# Intrinsic viscosity and hydrodynamic radius of atactic poly(methylphenylsiloxane)

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Viscosity and quasi-elastic light scattering measurements of poly(methylphenylsiloxane) samples with well defined tacticity and different molecular weights have been performed in several solvents. From these data, the mean dimensions of the chain have been estimated in terms of characteristic ratios. Similarities and differences between the results obtained with both techniques, and comparisons with results previously reported for other siloxanes, and with theoretical calculations are analysed and discussed.

**(Keywords: poly(methylphenylsiloxane); PMPS; light scattering measurements)**

## INTRODUCTION

The conformational properties of polysiloxanes have been extensively studied from the theoretical and experimental point of view[1–27]. The effect of side substituent groups on these properties with respect to the values corresponding to the similar poly(dimethylsiloxane) (PDMS) chain has been shown to be small in some properties such as the dipole moment[10,16,22,26]. However, this effect is more pronounced in the case of mean dimensions, obtained from hydrodynamic properties or light scattering measurements[15,17,18]. Moreover, the agreement between theoretical and experimental values is not good for some chains, e.g. poly(dipropylsiloxane)[17,21]. In the case of chains with asymmetric centres, the experimental studies have been restricted up to the present to samples with unknown tacticity[19] and this circumstance introduces a certain degree of ambiguity in the conclusions.

With the aim of overcoming this difficulty we have started a systematic investigation of different experimental properties of samples of poly(methylphenylsiloxane) (PMPS) chains of well defined tacticity. In previous work the results on dipole moment[26,26], fluorescence[28–30], partial specific volume[25] and Kerr constant[24] have been reported. Here we present two types of experimental data that can be directly related with the mean dimensions of the chain: viscosity and quasi-elastic light scattering measurements. The results obtained with these two different techniques are compared with theoretical values, and with results corresponding to other siloxane chains.

## EXPERIMENTAL

### *Polymers*

Four fractions of poly(methylphenylsiloxane), PMPS, denoted PMPS-2, PMPS-3, PMPS-4 and PMPS-5, were selected for the present work. The initial polymer sample was fractionated as reported previously[26]. The fractions were characterized by g.p.c. and light scattering (l.s.)[26] and their tacticity was determined by $^{1}$H n.m.r. (51% meso and 49% racemic, in diads)[31]. Molecular weights and polydispersity of the samples are reported in *Table 1*.

### *Solvents*

Cyclohexane (Ch), methylcyclohexane (MeCh) and tetrahydrofurane (THF) were Carlo Erba RPE for the viscosity measurements. BDH spectroscopic grade cyclohexane was used for quasi-elastic l.s. The refractive index, density and viscosity of the solvents were taken from the literature[32–34].

### *Viscometry*

Viscosity of the polymer solutions was measured in a modified Ubbelohde viscometer which had been previously calibrated. Precision in the efflux times was 0.1 s and temperature was controlled to ±0.05°C. Polymer solutions were obtained by successively diluting an initial PMPS solution, $c$ never exceeding $8\times10^{-3}\,\mathrm{g\,cm^{-3}}$. Kinetic energy corrections (always less than 2%) and density corrections (<1%) were introduced in the calculation of viscosities. Intrinsic viscosities were determined by means of Huggins ($\eta_{sp}/c$ *versus* $c$) and Kraemer ($\ln\eta_r/c$ *versus* $c$) extrapolations. The values of $[\eta]$, and the Huggins constant, $k_H$, were obtained by least-squares linear fitting of the experimental data.

### *Quasi-elastic light scattering*

The solutions for quasi-elastic l.s. measurements were prepared by dissolving a known quantity of the polymer in the solvent which was filtered prior to use. Filtrations were carried out through 0.5 $\mu$m Millipore Teflon filters. The concentrations ranged from 0.75 to 2.0 mg cm$^{-3}$. On the spectrometer, the cell was contained in an enclosure

**Table 1** Molecular weight and polydispersity of PMPS fractions

| Fraction | PMPS-2 | PMPS-3 | PMPS-4 | PMPS-5 |
|---|---|---|---|---|
| $M_w\times10^{-5}$ (l.s.) | 4.56 | 4.31 | 2.27 | 1.17 |
| $r=M_w/M_n$ (g.p.c.) | 2.53 | 2.04 | 1.65 | 1.76 |

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**Table 2** Limiting viscosity number, $[\eta]$, and Huggins constant, $k_H$, of several PMPS samples in different solvents

| | PMPS-2 | | PMPS-3 | | PMPS-4 | | PMPS-5 | |
|---|---|---|---|---|---|---|---|---|
| Solvent and temperature | $[\eta]$ (dl g$^{-1}$) | $k_H$ | $[\eta]$ (dl g$^{-1}$) | $k_H$ | $[\eta]$ (dl g$^{-1}$) | $k_H$ | $[\eta]$ (dl g$^{-1}$) | $k_H$ |
| $MeCh_{20°C}$ | 0.546 | 0.36 | 0.544 | 0.35 | 0.395 | 0.39 | 0.254 | 0.37 |
| $Ch_{25°C}$ | 0.641 | 0.40 | 0.637 | 0.46 | 0.478 | 0.40 | 0.286 | 0.40 |
| $Ch_{50°C}$ | 0.783 | 0.36 | 0.766 | 0.33 | 0.540 | 0.39 | 0.325 | 0.42 |
| $THF_{25°C}$ | 1.235 | 0.28 | 1.220 | 0.29 | 0.834 | 0.32 | 0.486 | 0.34 |

**Table 3** $K$ and $a$ Mark–Houwink parameters, together with unperturbed dimensions, $K_\theta$, interaction parameter, $B$, and characteristic ratio $C_\infty$ obtained from SF extrapolations, for PMPS in different solvents

| Solvent and temperature | $K\times10^2$ (cm$^3$g$^{-1}$) | $a$ | $K_\theta\times10^2$ (cm$^3$g$^{-1}$) | $B\times10^{29}$ (cm$^3$g$^{-1}$mol) | $C_\infty$ |
|---|---|---|---|---|---|
| $MeCh_{20°C}$ | 3.06 | 0.58 | 6.50 | 0.191 | 10.2 |
| $Ch_{25°C}$ | 2.73 | 0.60 | 7.15 | 0.293 | 10.8 |
| $Ch_{50°C}$ | 1.56 | 0.65 | 7.15 | 0.521 | 10.8 |
| $THF_{25°C}$ | 1.65 | 0.69 | 9.60 | 1.040 | 13.4 |

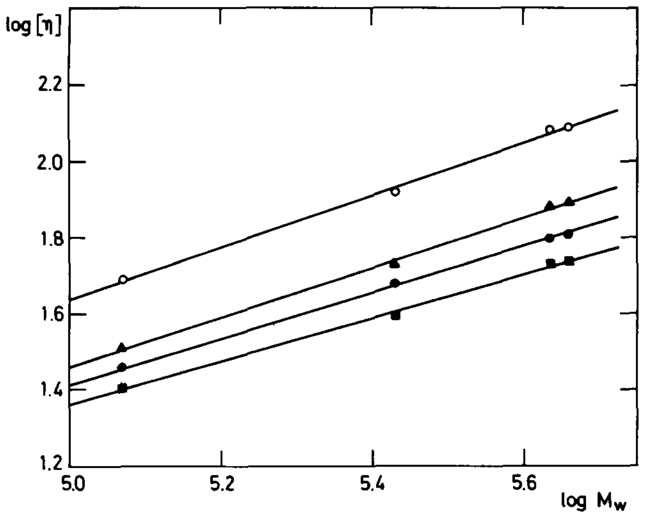

**Figure 1** Mark–Houwink representations for PMPS in different solvents: (○) THF at 25°C, (▲) Ch at 50°C, (●) Ch at 25°C and (■) MeCh at 20°C

which maintained the temperature constant to 0.1°C. The beam from a Coherent Radiation Model CR-2 argon ion laser operating at 488 nm was focused at the centre of the cell. The light scattering at the angle $\theta=90°$ was detected by an ITT FW130 photomultiplier tube. The pulses corresponding to individual photons were standardized, amplified and finally fed into a Malvern K7023 correlator. The normalized correlation functions were computer fitted to the function $1+A\exp(-\Gamma\tau)+\delta$ with $A$, $\Gamma$ and $\delta$ as adjustable parameters and the diffusion coefficients, $D$, were obtained from $\Gamma=2Dq^2$, where $q$ is the scattering vector, $q=(4\pi/\lambda)\sin\theta/2$ ($\lambda$ is the wavelength of the incident light).

## RESULTS

The limiting viscosity numbers for the different fractions are shown in *Table 2* together with the Huggins constants, $k_H$, in Ch at 25 and 50°C, THF at 25°C and MeCh at 20°C. In *Table 3* we show the $K$ and $a$ Mark–Houwink parameters, obtained from least squares linear fits in $\log[\eta]$ *versus* $\log M_w$ representations (see *Figure 1*).

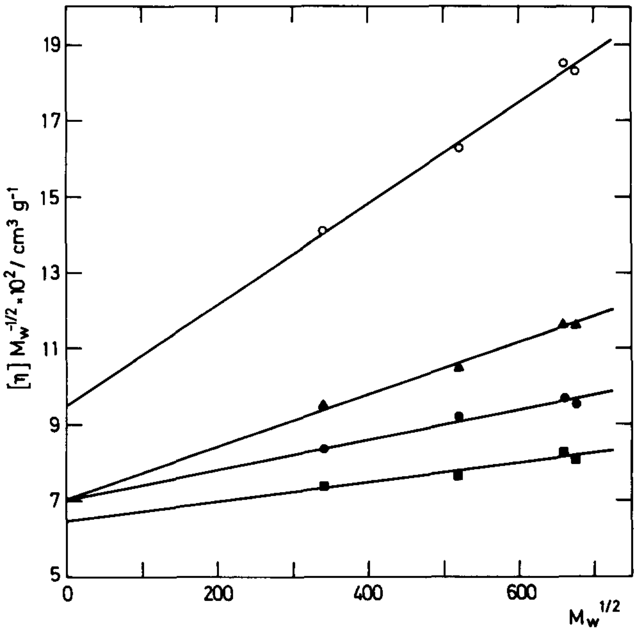

**Figure 2** Stockmayer–Fixman extrapolations for PMPS in different solvents: (○) THF at 25°C, (▲) Ch at 50°C, (●) Ch at 25°C and (■) MeCh at 20°C

We treated the $[\eta]$ results according to the extrapolation procedure of Stockmayer and Fixman (SF) in order to obtain the unperturbed dimensions of the polymer, $K_\theta$:

$$[\eta]M_w^{1/2}=K_\theta+C'\Phi BM_w^{1/2}$$

where $B$ is the interaction parameter, $C'$ is a purely numerical factor (usually 0.51) and we have adopted the value $2.5\times10^{23}\,\mathrm{mol}^{-1}$ for the Flory constant $\Phi$, in accordance with the most recent experimental data[35]. A SF plot of $[\eta]M_w^{1/2}$ *versus* $M_w^{1/2}$ is shown in *Figure 2* for the different solvents. A reasonably good linear behaviour is observed in all cases. The values of $K_\theta$ are calculated as intercepts of least squares linear fittings.

Our quasi-elastic l.s. experiments have allowed us to obtain values of $D$ within the low concentration range described in the experimental section. These values have been extrapolated to infinite dilution in order to calculate the hydrodynamic radius of the chains, $R_h$, from

$$D_{c=0}=k_BT/f_t=k_BT/6\pi\eta_0R_h$$

where $k_BT$ is the Boltzmann factor, $f_t$ is the chain

**Table 4** Hydrodynamic radius, $R_h$, obtained from quasi-elastic light scattering measurements of different PMPS fractions in cyclohexane at 25.4°C, together with the Flory–ScheragaMaldelkern parameter $\beta$ obtained from these measurements and the corresponding viscosity values

| Fraction | PMPS-2 | PMPS-3 | PMPS-4 | Extrapolated value (see text) |
|---|---|---|---|---|
| $R_h$ (Å) | 174 | 160 | 122 | |
| $\beta \times 10^{-6}$ | 2.03 | 2.16 | 2.19 | 2.66 |

translational friction coefficient and $\eta_0$ is the solvent viscosity. In *Table 4* we report the results for $R_h$ corresponding to measurements of the fractions PMPS-2, PMPS-3 and PMPS-4 in cyclohexane at 25.4°C. From the results in *Table 4* we have estimated the unperturbed mean dimensions of the chains. Assuming that the expansion of the friction coefficients is a function of the molecular weight of the type

$$\alpha_f = f_t/(f_t)_0 = 1 + a_f M^{1/2}$$

where the subscript 0 refers to unperturbed conditions (this relationship can be justified for small values of the excluded volume parameter, $z \approx M^{1/2}$, using perturbation theories[36]) one can write

$$R_h/M^{1/2} = (R_h)_0/M^{1/2} + a_f (R_h)_0$$

where $(R_h)_0 = (f_t)_0/6\pi\eta_0 \approx M^{1/2}$, according to the Kirkwood–Riseman theory[36]. From a plot of $R_h/M^{1/2}$ *versus* $M^{1/2}$ we have obtained the value $(R_h)_0/M^{1/2} = 0.180$ Å (mol g$^{-1}$)$^{1/2}$ for the least squares fitted intercept.

## DISCUSSION

In *Table 3* we present the results for $K_\theta$ from our SF plots intercepts. It can be observed that the values of $K_\theta$ for PMPS in different solvents depend slightly on the thermodynamic quality of the solvent. It should be remarked that the values of $K_\theta$ for PMPS in cyclohexane at 25 and 50°C and in methylcyclohexane at 20°C are in good agreement. The highest result obtained in tetrahydrofurane can be attributed to the good thermodynamic quality of this solvent. The value of Mark–Houwink parameter $a = 0.68$ confirms that THF is a good solvent. In this case the SF extrapolation may not completely eliminate the excluded volume effect.

The parameter $B$ of SF (*Table 3*) has values also correlated with the thermodynamic quality of the solvent. We can observe that it is smaller for systems with a lower value of the Mark–Houwink parameter $a$. *Table 3* includes the results of the characteristic ratio $C_\infty$ in the different solvents. These results are calculated from the following formula, based on the Kirkwood–Riseman theory

$$C_\infty = M_0(K_\theta/\phi)^{2/3}/l^2$$

where $M_0$ is the molecular weight per skeleton bond and $l$ is the bond length. The agreement between the values obtained is good except in the case of THF. However, these results differ from those previously reported by Buch *et al.*[19] for PMPS samples of unknown tacticity. The differences can be attributed either to the influence of tacticity or to the difficulties of eliminating excluded volume through the SF extrapolation method.

From the extrapolated result for $(R_h)_0/M^{1/2}$ we can also estimate $C_\infty$ according to the formula

$$C_\infty = 6p^2[(R_h)_0/M]^2 M_0/l^2$$

($\rho$ is the ratio between radius of gyration and hydrodynamic radius).

We have adopted the $\rho = 1.28$ value obtained recently by Schmidt and Burchard[37]. We have obtained $C_\infty = 8.05$. It can be observed that this estimation for $C_\infty$ is somewhat lower than that obtained from the viscosity data, perhaps as a consequence of the smaller influence of excluded volume on translational diffusion that may facilitate the extrapolation procedure. The quasi-elastic l.s. estimation for $C_\infty$ is in agreement with the rotational isomeric model calculations performed for the PMPS chain by Mark and Ko[20]. On the other hand, the value of $C_\infty$ estimated from viscosity is clearly above the theoretical results. This situation is also found in other substituted siloxanes as poly(dipropylsiloxane)[17,21].

An alternative comparison between the viscosity and the quasi-elastic l.s. data can be performed by combining directly the data corresponding to similar samples and systems into the Flory–Scheraga–Maldelkern parameter $\beta$

$$\beta = ([\eta]M/100)^{1/3}\eta_0/f_t$$

The results are shown in *Table 4*. These results are close to the theoretical limit for a hard sphere ($2.12 \times 10^6$) and also to the estimations for a flexible coil based on the value for $\Phi$ and $\rho$ described above ($2.26 \times 10^6$) though a slight but significant variation with molecular weights is observed. In fact the extrapolated estimations for $K_\theta$ and $(R_h)_0/M^{1/2}$ yield a higher value ($\beta = 2.66 \times 10^6$) in direct connection with the differences observed in the values of $C_\infty$ calculated from the two different techniques.

## CONCLUSIONS

In this work we have obtained viscosity and quasi-elastic l.s. data for PMPS samples of known tacticity in order to determine the unperturbed dimensions of these chains and compare them with theoretical results as well as the values previously reported for polysiloxanes with other side substituents.

The combination of intrinsic viscosity and quasi-elastic l.s. data for the same polymer samples in similar thermodynamic conditions provides values of the parameter $\beta$ in good accordance with the theory. This confirms the consistency between data obtained by using these different experimental techniques. The estimation of unperturbed dimensions, on $C_\infty$, from SF extrapolations of viscosity data in solvents of different thermodynamic qualities are in good agreement, except for THF (best solvent with higher excluded volume effects). A similar estimation from quasi-elastic l.s. in Ch by means of an elementary procedure based on perturbation theory yields a value of $C_\infty$ smaller than those obtained from viscosity. These differences can be attributed to the influence (higher in viscosity) of excluded volume in the extrapolation procedures. The quasi-elastic l.s.

estimation is in good agreement with theoretical calculations based on the rotational isomeric model chains of similar tacticities. Higher estimations of unperturbed dimensions based on viscosity data have also been previously found for siloxane chains with other side substituents.

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