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Short- and Long-range Interaction Parameters for Polydimethylsiloxanes with Different Terminal Groups

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SUMMARY: The paper discusses the behaviour of polydimethylsiloxanes with different terminal groups as induced by polymer molecular weight and solvent mixture composition in dilute solution.

Introduction

Due to their peculiar properties - high chain flexibility, very low glass transition temperature and very small bulk modulus[1-3] the polysiloxanes represent a group of quite unique polymers. However, these properties refer to those in the bulk state, so that it is not adequate to conclude that single, isolated polydimethylsiloxane chains in dilute solution are very flexible. Literature data[4] suggest that polydimethylsiloxane chains are rather stiff in this static sense. Due to these considerations, the study of oligo- and polysiloxanes in solution presents a great interest.

The present paper discusses the excluded volume effect of polydimethylsiloxanes with different terminal groups in dilute solution through the intrinsic viscosity, the mean dimension, the second virial coefficient as a function of the expansion factor.

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Experimental

The polymers under study were oligo- (ODMS) and polydimethylsiloxanes (PDMS) (I), α, ω-bis-hydride-polydimethylsiloxanes (II) and α, ω-bis-(3-aminopropyl)-oligo- and polydimethylsiloxanes (ODMS-NH_2, PDMS-NH_2) (III) obtained by anionic polymerization[5,6]. They were investigated by gel permeation chromatography (GPC), potentiometric titration, viscometry and interferometry.

The intrinsic viscosities $[\eta]$ (ml/g) in toluene (T) were determined in the 20-32°C temperature range using an Ubbelohde suspended-level viscometer, and were treated by the Huggins plots. The flow volume of the viscometer used was greater than 5 ml, making drainage errors unimportant[7]. Values of $[\eta]$ were accurate to within ± 2 %.

Using the Qian and Rudin[8,9] method, the mean dimensions for a large concentration range were obtained[10,11] (Tab. 1).

Results and discussion

Starting from chain dimension, second virial coefficient and intrinsic viscosity data, Tab. 1 presents the excluded volume effect for the studied sytems[10], through the interpenetration function $\psi(z)$ (according to eq. (1)), the hydrodynamic penetration function $\pi(z)$ (according to eq. (2)) and the expansion factor α_S (eq. (3)):

$$\psi(z) = \frac{A_2 M^2}{4\pi^{3/2} N_A < S^2 >^{3/2}} \tag{1}$$

$$\pi(z) = \frac{A_2 M}{[\eta]} \tag{2}$$

$$\alpha_s^2 = \frac{< S^2 >}{< S_\theta^2 >} \tag{3}$$

$< S^2 >^{1/2}$ and $< S_\theta^2 >^{1/2}$ being the perturbed and unperturbed radii of gyration at zero concentration and in theta condition, respectively, M the molecular weight of the polymer, A_2 the second virial coefficient and N_A Avogadro's number.

The second virial coefficient from Tab. 1 was determined for the studied systems[10] from viscosity data according to Qian and Rudin model[9, 12-14] which considers the polymer solution as a dilute suspension of hard spheres (eq. 4).

$$A_2^* = \frac{16\pi N_A [\eta]}{9.3 \cdot 10^{24} M\{1 + ([\eta] - [\eta]_\theta)(1 - \exp(-c/c^*)/[\eta]_\theta\}} \tag{4}$$

A_2^* as defined here differs from the conventional second virial coefficient A_2, which is independent on concentration over the experimental concentration range. Eq. (4) can be used to calculate the osmotic pressure π of a polymer solution with concentration c from eq. (5).

Tab. 1. Intrinsic viscosities $[\eta]$ (ml/g), intrinsic viscosities under theta conditions $[\eta]_\theta$, perturbed ($<S^2>^{1/2}$) and unperturbed ($<S_\theta^2>^{1/2}$ radii of gyration and unperturbed dimensions parameters ($<S_\theta^2>/M$) of polysiloxanes in toluene at different temperatures.

Code	M_n $(\cdot 10^{-4})$	T/°C	$[\eta]$ (ml/g)	$[\eta]_\theta$ (ml/g)	$<S^2>^{1/2}$ $(\cdot 10^7)$ (cm)	$<S_\theta^2>^{1/2}$ $(\cdot 10^7)$ (cm)	$\frac{<S_\theta^2>}{M}$ $(\cdot 10^{18})$ (cm^2)
I	0.17	25	3.1	2.8	1.196	1.212	8.59
	0.42	25	5.8	4.9	1.989	1.876	8.36
	0.80	30	2.0	7.1	1.738	2.624	8.60
	4.31	25	33.0	15.6	7.710	6.001	8.36
	5.82	25	49.4	18.1	9.754	6.980	8.36
II	0.20	25	3.2	2.5	1.275	1.166	6.80
	0.30		3.0	3.0	1.431	1.431	6.83
	0.70		6.5	4.6	2.451	2.182	6.80
	1.20		9.7	8.7	3.349	3.233	6.84
	2.50		16.0	8.7	5.054	4.124	6.80
III	0.23	30	3.1	3.8	1.324	1.420	8.69
	0.51		5.7	5.7	2.107	2.103	8.69
	1.27		9.0	8.9	3.332	3.327	8.69
	1.66		14.0	10.2	4.217	3.798	8.69
	2.42		16.3	12.4	5.033	4.590	8.69
	5.00		30.8	17.8	7.920	6.591	8.69
	10.00		50.6	25.1	11.770	9.322	8.69

$$\frac{\pi}{c}=\frac{RT}{M_n}\left(1+\frac{A_2^* M_n c}{2}\right)^2 \qquad (5)$$

To obtain a concentration-independent second virial coefficient A_2, one can plot calculated

$(\pi / c)^{1/2}$ (eq. (5)) values against c and fit a least-squares straight line to the results to derive A_2 from the slope. This procedure involves a direct simulation of the raw experimental data points, which are then treated exactly as in the real experiment, to predict the second virial coefficient of the real polymer solution [15,16].

If at high excluded volume $\psi(z)$ tends assymptotically to a constant value, at small excluded volume literature data present a dispersity of experimental $\psi(z)$ values[17-20]. Yamakawa[17,20] predicted a regularity of the experimental points in the low excluded volume region if either polymer molecular weight or solvent quality are modified.

In a previous paper[10] the excluded volume effect for ODMS-NH_2 was modified by changing solvent quality. Negative excluded volume effects were obtained in T, for the whole studied temperature range, as well as for different toluene/acetone (T/A) mixtures, i.e., for ϕ_1=0.7 (28-32°C), ϕ_1=0.54 (28-30°C) and ϕ_1=0.46 at 28°C. It is reasonable to consider that this behaviour is a consequence of the non-Gaussian character of the flexible chains tending to a collapsed state in a good solvent, a state vanishing with the increase of the amount of the nonsolvent in the system.

Figs 1 and 2 present the static and dynamic penetration functions $\psi(z)$ and $\pi(z)$ against the excluded volume effect, one side by changing the solvent quality and on the other side by changing the polymer molecular weight. These values are compared with the penetration functions for the PDMS/toluene system[21], obtained with eqs. (1), (2) - where the second virial coefficient was determined in the same way as in the present study, starting from viscometric data and using eq. (4) - as a function of the excluded volume effect modified changing the polymer molecular weight.

A dispersity of the experimental data for low values of the excluded volume effect was observed. However, in the low excluded volume region one can observe a slight difference between the variation of the functions $\psi(z)$ and $\pi(z)$ if either polymer molecular weight or solvent quality are modified. The same conclusion yielded from Yamakawa studies[20] for polystyrene and poly(methyl methacrylate), but the differences were more important.

Conclusions

The variation of the interpenetration function $\psi(z)$ and $\pi(z)$ as a function of polymer molecular weight for PDMS-NH_2/T were discussed. The data were compared with previous data obtained for the interpenetration function $\psi(z)$ and $\pi(z)$ by varying the solvent composition for ODMS-NH_2/T/A. It was pointed out that in the low excluded volume effect region these functions have a different behaviour and agree with Yamakawa et al. results for other polymers.

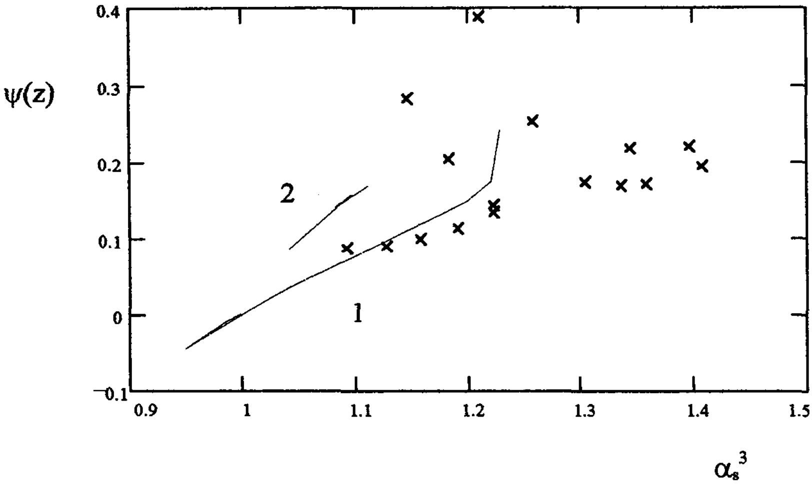

Fig 1. Plots of $\psi(z)$ *vs.* α_s^3 for PDMS/T (curve 1)[21)], PDMS-NH_2/T of different polymer molecular weights (x) and PDMS-NH_2/T/A of different solvent mixtures (curve 2).

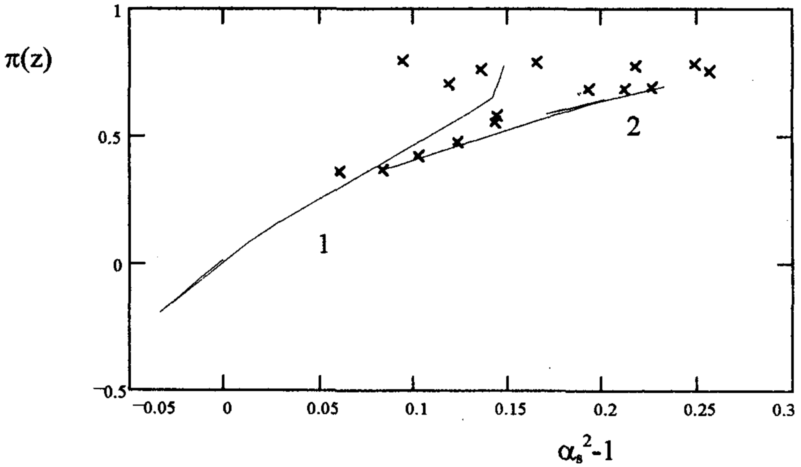

Fig 2. Plots of $\pi(z)$ *vs.* (α_s^2-1) for PDMS/T (curve 1)[21)] and PDMS-NH_2/T systems for different polymer molecular weights (x) and different solvent mixtures (curve 2).

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