Solution properties of poly(methylphenyl)silane

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The solution properties of poly(methylphenyl)silane are studied in tetrahydrofuran at room temperature. Combined measurements by gel permeation chromatography (g.p.c.) and light scattering indicate that the absolute molecular-weight values of poly(methylphenyl)silane do not differ from the g.p.c. values obtained using a classical g.p.c. calibration with polystyrene standards. Some calculations are performed on the molecular-weight values using the theory of Yamakawa and Fujii. These results allow one to conclude that the behaviour in solution of poly(methylphenyl)silane can be described using a model based on rigid-rod-like elements involving about 40 Si atoms.

(Keywords: poly(methylphenyl)silane; solution properties; molecular parameters; photochemical degradation; hydrodynamic properties; persistence length)

INTRODUCTION

Since their discovery in the early 1980s, tractable polysilanes have provoked great interest in the scientific world including chemists, silicon specialists and physicists[1]. The attention of polymer scientists however did not cover equally the polysilane field. For instance, few studies were devoted to the behaviour of polysilanes in solution especially by the light scattering (l.s.) technique. To our knowledge only one paper has appeared on the subject[2] so far. Fundamental information should have been gained by such a study. As an example, the molecular-weight values by gel permeation chromatography (g.p.c.) are always quoted in polystyrene equivalents owing to the lack of l.s. characterization. Moreover, numerous papers[3] report a probable planar zig-zag conformation of the polysilane chain in solution extending up to 40–50 Si atoms, but no l.s. measurements were made to support these conclusions. It is the purpose of the present work to study a member of this class of new polymers by the l.s. technique: poly(methylphenyl)silane (PSi).

EXPERIMENTAL

Synthesis and fractionation

Methylphenyldichlorosilane was purchased from Alfa Products and fractionally distilled before use. The polymer synthesis was performed, as usual, by Würtz coupling in toluene[4]. The reaction took place in brown glassware under argon in order to avoid any photochemical scission during synthesis. In a typical run, 100 ml of toluene (freshly distilled on Na) was first introduced in a 500 ml round-bottomed flask together with sodium chunks (20% weight excess on stoichiometry). The system was brought to reflux temperature under magnetic stirring. Then the dichloride (0.1632 mol) was carefully introduced from a lateral pressure-equalized flask. The reaction was continued for 6 h. After cooling down, 10 ml of methanol and 200 ml of deionized water were introduced to neutralize the excess of sodium and dissolve the salts produced by the reaction. After decantation, the crude polymer was recovered from the organic phase by precipitation into methanol. The fractionation was performed from a 10% (w/v) solution in toluene by successive additions of isopropanol. When filtered off, the fractions were dried overnight at 120°C under vacuum.

Polymer characterization

'Static' light scattering measurements were performed on a modified FICA 42000 photogoniodiffusometer. The source was a 4 mW He–Ne laser providing 632 nm vertically polarized light. Samples were clarified by centrifugation for 2 h at 14 000 rev min^{-1}.

Refractive index increments (dn/dc) were measured with Brice-Phoenix differential refractometer at $\lambda_0 = 632$ nm.

The experimental g.p.c. device included two mixed-bed (100–10^5 Å) Shodex columns on-line with a Chromatix CMX 100 small-angle light-scattering detector ('dynamic' light scattering). The latter was followed by a refractive index (r.i.) detector (Shimadzu RID 6A).

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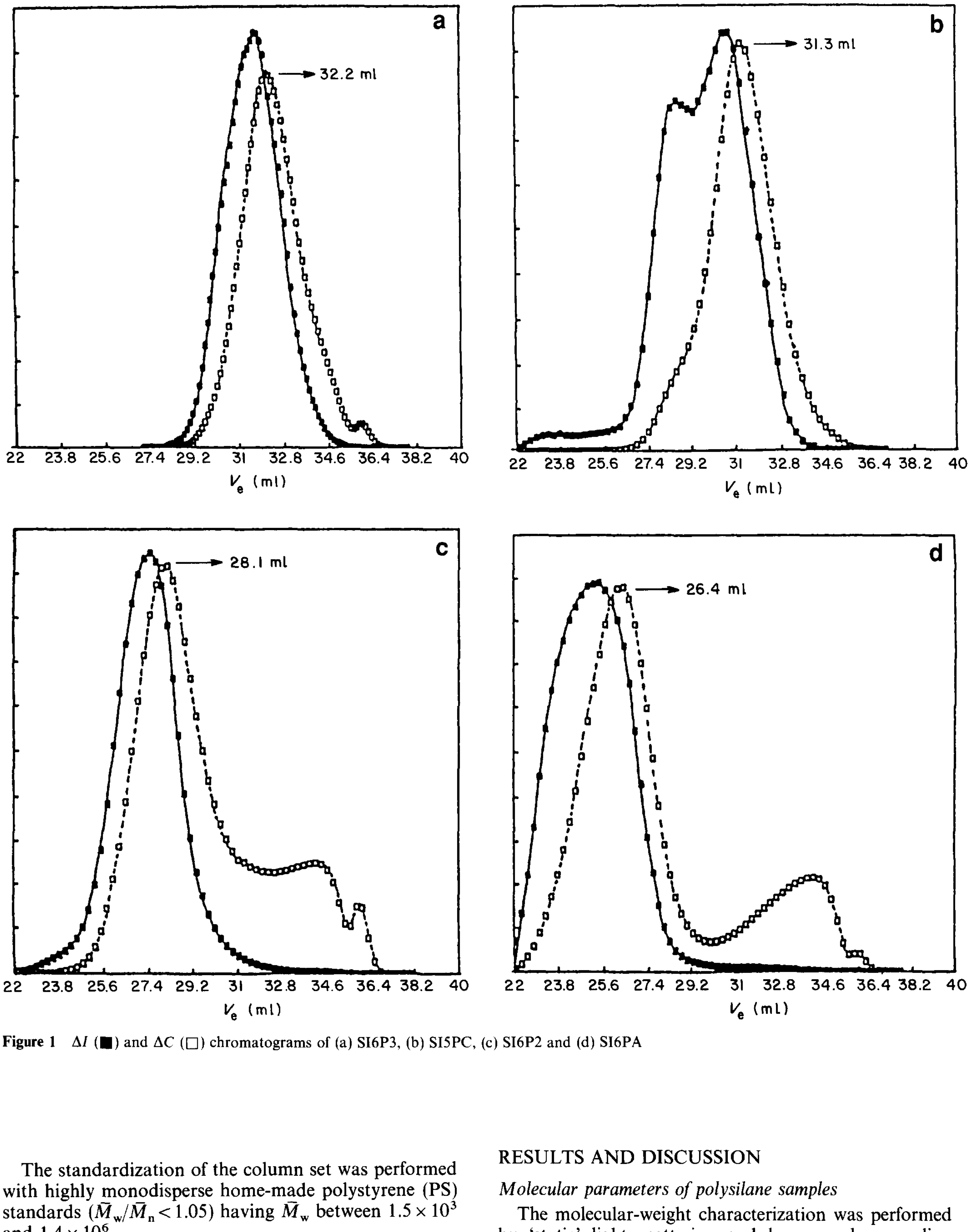

Figure 1 ΔI (■) and ΔC (□) chromatograms of (a) SI6P3, (b) SI5PC, (c) SI6P2 and (d) SI6PA

The standardization of the column set was performed with highly monodisperse home-made polystyrene (PS) standards ($\bar{M}_w/\bar{M}_n < 1.05$) having $\bar{M}_w$ between 1.5×10^3 and 1.4×10^6.

The resulting standardization curve provided 'apparent' polysilane molecular weights (so-called PS equivalent $\bar{M}_w$) $\bar{M}_w^{gpc}$. Absolute molecular weights (dynamic values) $\bar{M}_w^{dls}$ were obtained by coupling the ΔI (scattered intensity) signal with ΔC (concentration) signal from the r.i. detector.

In order to avoid any photochemical degradation, all of the operations were conducted in the absence of light.

RESULTS AND DISCUSSION

Molecular parameters of polysilane samples

The molecular-weight characterization was performed by 'static' light scattering and by g.p.c.–l.s. coupling ('dynamic' method) for six poly(methylphenyl)silane samples. Four ΔI (l.s.) and ΔC (r.i.) chromatograms are reported on *Figure 1*.

Absolute molecular weights (static method) $\bar{M}_w^{sls}$ of the samples were respectively 13800, 30200, 110000 and 420000 for SI6P3, SI5PC, SI6P2 and SI6PA.

The depolarization ratio ρ_v has been measured for the

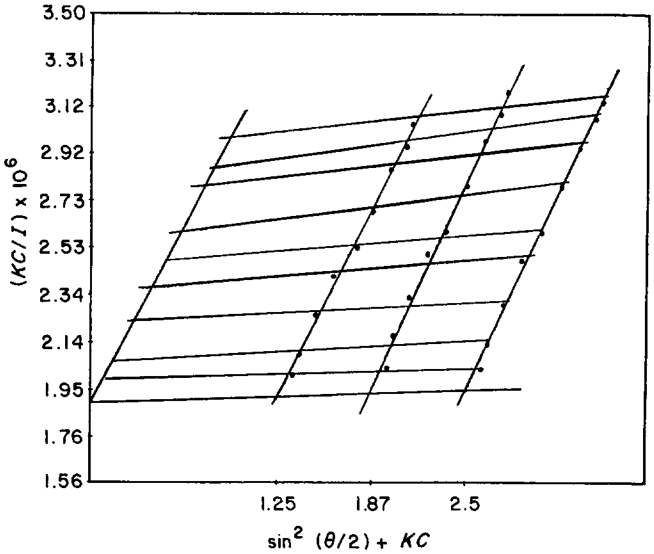

Figure 2 Zimm plot of SI5PA sample

Table 1 Molecular parameters of PSi samples (l.s. by static method $\bar{M}_w^{sls}$ and by dynamic method $\bar{M}_w^{dls}$)

	d*n*/d*c*				
Sample	Meas.	Calc.	$\bar{M}_w^{sls}$	$\bar{M}_w^{dls}$	$\bar{M}_w^{gpc}$
SI5P3	0.268	0.270	9 530	10 000	9 300
SI6P3	0.274	0.273	13 800	11 300	15 500
SI5PC	0.283	0.278	30 200	27 800	39 000
SI6P2	0.268	0.262	110 000	113 000	150 000
SI6P2[a]	0.268	0.266	100 000	115 000	158 000
SI6PA	0.258	0.254	420 000	435 000	512 000
SI5PA	0.262	0.263	478 600	598 000	708 300
SI5PA[a]	0.262	0.263	523 000	600 000	652 000

[a] Degraded samples: $t = 0$ (see *Table 2*)

two lowest molecular-weight samples (SI5P3 and SI6P3). The values are very low (<0.01) so that the correction for the molecular weight is negligible.

Figure 2 reports a typical Zimm plot (sample SI5PA; absolute $\bar{M}_w$ by static l.s. 526 000).

In *Table 1* are gathered the figures of $\bar{M}_w^{sls}$, $\bar{M}_w^{dls}$ and $\bar{M}_w^{gpc}$. Measured d*n*/d*c* are also reported in *Table 1* together with a d*n*/d*c* value calculated from the standardization constant of the refractometer for PS and PSi.

It can be observed in *Table 1* that the d*n*/d*c* values (measured and calculated) show limited but significant variations from sample to sample. As these variations are erratic they cannot be due to end-group concentrations. Most probably they arose from a small amount of foreign chemical groups (maybe siloxanes) resulting from the synthesis and exhibiting very different polarities. The present measurement of d*n*/d*c* suggests that the single d*n*/d*c* values of Cotts *et al.*[2] are perhaps oversimplified.

There is also very significant evolution for ΔI and ΔC chromatograms: Low-molecular-weight samples ($\bar{M}_w < 20\,000$) are characterized by a sharp distribution ($\bar{M}_w/\bar{M}_n < 2$) (see for instance *Figure 1a*). Medium-molecular-weight samples (*Figure 1b*) show a shoulder on the high-molecular-weight side. High-molecular-weight samples exhibit a bimodal distribution (*Figures 1c* and *d*) with a second peak on the low-molecular-weight side. This peak is characterized by a very low scattered intensity. The latter samples consequently show high polydispersity index ($\bar{M}_w/\bar{M}_n > 10$).

Another noticeable result in *Table 1* is the fairly good correspondence between $\bar{M}_w^{sls}$ and $\bar{M}_w^{dls}$ for all samples but the highest $\bar{M}_w$. This latter result is reproducible, and no explanation can be found so far.

More important is the correlation between $\bar{M}_w^{gpc}$ and both $\bar{M}_w^{sls}$ and $\bar{M}_w^{dls}$. As we have already published recently[5], the conversion factor of $\bar{M}_w^{gpc}$ (PS calibration) to obtain absolute values is close to 1, which is very different from the factor 2 or 3 reported in previous papers[6]. This point will be studied in more detail below.

Photochemical degradation

Two samples (SI6P2 and SI5PA) were photochemically degraded for increasing periods of time (15 min to 4 h) following a simple procedure described previously[7]. The degraded samples were analysed by the g.p.c.–l.s. on-line device. ΔC and ΔI chromatograms of SI6P2 sample after three different degradation times (0 h, 0.5 h, 4 h) are reported in *Figure 3*. As previously observed (for

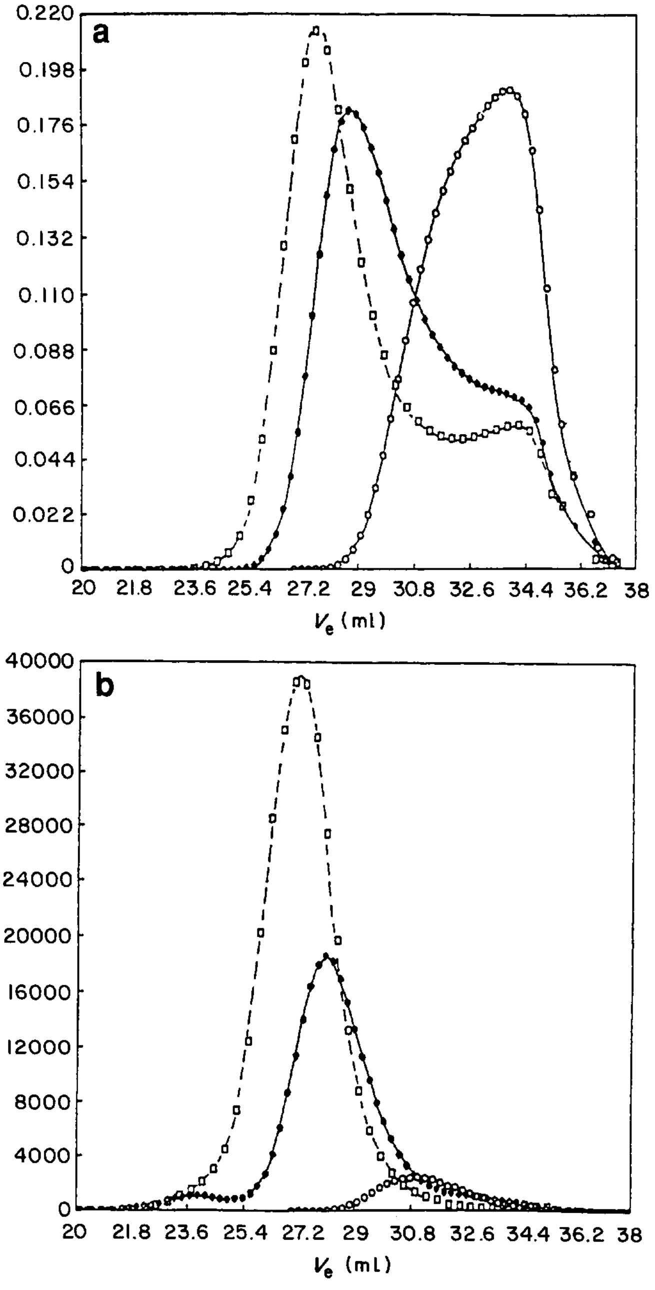

Figure 3 ΔC (a) and ΔI (b) chromatograms of SI6P2 sample after different degradation times: (□) 0 h, (●) 0.5 h and (○) 4 h

Table 2 Evolution of the molecular weight with the degradation times for PSi samples (daylight exposure)

Sample	t (h)	$\bar{M}_w$	$(\bar{M}_w/\bar{M}_w)_{t=0}$	I^a
SI6P2	0	115 000	1	~30
	0.50	59 600	0.518	17
	1	21 250	0.185	8
	2	15 980	0.138	5.4
	4	8 180	0.073	4.7
SI5P2	0	600 000	1	~24
	0.25	296 000	0.493	~26
	0.50	87 000	0.145	9.1
	1	61 000	0.102	7.7
	2	60 100	0.100	7.6

[a] $I = \bar{M}_w/\bar{M}_n$

poly(cyclohexylmethyl)silane[7]) a fast photoscission takes place. The peak of the ΔI chromatogram shows a fast decrease together with a shift to high retention times. The $\bar{M}_w$ variations induced by this treatment appear clearly in *Table 2*.

For instance, 2 h of daylight exposure suffices to lower $\bar{M}_w$ by a factor of about 10. The polydispersity (from ΔC chromatogram) decreases apparently up to 5 for the SI6P2 sample and up to 7.6 for the SI5PA sample. This should be related with the photosensitivity of high-$\bar{M}_w$ molecules of PSi to daylight ($\lambda > 330$ nm), known to be large compared to the insensitivity of the low-$\bar{M}_w$ fraction[8].

As a blank experiment it has been verified that SI6P2 sample in tetrahydrofuran (THF) did not undergo any observable degradation for 48 h in the dark.

Hydrodynamic properties of PSi

As reported before, the factor to convert $\bar{M}_w^{gpc}$ (PS calibration) into $\bar{M}_w^{dls}$ or $\bar{M}_w^{sls}$ is close to 1, lower by far than the previously reported values[6].

However, this factor is systematically lower than 1. Assuming a molecular-weight separation on the basis only of steric exclusion (no retention on columns), then the constancy of the hydrodynamic volume $[\eta]M$ leads to a significant viscosity difference between PS and PSi fractions of identical molecular mass M.

This can be written for a given elution volume (V_e):

$$[\eta]_{PS} M_{PS} = [\eta]_{PSi} M_{PSi} \qquad (1)$$

and

$$[\eta]_{PSi} = \frac{[\eta]_{PS} M_{PS}}{M_{PSi}} \qquad (2)$$

where M_{PS} is deduced from the PS standardization of the column and therefore equals $\bar{M}_w^{gpc}$ of the fraction eluting at V_e in our notation. $[\eta]_{PS}$ is the intrinsic viscosity of PS corresponding to this molecular weight ($[\eta]_{PS}$ (ml g^{-1}) $= 14 \times 10^{-3} M_{PS}^{0.7}$ in THF[9]). M_{PSi} is the molecular weight of polysilane as deduced from the g.p.c.–l.s. coupling, which means $\bar{M}_w^{dls}$ of the fraction eluting at V_e following our notation.

Equation (2) allows the calculation of a Mark–Houwink viscosity law from the g.p.c.–l.s. analysis of a large number of PSi fractions.

In a first step, only a few fractions were analysed. These fractions corresponded to the top of the peaks on ΔC chromatograms of the initial fractionated samples and of the SI6P2 photodegraded samples. The results are reported in *Table 3*. The viscosity law (in log–log correlation) is reported in *Figure 4*. The variation is far from the linear one that should be obtained for perfectly flexible chains. It corresponds to semi-rigid chain behaviour[10]. The slope is around 1.2 for low molecular weights and decreases when the molecular weight becomes higher.

In order to study this variation in closer detail, 35 fractions were selected on both sides of the ΔC chromatogram peaks. The results of the above analysis are reported in *Figure 5* and confirm the previous results. Two different Mark–Houwink relationships can be written depending on the molecular-weight range:

$$[\eta]_{PSi}\ (\text{ml g}^{-1}) = 8.1 \times 10^{-5} (M_w^{dls})^{1.28}$$

$$(8000 < M_w^{dls} < 30\,000) \qquad (3)$$

$$[\eta]_{PSi}\ (\text{ml g}^{-1}) = 15.8 \times 10^{-2} (M_w^{dls})^{0.56} \qquad (M_w^{dls} > 120\,000) \qquad (4)$$

In the intermediate region, linear viscosity laws can also be written but for limited molecular-weight ranges. For instance, three laws are reported in *Table 4*.

It can be deduced from this analysis that the hydrodynamic properties of poly(methylphenyl)silane are characterized by semi-rigid chain conformation or by a model of chain persistence length. The calculations of the parameters for such a model are proposed in the next section.

Table 3 Molecular weights (apparent and absolute) and viscosity of selected PSi fractions. $[\eta]_{PS}$ is the PS viscosity calculated from $[\eta]$ at the corresponding retention times

$\bar{M}_w^{dls}$	$\bar{M}_w^{gpc}$	$[\eta]_{PS}$	$[\eta]_{PSi}$
7 670	8 941	8.17	9.52
10 090	12 850	10.53	13.41
10 290	11 770	9.90	11.32
15 650	21 070	14.88	20.04
16 230	22 130	15.40	21.00
27 540	37 480	22.27	30.31
37 940	51 000	27.63	37.14
84 000	118 000	49.71	69.93
137 900	172 200	64.71	80.81
162 100	216 900	76.12	101.85
382 300	441 100	125.11	144.35
388 600	426 000	122.10	134.06
635 400	645 500	163.30	165.90

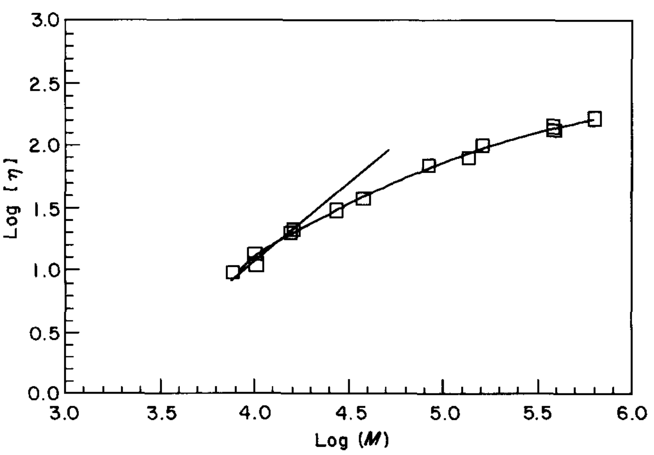

Figure 4 Variation of the intrinsic viscosity $[\eta]_{PSi}$ with the molecular weight (fractions at the top of ΔC peaks)

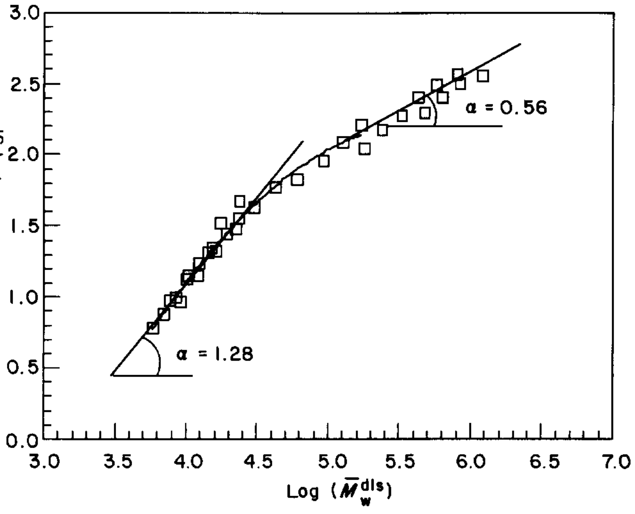

Figure 5 Variation of the intrinsic viscosity $[\eta]_{PSi}$ with the molecular weight for all studied fractions ($8000 < \bar{M}_w^{dls} < 10^6$)

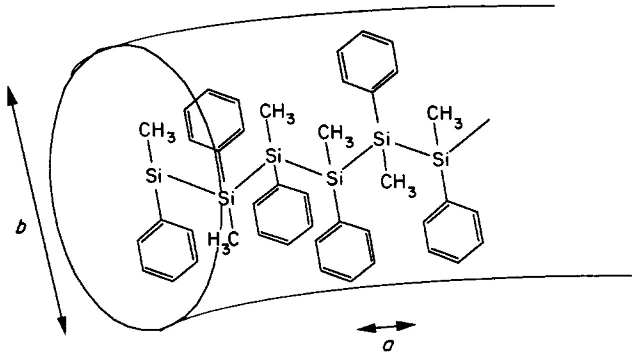

Figure 6 Representation of parameters *a* and *b* of the curved cylinder

Conformation of poly(methylphenyl)silane in THF solution

The theory of Yamakawa[11] for the hydrodynamic properties of chains displaying persistence length behaviour leads to two relationships for $[\eta]$.

On the low-molecular-weight side, where the full chain length is less than or of the same order of magnitude as the Kuhn statistical segment length:

$$[\eta]=\frac{\pi N_A}{24M_0}10^{-24}n^2a^3\frac{f(L)}{\ln(na/b)\{1+\sum_{i=1}^{4}A_i[\ln(b/na)]^{-i}\}} \tag{5}$$

with

$$f(L)=\frac{3}{2L^4}(e^{-2L}-1+2L-2L^2+\tfrac{4}{3}L^3)$$

where $L=na/2q$ and $A_1=1.84$, $A_2=8.24$, $A_3=32.86$ and $A_4=41.10$.

For higher molecular weights, i.e. for much longer chains, the relationship is:

$$[\eta]=\frac{\Phi_\infty(2aq)^{3/2}}{M_0}10^{-24}n^{1/2}\frac{1}{1-\sum_{i=1}^{4}C_iL^{-i/2}} \tag{6}$$

where $L=na/2q$ and

$$C_1=3.23-143.7b-1906.26b^2+(2.46-1422.06b^2)\ln b$$

$$C_2=-22.46+1437.08b+19387.4b^2 +(-5.92+13868.6b^2)\ln b$$

$$C_3=54.82-3235.4b-49357.06b^2 +(15.41-34447.63b^2)\ln b$$

$$C_4=-32.92+2306.79b+36732.64b^2 +(-8.52+25198.11b^2)\ln b$$

For both equations (5) and (6), *a*, *b* and *q* (in Å) are respectively the projection of the length of the monomer onto the contour length (approximately the monomer length), the hydrodynamic diameter of the chain and the persistence length. *n* is the number of monomer units having a mass M_0 and Φ_∞ is Flory's constant ($\Phi_\infty=2.87\times10^{23}$).

In both expressions (5) and (6), all dimensions are ratioed to the length of the Kuhn statistical element: $\lambda^{-1}=2q$. Therefore $[\eta]$ is a 'reduced' intrinsic viscosity.

The application of the calculation of Yamakawa and Fujii[12] to poly(methylphenyl)silane needs the adjustment of the three parameters *a*, *b* and *q* of the curved cylinder (*Figure 6*) to this polymer. Simple estimations lead us to choose 2 Å and 12 Å for *a* and *b* respectively.

Taking these values into account, an estimation of *q* has been obtained by comparison of the experimental results for a few low-molecular-weight ($\bar{M}_w < 40\,000$) fractions (corresponding to some results in *Figure 4*) with the calculated curves from equation (5). The best fit is obtained for *q* values lying between 35 and 40 Å (*Figure 7*).

Table 4 Evolution of the viscosity law $[\eta]_{PSi}=K(\bar{M}_w^{dls})^\alpha$ in the intermediate molecular-weight range

t (h)	$[\eta]_{PSi}=K(\bar{M}_w^{dls})^\alpha$	ΔM^a
0	$[\eta]=10.6\times10^{-3}M^{0.77}$	1×10^5–8×10^5
0.5	$[\eta]=2.81\times10^{-3}M^{0.88}$	3×10^4–2×10^5
1	$[\eta]=1.41\times10^{-3}M^{0.97}$	2×10^4–8×10^4

[a] Molecular-weight range where the viscosity law applies

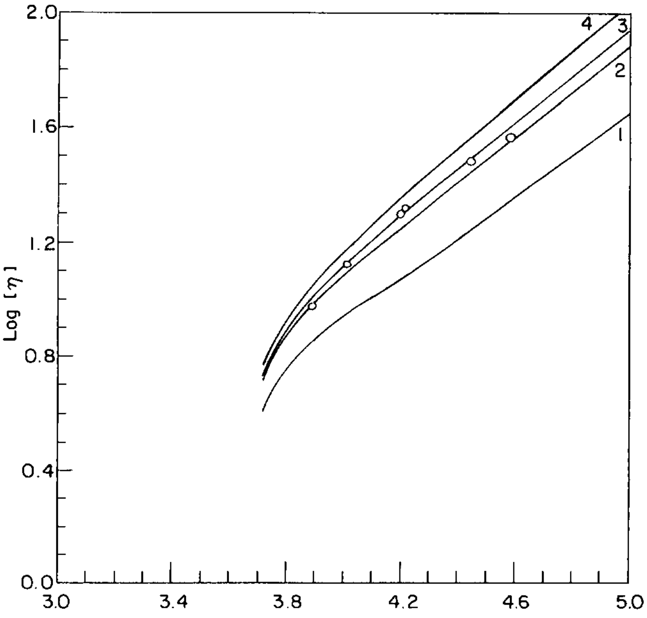

Figure 7 Variation of the intrinsic viscosity $[\eta]$ for low-molecular-weight fractions ($\bar{M}_w < 40000$). Comparison with the curves calculated from equation (5) (see text) with $a=2$ Å and $b=12$ Å: curve 1, $q=25$ Å; curve 2, $q=35$ Å; curve 3, $q=40$ Å; curve 4, $q=50$ Å

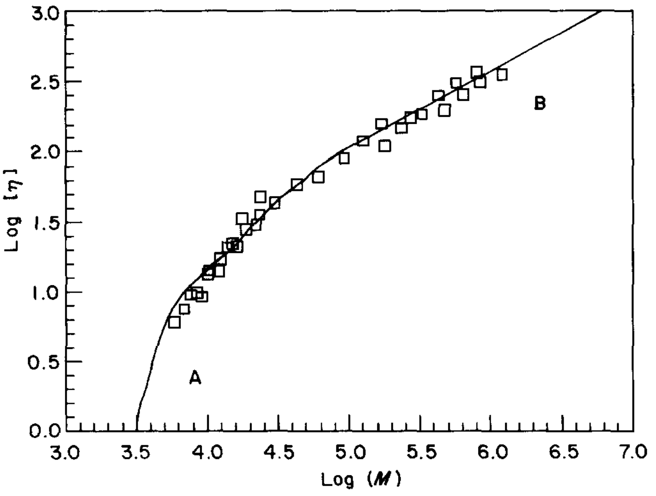

Figure 8 Variation of the intrinsic viscosity [η] with the molecular weight for all studied fractions. Comparison with curves calculated with $q=40$ Å, $a=2$ Å and $b=12$ Å: A, equation (5), $na \leqslant 2.28(2q)$; B, equation (6), $na > 2.28(2q)$

The curve fitting was then extended to all results of *Figure 5* and to both relationships (5) and (6), and the results are reported on *Figure 8*. The two theoretical curves were calculated respectively using equation (5) for $\bar{M}_w$ between 3×10^3 and 2×10^4 ($na \leqslant 2.28(2q)$) and equation (6) for $\bar{M}_w$ between 2×10^4 and 8×10^6 ($na > 2.28(2q)$).

The adjustable parameters were $q=40$ Å, $a=2$ Å and $b=12$ Å. It can be observed that the experimental values correlate very well with the calculated curves over the full $\bar{M}_w$ range. Moreover, a slight modification of the hydrodynamic diameter b (± 1 Å) does not influence significantly the optimized q value, which remains between 35 and 40 Å.

It is also possible to estimate the persistence length q (or the length of the Kuhn statistical element: $\lambda^{-1}=2q$) from the radius of gyration $R_{g,z}$ obtained by static light scattering. The values of $R_{g,w}$ ($R_{g,z}$ corrected for the polydispersity in a first approximation) are respectively 88, 150 and 320 Å for SI5PC, SI6P2 and SI6PA. From these data, one obtains $q=40$ Å for the persistence length deduced from the relation:

$$\lambda^{-1}=2q=\frac{6R_{g,w}^2}{n_w a} \qquad (7)$$

where n_w is the weight-average number of elements in the chain.

CONCLUSIONS

Combined measurements by g.p.c. and l.s. of fractionated poly(methylphenyl)silane were performed in THF. They indicate that the absolute weight-average molecular-weight values of PSi do not differ greatly from the g.p.c. values previously obtained using a classical g.p.c. calibration with monodisperse PS standards. This observation seems to rule out for this polymer the proposition of Cotts *et al.*, who announced previously a ratio $\bar{M}_w^{ls}/\bar{M}_w^{gpc}$ lying between 2 and 3 for a range of polysilanes.

Further calculations were also performed on $\bar{M}_w$ values of g.p.c. 'slices' using the persistence length theory of Yamakawa and Fujii. A best fit was obtained using this model, which leads to a semi-rigid conformation of the PSi chain in THF solution characterized by a persistence length of about 40 Å, or a Kuhn statistical element of about 75 ± 5 Å.

These calculations allow one to conclude that the poly(methylphenyl)silane chain in THF solution is characterized by rigid-rod-like elements involving about 35–40 monomer units. The correspondence with other values deduced from spectroscopy measurements is exceptionally good.

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