

MOLECULAR WEIGHT DISTRIBUTION OF POLY(PHENYLSILSESQUIOXANES)

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The distribution curves of four samples of poly(phenylsilsesquioxane) were constructed by using data of precipitation fractionation in the benzene-methanol system. The differential curves exhibited a sharp maximum and an elongated tail in the high molecular weight region. The polydispersity index of the polymers was high ($\overline{M}_w/\overline{M}_n = 5-10$).

Although ladder-type poly(phenylsilsesquioxanes)¹ have been known for more than ten years, only very scarce information about their polydispersity is available. A survey by Brown² gives only the interval within which the polydispersity index ($\overline{M}_w/\overline{M}_n$) varies for various samples. In papers by Janin and coworkers³⁻⁵ there is a number of GPC curves, but they have not been evaluated in terms of the molecular weight distribution. In connection with the study of the solution properties of poly(phenylsilsesquioxane)¹ we carried out preparative fractionation of four laboratory samples. The results summarized in this communication provide first information about the shape of the molecular weight distribution of ladder-type poly(phenylsilsesquioxanes).

EXPERIMENTAL

Polymer samples prepared by Brown's method² were supplied by courtesy of the Research Institute of Organic Syntheses, Pardubice (PFS-S, P1, P2, P3).

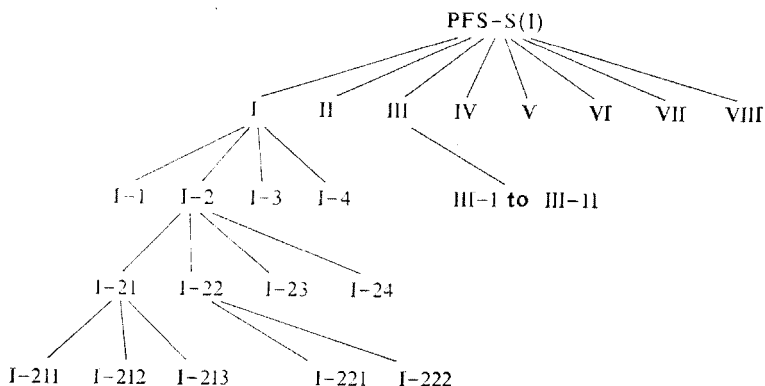
The fractionation was carried out by successive precipitation from benzene solution with methanol (starting concentration 0.2-0.5%). After the addition of methanol up to a slight opalescence at 25°C the solutions were heated until they had cleared up, left to cool down to 25°C with stirring (2-3 h), stirred at this temperature another three hours and then left to stand overnight. Separated fractions were reprecipitated twice by pouring benzene solutions (0.5-1%) into a tenfold excess of methanol and dried *in vacuo* at 50°C.

The polymer PFS-S was fractionated twice. In the first experiment, PFS-S(1), some fractions were refractionated according to the scheme.

In the second fractionation of the same polymer and with polymers of the PFS-P series no refractionation was carried out.

The weight average molecular weights of the fractions were determined by the light scattering method or (for some secondary and tertiary fractions) from intrinsic viscosities in toluene by an

interpolation in the dependence $[\eta]-M_w$ (ref.¹). For some fractions also the M_n values were determined osmotically. Details concerning these measurements are given in ref.¹.



RESULTS AND DISCUSSION

Fractions of poly(phenylsilsesquioxane), molecular weight higher than $5 \cdot 10^6$, separated in the form of a clear liquid phase. Heating by c. 10°C was sufficient to make them dissolve again. On the other hand, fractions whose molecular weight was lower were sometimes precipitated in the form of white solid gels or even powders; heating by 10°C was not sufficient to dissolve them in this case. The same was observed for refractionation. In spite of this, however, the fractionation was well reproducible as shown by the integral distribution curve of the polymer PFS-S (Fig. 1a).

In order to estimate the effectivity of fractionation and the reliability of the distribution curves one has to know the quality of fractions. As far as it was possible for the given range of molecular weights, the M_n values were determined osmotically for some fractions in addition to the M_w values, and the polydispersity index (M_w/M_n) was calculated. For fractions I and III obtained in the first fractionation of the polymer PFS-S refractionation was carried out (*cf.* Scheme in the Experimental), and the results were used for calculating the polydispersity index in the usual way⁶. Surprisingly enough, the index was low for fraction I (1.33). For fraction III the M_w/M_n values, both determined directly and from the results of refractionation, could be compared; the agreement between the values (1.87 and 1.70) was satisfactory.

The considerable polydispersity of fractions imposes carefulness in the discussion of the results presented in this paper. Since M_w averages of fractions were used for calculating the \bar{M}_w and \bar{M}_n values of unfractionated polymers, the \bar{M}_w values will be correct, but the \bar{M}_n values will be higher than correct⁷. As a result, the polydispersity indices given in Table I are somewhat lower than the real values.

By employing the usual procedure⁶, we constructed integral distribution curves and calculated polydispersity indices of unfractionated polymers from the weight fractions and molecular weights of fractions (Table I). The integral curves $I(M)$ vs M are shown in Figs 1a, and as the plot of $I(M)$ vs x (where $x = M_i/\bar{M}_w$ and M_i is the molecular weight of the i -th fraction) in Fig. 2. This form allows a better comparison of the distribution curves of the individual samples. All samples, even though

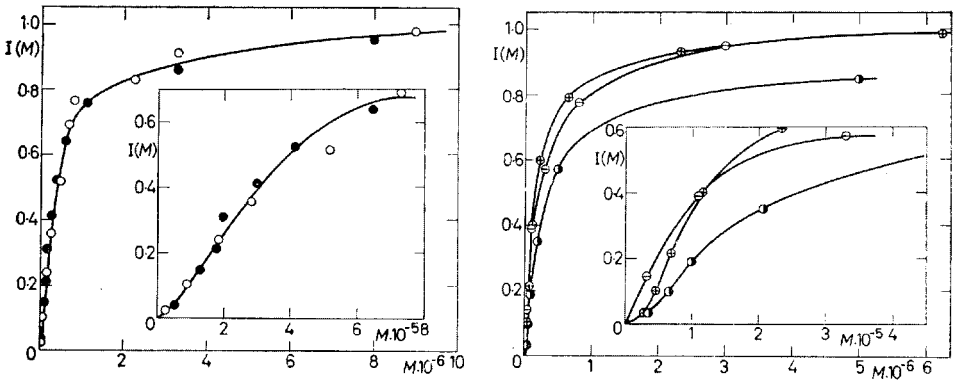


FIG. 1

Integral Distribution Curves of Poly(phenylsilsesquioxanes) (PFS-S)

a) ○ PFS-S(1), ● PFS-S(2); b) □ PFS-P1, ⊙ PFS-P2, ● PFS-P3.

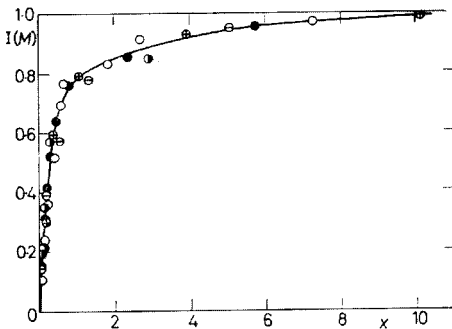


FIG. 2

Reduced Integral Distribution Curve

$x = M_i/\bar{M}_w$. Points designated as in Fig. 1.

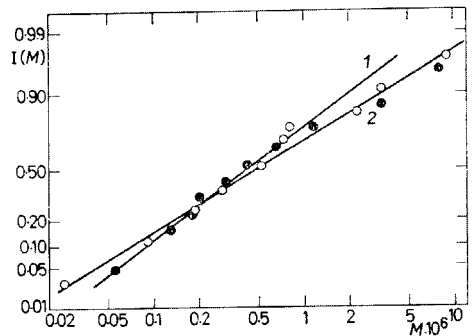


FIG. 3

Plot $I(M)$ vs M on Probability Paper

Points designated as in Fig. 1. Linear approximation: 1 for $0 < M < 10^6$, 2 for $0 < M < 10^7$.

they greatly differ in the average molecular weights and conditions of preparation, have that in common that 80% of the polymer mass is held by molecules having $x \leq 1$. The curves of the samples do not virtually differ within a broad range of x ($0.2 \leq x \leq 8$); only at $x \leq 0.2$ we find some differences between the positions of the inflexion points and the steepness of curves in their neighbourhood. It may be inferred from the course of the integral curves that the differential distribution curves will have their maximum at low molecular weights ($M_{\max} \cdot 10^{-3} = 20-200$), but that they will be very elongated in the region of high molecular weights (almost up to $1 \cdot 10^7$).

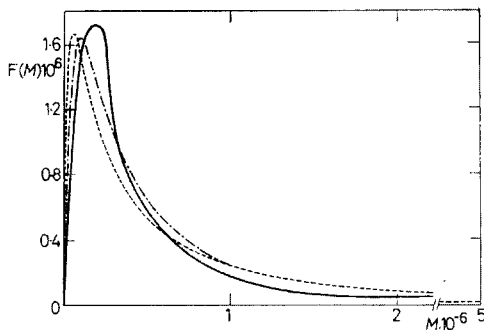


FIG. 4

Differential Distribution Curves $F(M)$ of Polymer PFS-S

Methods of construction: ——— numerical differentiation of integral distribution curve; ······ calculated by using parameters of straight line 1 in Fig. 3, -·-·-· calculated by using parameters of straight line 2 in Fig. 3.

We attempted to use several ways of obtaining differential distribution curves: the Tung plot⁶ $\log \log [1 - I(M)]^{-1}$ vs $\log M$, the $I(M)$ vs $\log M$ plot on a probability paper⁶ (used for the construction of logarithmic normal distribution curve) and also the numerical differentiation of the integral distribution curve⁸. The dependences obtained in the Tung plot were strongly curved. Their approximation by means of two straight lines makes necessarily the differential distribution curves discontinuous and thus almost useless. We therefore abandoned the idea of using this type of construction of the differential distribution curves.

Another two procedures appeared to be useful only in the treatment of the results of fractionation of the polymer PFS-S, because in this case we had at disposal the greatest number of experimental data (for numerical differentiation) and because the plot on the probability paper was approximately linear (Fig. 3). The same plot

for other samples was more or less curved and there were too few data for numerical differentiation. Fig. 4 shows various ways of constructing the differential distribution curves of the polymer PFS-S. The basic shape of the curve remains the same in all cases, differences are found predominantly in the position and less in the height of the maximum. This is by no means surprising bearing in mind how inaccurate all procedures leading from the integral distribution curves to the differential ones are. In spite of this we still can give a reliable interval for the position of the maximum ($1 < M \cdot 10^{-5} < 2$).

For other polymers (PFS-P1 to P3), and according to what has been said about Fig. 2, one may expect that their differential distribution curves will be very similar to that of the polymer PFS-S; only the maxima will be steeper and will be situated at lower molecular weights (especially for polymers PFS-P1 and PFS-P3 with a lower \overline{M}_w).

TABLE I

Results of Fractionation of Samples of Poly(phenylsilsesquioxanes)

\overline{M}_w and \overline{M}_n calculated from results of fractionation.

Polymer	$\overline{M}_w \cdot 10^{-6}$	$\overline{M}_n \cdot 10^{-6}$	$\overline{M}_w/\overline{M}_n$	Intrinsic viscosity, dl/g	
				determined ^a	calculated ^b
PFS-S(1) ^c	1.24 ^d	0.188	6.60	2.28 ^e	2.06
PFS-S(2) ^c	1.40	0.235	5.94	2.28 ^e	1.89
PFS-P1	0.593	0.087	6.79	1.08	1.03
PFS-P2	1.71	0.177	9.68	1.58	1.78
PFS-P3	0.596	0.115	5.18	0.830	0.847

^a Viscosities of toluene solutions of fractions measured at 25°C. ^b Calculated from results of fractionation. ^c Double fractionation of polymer PFS-S. ^d By light scattering $\overline{M}_w = 1.4 \cdot 10^6$. ^e Benzene, 25°C.

The differential distribution curves of the samples of poly(phenylsilsesquioxanes) under investigation resemble those of branched polymers, particularly by a long tail in the region of high molecular weights⁹. This similarity supports the conclusion derived from solution properties¹ that molecules of our samples are branched. Yet no quantitative analysis seems to be justified because of the complexity of reactions taking place in the synthesis of poly(phenylsilsesquioxanes)^{2,4,5}. For the same reason one has to take into account that under other conditions of preparation no branching will occur, the distribution curves will have a different shape and the polydispersity index will be lower (*cf.* Table V in ref.⁵ and Table I in ref.²).

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