Solution properties of ultrahigh molecular weight polymers: 11. A viscometric study on the excluded volume effect of poly(butyl methacrylate)

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The intrinsic viscosities and the viscosity constants of ultrahigh molecular weight poly(butyl methacrylate) fractions were obtained by the Huggins, the Kraemer, the Martin, the Schulz–Blaschke and the Fedors methods in methyl ethyl ketone. It was concluded that the averaging procedures suggested by Sakai for intrinsic viscosities are close to the values resulting from Fedors' method. The Mark–Houwink constants were obtained. The interpenetration functions $\Psi(z)$ and $\Pi(z)$ were discussed on the basis of different theoretical approaches through the expansion factors $\alpha_s(z)$; the renormalized group theory of Douglas and Freed was found to confirm best with the experimental results.

(Keywords: intrinsic viscosity; Mark–Houwink equation; ϕ and ϕ_0 Flory constants; $\Psi(z)$ and $\Pi(z)$ interpenetration functions; poly(butyl methacrylate))

INTRODUCTION

An extensive investigation of ultrahigh molecular weight polymers in dilute solution is much more complicated as compared with the investigation of usual length polymer–solvent systems. Short- and long-range interactions, influenced by different parameters, as determined by classical methods through the known theoretical approximations, undergo some modifications which can be considered either as interpretation errors or as physical phenomena. Therefore, systematic studies, arising from the coupling of different experimental methods, are needed for the elucidation of diverse theoretical and experimental aspects.

In some previously published papers, a light scattering technique was used to characterize ultrahigh molecular weight (10×10^6–48×10^6) poly(butyl methacrylate) (PBuMA) samples[1–3] obtained by a new polymerization method—plasma-induced polymerization[4–6]. In the present work a viscometric study on PBuMA samples ($\bar{M}_w = 9.6 \times 10^6$–$21.6 \times 10^6$) is reported.

EXPERIMENTAL

PBuMA samples were obtained by plasma-induced polymerization; the conditions of this polymerization technique were previously described in detail[4–6]. The syntheses yielded five samples with weight average molecular weights ($\bar{M}_w$) ranging from 1×10^7 to 2.1×10^7. All samples ($\bar{M}_w/\bar{M}_n = 1.4$–$1.6$) were submitted to fractionation by use of toluene–methanol mixtures as solvent–precipitant systems. Only very slight stirring was applied to solutions at any stage. The fractions were purified by reprecipitating their toluene solutions three times into methanol, followed by drying in vacuum.

Ten PBuMA fractions ($\bar{M}_w/\bar{M}_n \simeq 1.1$) were selected for the present study (*Table 1*).

The viscometric measurements were carried out in methyl ethyl ketone (MEK) in the 20–30°C temperature range (±0.01°C), by use of an Ubbelohde suspended-level viscometer. The concentration range was 5×10^{-4} to 2×10^{-3} g cm^{-3}. The solutions were maintained for 2 days in the dark, at 40°C, until complete dissolution was attained, and made optically clean by centrifuging for about 1–2 h, at 11 000*g* in a Janetzki centrifuge.

The kinetic energy corrections were found to be negligible. The flow volume of the viscometer used was greater than 5 ml, making drainage errors unimportant. Flow times were obtained with an accuracy of ±0.035%.

RESULTS AND DISCUSSION

Intrinsic viscosities

Intrinsic viscosities $[\eta]$ were obtained by use of the methods of Huggins[7] (equation (1)), Kraemer[8] (equation (2)), Martin[9] (equation (3)), Schulz and Blaschke[10] (equation (4)) and Fedors[11] (equation (5)):

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \qquad \mathrm{H} \qquad (1)$$

$$\ln \eta_r/c = [\eta] - k_K[\eta]^2 c \qquad \mathrm{K} \qquad (2)$$

$$\ln(\eta_{sp}/c) = \ln[\eta] + k_M[\eta]c \qquad \mathrm{M} \qquad (3)$$

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Table 1 Intrinsic viscosities using the Huggins (H), Kraemer (K), Martin (M), Schulz–Blaschke (SB) and Fedors (F) methods (equations (1)–(5)) for PBuMA samples in MEK at 25°C, and average values

Sample	$\bar{M}_w \times 10^{-7}$	$[\eta]_{H,K}$	$[\eta]_M$	$[\eta]_{SB}$	$[\eta]_F$	$[\eta]_{ave}$	$\frac{1}{2}([\eta]_H+[\eta]_M)$	$\frac{1}{2}([\eta]_H+[\eta]_{SB})$
1	0.9593	7.05	7.24	7.30	7.25	7.18	7.15	7.18
2	1.2311	8.50	8.58	8.60	8.63	8.56	8.54	8.55
3	1.2730	8.62	8.80	9.18	8.87	8.82	8.71	8.90
4	1.5070	9.75	9.88	10.20	10.28	9.97	9.81	9.97
5	1.5870	9.95	10.54	10.75	10.72	10.35	10.25	10.35
6	1.6870	10.25	10.65	11.00	10.84	10.60	10.45	10.62
7	1.7940	11.00	11.34	11.80	11.43	11.31	11.17	11.40
8	1.8370	11.20	11.47	12.02	11.65	11.51	11.34	11.63
9	2.0661	12.32	12.52	12.70	12.78	12.78	12.42	12.51
10	2.1633	12.93	12.95	12.99	12.99	12.96	12.94	12.96

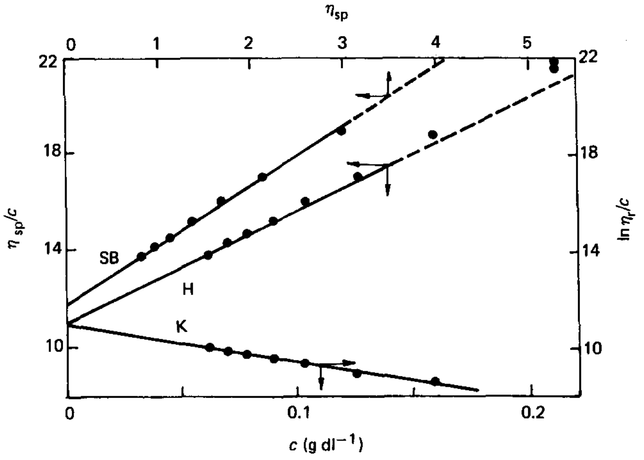

Figure 1 Huggins (H), Kraemer (K) and Schulz–Blaschke (SB) plots for PBuMA (sample 7, *Table 1*) in MEK at 25°C

$$\eta_{sp}/c = [\eta] + k_{SB}[\eta]\eta_{sp} \qquad \text{SB} \qquad (4)$$

$$1/2(\eta_r^{1/2} - 1) = -1/[\eta]c_m + 1/[\eta]c \qquad \text{F} \qquad (5)$$

where η_{sp} is the specific viscosity, η_r is the relative viscosity, c is polymer concentration (g dl^{-1}) and c_m is the concentration to which the particles can pack.

The values of $[\eta]$ obtained through the mentioned methods for PBuMA fractions in MEK at 25°C are given in *Table 1*. Weight average molecular weights were previously determined[2] by a light scattering technique.

Figures 1 and *2* present the dependences according to equations (1)–(5) for sample 7 (*Table 1*) in MEK at 25°C. One can see that for concentrations higher than 0.14 g dl^{-1} the data deviate from linearity, except for Fedors' plot. In a previous study (part 10 in this series)[12] it was shown that Fedors' method is only slightly sensitive to the possible errors appearing in the determination of η_r at high concentrations, including the semidilute region, and is sensitive for $c \to 0$.

By comparing the first four methods (*Table 1*), Sakai[13] concluded that for homopolymers the Schulz–Blaschke method yields the largest $[\eta]$ value, being followed in order by the Martin and the Huggins methods, and the best value of $[\eta]$ is obtained from

$$[\eta] = \tfrac{1}{2}([\eta]_H + [\eta]_M) \qquad \text{for good solvents} \qquad (6)$$

$$[\eta] = \tfrac{1}{2}([\eta]_H + [\eta]_{SB}) \qquad \text{for poor solvents} \qquad (7)$$

Table 1 shows the data of the present investigation and confirms Sakai's conclusion. By calculating the deviations for the studied fractions, $[\eta]_M$ and $[\eta]_{SB}$ appear to be higher by about 2.3% and 4.6%, respectively, as compared to $[\eta]_{H,K}$. Also, $[\eta]_F$ is higher than $[\eta]_{H,K}$ by about 3.7%, its value lying between $[\eta]_M$ and $[\eta]_{SB}$.

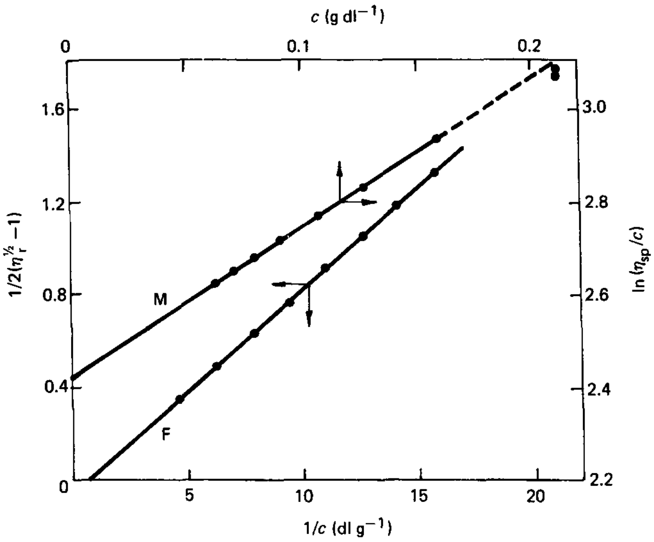

Figure 2 Fedors (F) and Martin (M) plots for PBuMA (sample 7, *Table 1*) in MEK at 25°C

The intrinsic viscosity values in *Table 1* were not corrected for shear stress (τ) so that the values are lower than those corresponding to $\tau \to 0$. Literature data[14], reported for polyisobutylene samples with molecular weights 1.46×10^6–15×10^6, show that neglect of the shear stress dependence affects the η_{sp} values by up to about 5%. About the same error should be transmittable to $[\eta]$. In the present study, this error is anyway within the limit of the errors given by the methods used to calculate $[\eta]$, and, at the same time, even the light scattering determination of ultrahigh molecular weights yields errors up to ±15% (ref. 15) (increasing with the molecular weight).

In the ensuing discussion the average values of $[\eta]$ obtained by use of all five methods have been considered. These values are close to those yielded by Sakai's relations (6) and (7), particularly to equation (7), and are higher than the values given by equation (6) by only about 0.97%.

It was found that there was no trend in any of the four initial slope constants (k_H, k_K, k_M and k_{SB}) with changing molecular weight for PBuMA samples in MEK at 25°C. Thus, an average value of each slope constant (±standard deviation) was determined (*Table 2*).

Intrinsic viscosity–molecular weight relationship

From intrinsic viscosity studies performed by use of the five mentioned methods at 20, 25 and 30°C, differences of $\pm1.16\%$ were observed between $[\eta]$ at 25°C and the values found at 20 and 30°C, respectively. However, these deviations are within the estimated average error for $[\eta]$ ($\pm1.2\%$).

From the double logarithmic plots of $[\eta]$ *versus* $\bar{M}_w$ the following relation has been established by the method of least squares (*Figure 3*):

$$[\eta]=0.613\times10^{-4}\bar{M}_w^{0.7258} \quad \text{(at 25°C)} \qquad (8)$$

The literature[16] presents the following dependences established for PBuMA in MEK:

$$[\eta]=0.156\times10^{-4}\bar{M}_w^{0.81}$$

$$(23°\text{C},\ \bar{M}_w=0.25\times10^6\text{–}2.6\times10^6,\ 1.3\leqslant\bar{M}_w/\bar{M}_n\leqslant1.75) \qquad (9)$$

$$[\eta]=0.970\times10^{-4}\bar{M}_w^{0.68}$$

$$(25°\text{C},\ \bar{M}_w=11\times10^4\text{–}67\times10^5,\ \bar{M}_w/\bar{M}_n\leqslant1.25) \qquad (10)$$

$$[\eta]=0.115\times10^{-4}\bar{M}_w^{0.89}$$

$$(30°\text{C},\ \bar{M}_n=67\times10^4\text{–}132\times10^4,\ 1.8\leqslant\bar{M}_w/\bar{M}_n\leqslant2.4) \qquad (11)$$

The exponent in equation (8) is higher by 0.046 as compared to that given in the literature for the same temperature, reflecting a tendency of the macromolecular chain to extend in the molecular weight domain studied in the present paper. Also, considering that in the 20–30°C temperature range no modifications of $[\eta]$ have been observed, one can suppose that for ultrahigh molecular weight PBuMA in MEK the additional energy given by temperature rise is insufficient to impart evident conformational changes.

Table 2 Viscosity slope constants (average values) for PBuMA in MEK at 25°C

k_H	k_K	k_M	k_{SB}	k_H+k_K
0.356 ±0.05	0.139 ±0.03	0.275 ±0.04	0.216 ±0.04	0.495

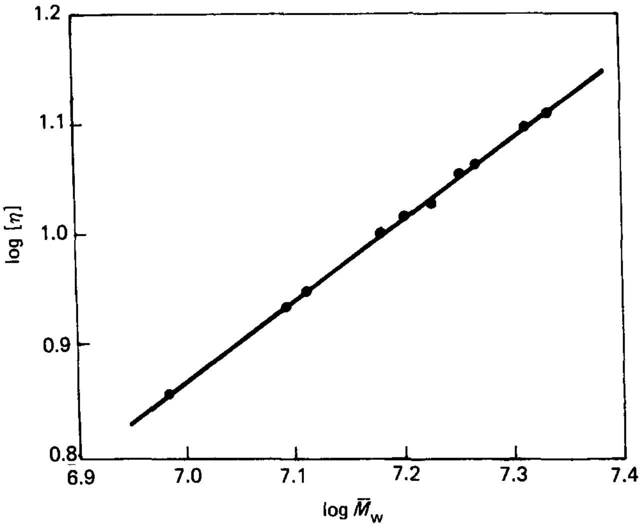

Figure 3 Log$[\eta]$ vs. log $\bar{M}_w$ for PBuMA samples in MEK at 25°C

Experimental evaluation of ϕ parameters

According to Flory and Fox[17], $[\eta]$ can be given by

$$[\eta]=6^{3/2}\phi(\langle S^2\rangle/M)^{3/2}M^{1/2} \qquad (12)$$

$$[\eta]_0=6^{3/2}\phi_0(\langle S_0^2\rangle/M)^{3/2}M^{1/2} \qquad (13)$$

where the subscript '0' refers to the unperturbed chain, and ϕ is the Flory viscosity factor. According to equations (12) and (13), the viscosity expansion factor α_η will be a function of the linear expansion factor α_s as reflected by

$$\alpha_\eta^3=(\phi/\phi_0)\alpha_s^3 \qquad (14)$$

Table 3 presents the values of ϕ obtained according to equation (12), with $\langle S^2\rangle_w^{1/2}$ determined from light scattering data[2] by use of the Schulz–Zimm distribution, with $\bar{M}_w/\bar{M}_n=1.1$. The value of $\phi_0=2.51\times10^{21}$, calculated by Zimm[18] and obtained in a numerical simulation, has been used. There is still some controversy regarding Zimm's simulation, so that it must be regarded as a tentative result.

Figure 4 presents the most probable dependence of ϕ/ϕ_0 on the expansion factor α_s (data summarized and interpreted by Douglas and Freed[19]) for polychloroprene in different solvents[20,21] (curve A) and also includes the curve resulting from the renormalized group (RG) theory

Table 3 Light scattering[2] and viscometric data for PBuMA in MEK at 25°C

Sample	$\langle S^2\rangle_z^{1/2}\times10^5$	$\langle S^2\rangle_w^{1/2}\times10^5$	$A_2\times10^5$ (cm^3 mol g^{-2})	α_s^3[a]	$\phi\times10^{-21}$
1	1.335	1.270	0.884	3.54	2.288
2	1.565	1.489	0.839	3.92	2.172
3	1.591	1.514	0.833	3.92	2.202
4	1.766	1.680	0.804	4.16	2.156
5	1.829	1.740	0.795	4.28	2.121
6	1.862	1.772	0.785	4.12	2.187
7	1.964	1.869	0.775	4.41	2.115
8	1.997	1.900	0.771	4.47	2.097
9	2.145	2.041	0.755	4.65	2.072
10	2.204	2.097	0.739	4.71	2.068

[a] Determined with $\langle S_0^2\rangle/M=0.724\times10^{-17}$ cm^2 (ref. 1)

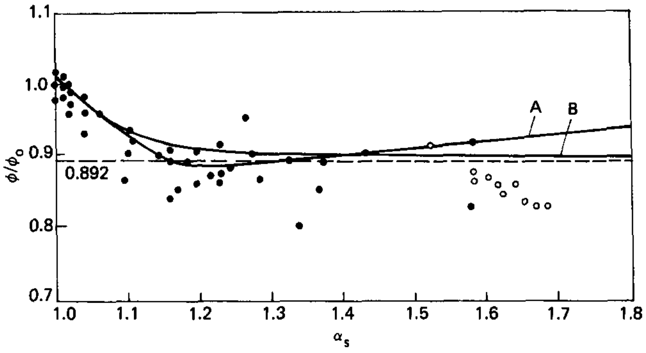

Figure 4 Plots of ϕ/ϕ_0 vs. α_s: data summarized by Douglas and Freed[19] (●); present data (○). Curve A is the most probable dependence[20,21], while curve (B) results from RG theory

of Douglas and Freed (curve B). The ratio is predicted in the non-draining limit from Douglas and Freed as

$$\phi/\phi_0 = \alpha_\eta^3/\alpha_s^3 = (1-0.276\lambda_1)/(1-0.130\lambda_1)^{3/2} \qquad (15)$$

where

$$\lambda_1 = (32z/3)/(1+32z/3) \qquad z \geqslant 0.75 \qquad (16)$$

Here z is to be treated as an empirical parameter as is the z variable (excluded volume parameter) in the two-parameter model, and $\phi^*/\phi_0 = 0.892$, where the asterisk * denotes a property for self-avoiding chains in the good solvent limit. Our experimental data points in *Figure 4* (with $\phi_0 = 2.51 \times 10^{21}$) yield an average value of 0.855, lower by 4.15% than that resulting from RG theory.

On the excluded volume effect

In a previous study[3], by examining the interpenetration function $\Psi(z)$ as given by different theoretical approximations, it was shown that $\Psi(z)$ calculated from experimental data for PBuMA in MEK at 25°C and in CCl_4 at 20°C is close to $\Psi(z)$ obtained from Kurata–Yamakawa theory with z calculated from $\alpha_s = f(z)$ dependence according to Yamakawa–Tanaka theory, and is in very good agreement with the RG theory of Douglas and Freed[19]. In the RG theory, for $\alpha_s^3 > 4$, the $\Psi(z)$ function presents only a very slight variation, tending to a constant value of 0.269 for the good solvent limit for highly expanded coils.

Similarly to the interpenetration function $\Psi(z)$, Douglas and Freed define the 'hydrodynamic penetration function' as a universal function of z only in the non-free-draining limit:

$$\Pi(z) = (A_2M/[\eta]) = [2^{1/2}(2\Pi/6)^{3/2}(N_A/\phi_0)]\Psi\alpha_s^3/\alpha_\eta^3 \qquad (17)$$

which in the RG theory turns to

$$\Pi(z) = 3.64(0.207\lambda_2 + 0.062\lambda_2^2)(1-0.130\lambda_2)^{3/2}(1-0.276\lambda_2)^{-1} \qquad (18)$$

where

$$\lambda_2 = 6.441z/(1+6.441z) \qquad (19)$$

The general shape of this function is very similar to that for $\Psi(z)$, tending to a limit of 1.1 for high excluded volume (*Figure 5*). By calculating $\Pi(z)$ experimentally based on equation (17) (with A_2, $\bar{M}_w$ and $[\eta]$ values from *Tables 1* and *3*) one observes from *Figure 5* that the data obtained give an average value of 1.22 ± 0.02, which verifies the limit of the theoretical expression of $\Pi(z)$ given by equation (18). Certainly, the agreement with the theoretical limit would be even better if the $[\eta]$ values at zero shear stress were used instead of those given in *Table 1*.

It is estimated that for high excluded volume (for $z \to \infty$) the values of $\Psi(z)$ and $\Pi(z)$ functions express the fact that the degree of penetration of the chain in dilute solution becomes constant.

CONCLUSIONS

Viscometric studies on poly(butyl methacrylate) ($\bar{M}_w = 9.6 \times 10^6$–$21.6 \times 10^6$) in MEK at 20–30°C, supplemented by light scattering data, allow the following conclusions.

(1) The intrinsic viscosities, determined in the dilute domain by different extrapolation methods, are placed in the following order: $[\eta]_{H,K} < [\eta]_M < [\eta]_{SB}$, while the viscometric constants are $k_H > k_M > k_{SB}$, thus confirming the conclusions of Sakai. Fedors' method, valid in a larger concentration domain, yields $[\eta]$ values close to the mean proposed by Sakai.

(2) The Mark–Houwink relation, established at 25°C from the values of $[\eta]$ determined by the five methods, differs from the literature relation given for the same temperature but for lower molecular weights. The increase of the exponent in the Mark–Houwink relation for higher molecular weights could be due to a tendency of the macromolecular chain to become more rigid. Similar conclusions have been previously reported[23].

It is significant that the obtained value of ~0.73 is smaller than the value of 0.80 which is usually considered as the asymptotic limit for very non-ideal polymer solutions. However, considering also our previous data[2] on the molecular dimensions and second virial coefficients of PBuMA in MEK, this relation exhibits the theoretically predicted asymptotic behaviour in the range of ultrahigh molecular weights.

The tendency towards an asymptotic behaviour in the ultrahigh molecular weight range also appears from the

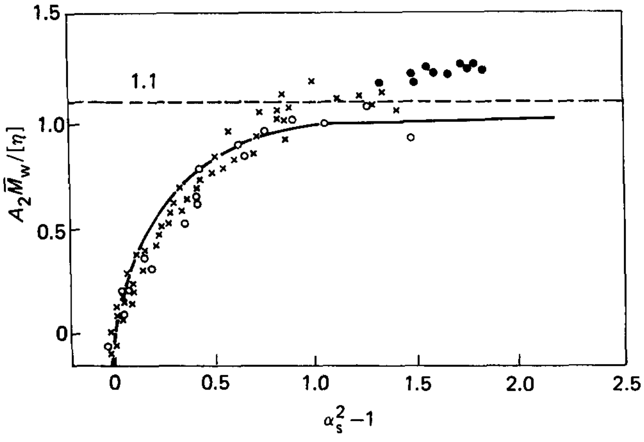

Figure 5 Plot of $A_2\bar{M}_w/[\eta]$ vs. $\alpha_s^2 - 1$ for polychloroprene in different solvents (○), for poly(*p*-methylstyrene) in different solvents (×) (data reproduced from Douglas and Freed[19] and summarizing the literature of Yamakawa[22]) and for PBuMA (●) (present data). The full curve shows data obtained from RG theory

behaviour of $[\eta]$ in the 20–30°C temperature range, where no conformational changes have been observed.

(3) The ϕ/ϕ_0 ratios were determined for the studied PBuMA fractions, an average value of 0.855 being found. This value is close to the asymptotic one (0.892) of Douglas and Freed, within the limit of the errors appearing in studying ultrahigh molecular weight polymers.

(4) The experimental data obtained for $\Psi(z)$ and $\Pi(z)$ functions satisfactorily approach those resulting from the renormalized group theory of Douglas and Freed which lead to the asymptotic values of 0.269 and 1.1, respectively, for $z \rightarrow \infty$.

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