2(F,o) [Eq. (2)], (2) the modified FKO (FKO,m) ψ [Eq. (3)] and the modified Flory theory of α_s^2 (F, m) [Eq. (4)], and (3) the Kurata-Yamakawa theory of ψ (KY) [Eq. (5)] and the Yamakawa-Tanaka theory of α_s^2 (YT) [Eq. (6)]. These theories are described in detail in Refs. 16 and 17.

$$\psi = \frac{\left[\ln\left(1+2.30\frac{z}{\alpha_s^3}\right)\right]}{2.30} \tag{1}$$

$$\alpha_s^2 - 1 = 2.60\frac{z}{\alpha_s^3} \tag{2}$$

$$\psi = \frac{\left[\ln\left(1+5.73\frac{z}{\alpha_s^3}\right)\right]}{5.73} \tag{3}$$

$$\alpha_s^2 - 1 = 1.276\frac{z}{\alpha_s^3} \tag{4}$$

$$\psi = 0.547\left[1-\left(1+3.903\frac{z}{\alpha_s^3}\right)^{-0.468}\right] \tag{5}$$

$$\alpha_s^2 = 0.541 + 0.459\left(1+6.04z\right)^{0.45} \tag{6}$$

This paper gives the results of analyzing the second virial coefficient (A_2) in a good solvent (toluene) for the following polysiloxanes: poly(dimethylsiloxane) (PDMS), poly (diethylsiloxane) (PDES), poly(methylhexylsiloxane) (PMHS), poly(methylhexadecyl siloxane) (PMHDS), and poly(methylphenylsiloxane) (PMPS). The calculation of A_2 was performed using a Helical Wormlike (HW) chain model. The analysis of ψ was carried out using the two-parameter (TP) scheme. The results were compared with the experimental data from the GPC/LS coupled system. This coupled system gives information about the molecular conformation and second virial coefficient as well as polymer size.

2. The polysiloxane samples analyzed

The polysiloxanes analyzed were commercial samples supplied by Scientific Polymer Products, Inc. (sp^2). All the polysiloxane samples used in this work are the same as those used in the previous studies of the effect of side groups on the conformation of a series of polysiloxanes in solution [18]. In our analysis, the samples were characterized in toluene using the GPC/LS coupled system, which has been described in detail by Villegas *et al.* [19]. A light scattering detector coupled with makes possible the measurements of the square root of the mean square radius (*RMSradius*)^2 and the mean molecular weight of polymer fractions eluting from a size-exclusion chromatography column without using standard polymers. The mean molecular weight, molecular size, and A_2were obtained from the concentration dependence at low concentrations of molecular weight. Molecular size for a polymer fraction (this is a particular volume retention or a slice of plot) can be determined from the Debye plot, *i.e.*, $R_\theta \,/\, K^* \, c$ plotted against $\sin^2(\theta/2)$; where $R_\vartheta$is the Rayleigh ratio, the optical constant is K^*, c is the slice concentration, and θ is the scattering angle. In this plot, the intersection gives the molecular weight, and the slope at low angles gives the molecular size for that slice. In contrast, the Zimm plot, using the slope of the projection at zero angle limits, gives the second virial coefficient A_2 [20]. For the polysiloxane samples, this plot was also obtained using the GPC/LS coupled system. The molecular conformation in solution is calculated from the relationship between the radius of gyration and the molecular weight measured by light scattering for each slice (M) [Eq. (7)]:

$$RMSradius = K\,M^p \tag{7}$$

Therefore, the molecular conformation can be determined from the slope of the log of the radius of gyration plotted against the log of the molecular weight M. Note that the radius of gyration as a function of the molecular weight plot depicts the relationship between the two quantities measured directly by light scattering. On the basis of Eq. (7), to obtain the molecular conformation of a polymer, it is necessary to measure the entire size distribution. In GPC/LS experiments, (*RMSradius)*^{2} is the polymer root mean square radius of gyration of the size distribution and M_w is the weight average molecular weight of the molecular distribution. Thus, from Eq. (7), a slope of $0.5 \leq p \leq 0.6$ is related to the random coil, p = 1 is a rigid rod, and p = 0.33 is a sphere [20].

The results of the characterization are shown in Table I [18]. It is necessary to take into account that the GPC/LS coupled system uses the *dn/dc* value to calculate the concentration at each elution volume and the mass recovered from the column. These quantities are important for obtain both (*RMSradius)*^{2} and M_w.

3. Results and discussion

3.1. Second Virial Coefficient of PDMS

For our analysis, information was needed concerning the molecular conformation and molecular size (*RMSradius)*^{2} in a good solvent of the polysiloxane samples (see Table I). On the other hand, in a polymer solution, the principal effect of the solvent molecules is on the relation between root-mean-square end-to-end distance or the unperturbed radius of gyration and chain length. In this work, two samples of PDMS (PDMS1 and PDMS2) show experimental values for (*RMSradius)*^{2} as large as the $\langle s^2 \rangle o$ values calculated from Eq. (8), which is consistent with the fact that these polysiloxanes show a slope value indicating that in dilute solutions there are semi-flexible coils, *i.e.*, the chains have intermediate properties between those of rigid rods and highly flexible coils (see Table I). However, it is interesting to note that the PDMS3 slope is approximately 0.6. In this case, the *RMSradius* value increases with $M_w^{3/5}$ and this sample shows properties of a dilute (nonoverlapping) coil in a good solvent. In a good solvent the attractive polymer bead-solvent contacts suppress bead-bead self-contacts and cause chain expansion relative to unperturbed conditions and, in the high molecular weight limit, the exponent in the coil size as a function of chain length power law relation approaches 3/5 [21]. As a result, this sample, which has of relatively low molecular weight, contains coil chains that are more compact than those in PDMS1 and PDMS2, samples of relatively high molecular weight (see Table 1).

TABLE I. Characterization of the samples in toluene using the GPC/LS coupled system.

Polysiloxane	$M_w \times 10^{-3}$ (g mol^{-1}) $\lvert dn/dc \rvert$	(ml g^{-1})	Slope	(*RMSradius)*^{2}(nm^2)
PDMS1	273.4	0.101	0.74	566.44
PDMS2	97.6	0.093	0.70	187.69
PDMS3	34.3	0.085	0.61	54.76
PDES	27.6	0.043	0.80	2256.25
PMHS	4.1	0.050	0.32	88.36
PMHDS	8.1	0.045	0.36	320.41
PMPS	11.5	0.034	1.02	445.21

TABLE II. Values of the unperturbed square of the root-mean-square radius from the "draining effect" [Eq. (8)] and α_s^2 of PDMS.

Samples	$\langle s^2 \rangle o$ (nm^2)*	(*RMSradius*)^2 (nm^2)**	α_s^2
PDMS1	240.25	566.44	2.36
PDMS2	82.81	187.69	2.27
PDMS3	31.36	54.76	1.75

*Values obtained using the "draining effect.

**(*RMSradius)*^{2}values from Table I.

TABLE III. Values of A_2 and Ψ for the poly(dimethylsiloxane) samples.

Sample	$A_2 \times 10^4$ (g^{-2} ml)*	Ψ (mol^{-1})*	$A_2 \times 10^4$ (g^{-2} ml)**	Ψ (mol^{-1})**
PDMS1	10.9	0.45	6.60	0.34[a]
PDMS2	10.7	0.29	9.77	0.27[b]
PDMS3	28.0	0.60	12.01	0.50[c]

$^*A_2$ values from SLS data.

$^{**}A_2$ and Ψ from theoretical values: [a] (FKO,o) for Ψ and (F,o) for α_s^2; [b,c] (FKO,m) for Ψ and (F,m) for α_s^2.

TABLE IV. Values of the square of the unperturbed root-mean-square radius of gyration from the blob model and α_s^2 of PDES.

Samples	$\langle s^2 \rangle o$ (nm^2)	(*RMSradius*)^2 (nm^2)*	α_s^2
PDES	1506.63	2256.25	1.50

*(*RMSradius*)^2 value from Table I.

TABLE V. Values of A_2 and Ψ for the poly(diethylsiloxane) sample.

Sample	$A_2 \times 10^2$ (g^{-2} ml)*	Ψ (mol^{-1})*	$A_2 \times 10^2$ (g^{-2} ml)**	Ψ (mol^{-1})**
PDES	10.0	0.06	7.74	0.15

$^*A_2$ values from SLS data.

** A_2 and Ψ from theoretical values: (FKO,o) for Ψ and (F,o) for α_s^2.

The gyration-radius expansion factor α_s^2 is defined as the ratio of (*RMNradius*)^2 to its unperturbed value $\langle s^2 \rangle o$. Remember that a criterion of an approximate theory that represents short-range and long-range interferences in the polymer chain is used in terms of α_s^2. But before evaluating α_s^2, it is necessary to determine values of the unperturbed mean-square of gyration $\langle s^2 \rangle o$. In studies on α_s^2, Horita *et al.* give particular attention to its correct determination by properly selecting a pair of good, plus θ-solvents so that the values of the unperturbed $\langle s^2 \rangle o$ in a good solvent coincides with those of $\langle s^2 \rangle o$ in the θ-solvent taken as the reference standard [16]. The agreement of the former with the latter was then confirmed by comparing the values of $\langle s^2 \rangle o$ in the good and θ-solvents in the oligomer region where the excluded-volume effect may be negligible [22]. In previous work, we calculated the values of $\langle s^2 \rangle o$ for the PDMS samples using the so-called "draining effect" (DE) in bromocyclohexane at 29.5°C (θ-solvent for PDMS) [Eq. (8)] [18,22].

$$\left(\frac{\langle s^2 \rangle_\theta}{M_w} \right)_\infty = 8.88 \times 10^{-4} \frac{nm^2 - mol}{g} \tag{8}$$

The values obtained for α_s^2 using the (*RMSradius)*^{2} experimental values and $\langle s^2 \rangle o$ from DE are listed in Table II. It was shown that these results gave values of α_s^2 from the DE similar to that obtained by Horita *et al.* for comparable M_w samples [16].

On the basis of the HW model chain, the effect of chain ends is not considered. If the A_2 measurements are carried out at the θ point, this quantity depends upon the relationship given by Eq. (9) [11,17],

$$A_2 = N_A \frac{\left((\,RMSradius\,)^2 \right)^{3/2}}{M_w^2} f(\psi), \tag{9}$$

where N_A is Avogadro's number, M_w weight average-molecular weight and f is a factor that depends only on the interpenetration function ψ. Several approximate expressions have been derived for ψ as a function of the excluded-volume parameter (z). This parameter is given by

$$z = \left(\frac{3}{2\pi a^2} \right)^{3/2} \beta \eta^{1/2} \tag{10}$$

where β is the binary cluster integral and η is the number of statistically independent segments of effective bonds of a length. The Two-Parameter Theory (TP) based on the Gaussian chain model involves the only combinations ηa and $\eta^2\beta$ that are proportional to molecular weight (M_w) [23]. Thus, the TP theory, which applies in the coil limit ($M_w \rightarrow \infty$ or $\eta a \rightarrow \infty$), requires that when $\alpha_s^2 = 1$ then z, ψ and $A_2 \rightarrow 0$. Note that z cannot be determined directly by experiment, but $\alpha_s^2\,(z)$ can. Therefore, a plot of $\psi\,(z)$ as a function of $\alpha_s^2\,(z)$ eliminates z and provides a valuable test for the two-parameter theory [23].

The Flory and Krigbaun thermodynamics theory has shown that polymer coils in good solvents may be regarded as thermodynamically non-interpenetrating spheres. Consequently, A_2becomes proportional to

$$\left((RMSradius)^2\right)^{3/2}/M_w^2$$

with the approximation $\alpha* = \alpha_s$, where $\alpha*$ is the expansion factor of one polymer molecule in contact with another. This form of A_2represents the chain-like rigid sphere molecules with a diameter proportional to *RMSradius*. In this work, the polysiloxane A_2 was obtained using the Flory and Krigbaum theory for chains with excluded-volume effects from Eq. (9). In this theory the factor f is given by [17]:

$$f = 4\,\pi^{3/2}\,\psi. \qquad (11)$$

Experimental values of ψ may be calculated from Eqs. (9) and (11) with values of M_w, A_2 , and (*RMSradius*)^2 obtained from light-scattering measurements. Theoretical values of ψ were obtained from thermodynamics basic theories: the (FKO,o) theory of ψ [Eq. (1)] and the (F,o) theory of α_s^2 [Eq. (2)] were used for PDMSI while the modified (FKO,m) of ψ [Eq. (3)] and the modified (F,m) theory of α_s^2 [Eq. (4)] were used for PDMS2 and PDMS3. The A_2 experimental value was obtained from the Zimm plot (Static Light Scattering: SLS data) generated by the GPC/LS coupled system. The PDMS A_2 and ψ values are shown in Table III.

According to the results in Table III, the combination theory (2) is very satisfactory for PDMS2 and is a good approximation for PDMS3. However, for PDMS1, a relatively large deviation between the ψ value measured by SLS and those calculated theoretically is found from combination theory (1). As α_s^2 decreases (PDMSI2 and PDMS3), experimental Ψ in a given good solvent increases from the asymptotic value, while theoretical Ψ decreases toward zero (see Table III) [23]. Yamakawa explained this discrepancy as due to the effect of molecular conformation (stiffness) on A_2 and α_s^2 on the basis of the HW model [24]. However the HW chain model does not consider the effect of chain ends, and this effect is important in low molecular weight polymers. Thus, the above results indicate that A_2 increases with decreasing values of M_w (case of PDMS3) due to the effects of chain ends, which is consistent with results obtained from the HW model (see Table III) [25]. Subsequently, for PDMS1 and PDMS2, the behaviour of Ψ is explained by the values of the HW model parameters determined from an analysis of the unperturbed mean-square radius of gyration $\langle s^2\rangle o$ and α_s^2. Thus, the values obtained depend basically on the theory used for ψ, which suggests application limitations in the theoretical model used in the poly(dimethylsiloxane) samples. In the case of PDMS3, it may be necessary to use a different A_2 model, namely the HW model and in addition, the effects of chain ends. Data in Tables III, show a decrease in Ψ (PDMS2 and PDMS3) with increasing molecular weight (M) in a good solvent [26]. This has been observed experimentally, and has been explained for the low M region by Huber and Stockmayer, who examined the effect of chain stiffness by using the Yamakawa-Stockmayer (YS) theory [27].

3.2. Second virial coefficient of PDES, PMHS and PMHDS

The SiOSi bond angle in polysiloxanes is characterized by an angle measuring between 102 and 112°, depending on the nature of the two substituents on Si. The pendant group plays an important role in the polysiloxane flexibility [1]. Thus, the configuration of a PDMS chain can be adequately defined by giving the relative positions of its Si and O atoms; the angles of rotation of pendant methyl groups about the Si-CH_3 bonds may usually be ignored. However, this is not true in polysiloxanes with larger side groups than PDMS because the configuration is controlled basically by the flexibility and reorientation of the pendant groups. PDES, PMHS, and PMHDS have a larger alkyl group than PDMS (PLAG), which leads to lower chain flexibility. When the molecular conformation is extended to a PLAG solution along with the (solvent-solute) and (solute-solute) interactions, we must consider the influence of the side groups. PDES chains are extended coils almost rigid rods, whereas, surprisingly, PMHS and PMHDS have a spherical conformation in a good solvent (see Table I). The molecular conformation results indicate that the exclude-volume effect in PDES is greater than in PDMS. Thus, the source of the coil's expansion is the high mobility in the side chains of PDES because the backbone rotation angles are small. The methyl groups in PDMS, in contrast, are relatively free to rotate and the polymer remains flexible [18]. Thus, the molecular conformation is influenced by the increasing length of the side groups on the unperturbed dimensions of these polysiloxanes, especially over PMHDS, the member of the polysiloxanes which is distinguished by a large side group ($C_{16}H_{33}$).

In previous work, we described in detail how the PDES $\langle s^2\rangle o$ value (1506.63 nm^2) was obtained. According to the blob model (unperturbed chain model), this $\langle s^2\rangle o$ value is consistent with the Gaussian scaling of PDES coils in a melt state [18]. The comparison between the $\langle s^2\rangle o$ value and the GPC/LS measurement shows that the (*RMSradius)*^{2} value of PDES deviates significantly from its unperturbed analogue (see Table IV). In this study, as the $\langle s^2\rangle o$ value indicates, it was used to describe the unperturbed dimensions of PDES. The (FKO,o) theory of ψ [Eq. (1)] and the (F,o) theory of α_s^2

[Eq. (2)] were used for PDES chains. These results and the A_2 value are reported in Table V.

Looking at the above results, the PDES A_2 theoretical model is not extremely different from the experimental value, if we take into consideration that the PDES chains are more extended coils than the PDMS chains (see Table I). In the TP theory for a linear flexible chain, the chain stiffness has a significant effect on ψ, according to those on the intra-and intermolecular excluded-volume interactions, even for such a large molecular weight M_w that the ratio of the unperturbed mean-square radius of gyration to M_w is independent of M_w [14]. As a result, it is probable that the deviation between the theoretical and experimental values is a consequence of the stiffness of the coiled chains of PDES. It must be remembered that the HW model is true to the coil limit.

In the case of the PMHS and PMHDS samples, that have highly unsymmetrical sizes of their side groups, it was not possible to obtain a $\langle s^2 \rangle o$ value because we do not have a model that can be applied to these chains. As a result, no A_2 value could be derived from the combination theory for ψ and α_s^2. A more complete model may be obtained using the Yamakawa-Stockmayer-Shimada (YSS) theory, which takes into account the effects of excluded volume and chain stiffness [28]. Corresponding to the YSS theory of α_s^2, Yamakawa has extended the theory of A_2 to the HW model with a modification of the functional form of ψ, but here it is necessary to know the $\langle s^2 \rangle o$ value. On the other hand, to note that the slope for PMHS and PMHDS shows polymer chains consistent with a spherical conformation but surprisingly, the A_2 experimental value indicates that toluene is a good solvent, so long-range interactions occur (see Table VI). This unusual behaviour indicates that large alkyl groups have a profound effect on the molecular conformation because they adopt a compact conformation in a good solvent [12]. In addition, many properties of these polysiloxanes are still unknown today. We paid particular attention to the calculation of $A_2$by choosing a theoretical model in which the value of A_2 from SLS is in quantitative agreement with the value of the A_2 calculated by the theoretical model. Then, we considered rigid sphere molecules of radius $((\mathit{RMSradius})^2)^{1/2}$. PMHS and PMHDS A_2 can be calculated from Eq. (12) [see Appendix IV B of Ref. 17],

$$A_2 = \frac{4 N_A v_m}{{M_w}^2} \tag{12}$$

where $v_m = {}^4\!/_3 \pi \, (RMSradius)^3$ is the volume of the solute molecule. Since the volume of a spherical molecule is proportional to the molecular weight M_w, the second virial coefficient for a rigid sphere molecule is inversely proportional to M_w. The values of A_2 thus obtained and the ψ values from a model of rigid sphere molecules for PMHS and PMHDS are reported in Table VI.

With respect to PMHS, surprisingly, the theoretical value using rigid sphere molecules of radius $((\mathit{RMSradius})^2)^{1/2}$ and a simple model of the function f [Eq. (12)] agrees with the A_2 experimental value of PMHS from the GPC/LS coupled system. However, the A_2 value of PMHDS from the theoretical model becomes larger than the A_2 values from SLS. PMHS and PMHDS samples were of low molecular weight early oligomers. The weight-average degrees of polymerization, N, are 34.65 (PMHS) and 35.14 (PMHDS), *i.e.*, they are of similar N. However, the *RMSradius* values from the GPC/LS coupled system were very different, between PMHS (9.4 nm) and PMHDS (17.9 nm), indicating that the determination of the *RMSradius* value from the GPC/LS system was strongly influenced by the interaction between the bulky side group and the main chain. It is possible that the A_2 experimental value is obtained because the effects of screening originate in a bulky side group. In addition, the effects of chain ends seem to be important because the samples are of a low molecular weight [25].

3.3. Second Virial Coefficient of PMPS

In this paper, the study of A_2 was conducted with a poly(arylalkylpolysiloxane) (PMPS). In this polymer, the chains show stiffness in toluene according to the slope value (see Table I). Of the all samples studied here, the PMPS chains showed the most extended conformation. It is quite possible that this conformation with its excluded volume effects may arise from the orientation of the phenyl groups coupled with an attractive interaction between the side groups. This interaction is a consequence of the separation of adjacent phenyl rings and their orientation parallel to the siloxane bond [18, 29]. Also, in our previous work related to polysiloxanes, we obtained the PMPS $\langle s^2 \rangle o$ using the blob model [18]. With this value, an α_s^2 value of 1.21 was calculated (Table VII). The value in the bulk state must be 1.0. This result shows that the $\langle s^2 \rangle_o$, according to the blob model agrees with the Gaussian scaling of PMPS coils in the bulk state.

TABLE VI. Values of A_2 and Ψ for the poly(methylhexylsiloxane) and poly(methyl- hexadecylsiloxane).

Sample	$A_2 \times 10^2$ (g^{-2} ml)*	Ψ (mol^{-1})*	$A_2 \times 10^2$ (g^{-2} ml)**	Ψ(mol^{-1})**
PMHS	23.0	0.35	20.10	0.30
PMHDS	35.0	0.30	52.00	0.44

*A_2values from SLS data.

**A_2values from a model of rigid sphere molecules for ψ

TABLE VII. Values of the square of the unperturbed root-mean- square radius of gyration from the blob model and α_s^2 of PMPS.

Samples	$\langle s^2 \rangle_o$ (nm^2)	(*RMSradius*)^2 (nm^2)*	α_s^2
PMPS	366.08	445.21	1.21

*(*RMSradius*)^2 value from Table I.

TABLE VIII. Values of A_2 and Ψ for the poly(methylphenylsiloxane) sample.

Sample	$A_2 \times 10^3$ (g^{-2} ml)*	Ψ (mol^{-1})*	$A_2 \times 10^3$ (g^{-2} ml)**	Ψ (mol^{-1})**
PMPS	21.1	0.02	5.3	0.07

*A_2 values from SLS data.

** A_2 and Ψ from theoretical values: (FKO,o) for Ψ and (F,o) for α_s^2.

TABLE IX. Values of Ψ for the series of polysiloxanes.

Sample	Ψ (mol^{-1})*	Ψ (mol^{-1})**
PDMS1	0.45	0.34^a
PDMS2	0.29	0.27^b
PDMS3	0.60	0.50^c
PDES	0.06	0.15^d
PMHS	0.35	0.30^e
PMHDS	0.30	0.44^f
PMPS	0.02	0.07^g

Using M_W, A_2 ,and *RMSradius* obtained from light-scattering measurements in Eqs. (9) and (11).

** Theoretical values from: ^{a,d,g} (FKO,o) for Ψ and (F,o) for α_s^2 , ^{b,c} (FKO,m) for Ψ and (F,m) for α_s^2, ^{e,f} model of rigid sphere molecule for Ψ.

For PMPS, the A_2 theoretical value was calculated considering a rigid rod molecule model (extended cylinder) with a length of L=25.27 nm (PMPS end-to-end distance at full extension) and a diameter of d = 0.58 nm (total-trans stable conformation: TT). The theoretical model used considers L$\gg$d using a rod molecule. In this study, the TT zig-zag stable conformation is used to calculate the PMPS diameter [30,31]. In this conformation, the geometry of the Si-O-Si backbone forces the aromatic rings out of coplanarity with an angle of 33.5°. Horta *et al.* give an excellent analysis of the local conformation of PMPS in Ref. 29. The A_2 for rigid rod molecules has been calculated from Eq. (13),

$$A_2 = \frac{\pi}{4} \frac{N_A d L^2}{M^2} \tag{13}$$

This expression contains ψ in approximation to a rigid rod conformation developed in Appendix IVA of Ref. 17. The ψ values and A_2 values according to the theoretical model and from SLS of PMPS are reported in Table VIII.

The value of A_2 obtained from the GPC/LS system was considerably larger than the value of A_2 from the theoretical model. This difference can be a consequence of several factors: (1) the theory for the HW model predicts that the chain stiffness has a significant effect on A_2 and α_s^2 (the PMPS chains are rod-like); (2) the TP theory is true to the coil limit ($M_w \rightarrow \alpha$) but our PMPS sample had a low M_w (see Table I), and in this region the effects of the chain ends are important; and finally, (3) the value of L/d radio was $\sim$ 43.6 and the PMPS A_2value obtained is for a relatively short chain ($\sim$ 21 nm). Therefore, we conclude that the criterion of validity (L$\gg$d) cannot be true in this case [23, 24].

With respect to the difference between the ψ value using the M_w, (*RMSradius*)^2, and A_2 values from SLS data and from thermodynamics basic theories, we noted that this could be due to the difficulty in obtaining a complete quantitative agreement between theory and experiment (see Table IX). Therefore, the polysiloxanes present opportunities for extensive theoretical studies which could result in generating a model that would include the effect of a rigid rod and a compact chain in a good solvent with chain ends. Beyond this, it will be very complicated to obtain any model for ψ [11,15-17,25].

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