

Interpenetration functions and excluded-volume theories in relation to light scattering data from poly(phenyl acrylate) solutions

Malcolm B. Huglin, Mohamad K. H. Khorasani* and Pedro M. Sasiat

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

(Received 28 January 1988; accepted 5 April 1988)

Light scattering measurements have been made on dilute solutions of poly(phenyl acrylate) in ethyl lactate at 10 temperatures ranging from the θ temperature (284.7 K) up to 379 K to yield the weight-average molar mass \bar{M}_w ($= 1.46 \times 10^6 \text{ g mol}^{-1}$), the second virial coefficients A_2 and the mean-square radii of gyration $\langle S^2 \rangle$. Chain expansion factors α_s obtained via $\langle S^2 \rangle$ were used to calculate the excluded-volume functions according to different theories, and the interpenetration function ψ was calculated from \bar{M}_w , A_2 and $\langle S^2 \rangle$. The results are discussed in relation to consistent pairs of theoretical expressions for the excluded-volume function and ψ .

(Keywords: poly(phenyl acrylate); light scattering; interpenetration function; excluded volume; chain expansion factor)

INTRODUCTION

In previous communications on dilute solutions of poly(phenyl acrylate) (PPA) the upper critical solution temperature (θ) was reported as 284.7 K in ethyl lactate (EL) and both the unperturbed dimensions and their temperature coefficient were derived from viscometric data^{1,2}. Comparisons have been made² on the applicability of various excluded-volume theories to these solutions, such theories involving the viscometric chain expansion factor α_r . The present report also deals with excluded-volume theories, but in terms of the expansion factor α_s , which is obtainable from the z -average value of the mean-square radius of gyration $\langle S^2 \rangle$:

$$\alpha = [\langle S^2 \rangle / \langle S^2 \rangle_0]^{1/2} \quad (1)$$

In (1) $\langle S^2 \rangle_0$ denotes the mean-square radius of gyration in the unperturbed state and, as will be adopted henceforth for ease of notation, α_s has been denoted simply as α . For a polymer sample of a particular weight-average molar mass \bar{M}_w , changes in $\langle S^2 \rangle$ and thus in α can be effected by altering the temperature T . Strictly, the values of $\langle S^2 \rangle$, $\langle S^2 \rangle_0$ and α should all relate to the same T and variations in α should be made by altering the nature of the solvent at a fixed T . However, in accord with commonly adopted, albeit somewhat imprecise, practice³⁻⁶, we follow the procedure adopted previously with viscometric results² and obtain values of α at different values of T from the measured values of $\langle S^2 \rangle$ at these temperatures.

* Present address: Center for Materials Science and Bioengineering, College of Engineering, University of New Orleans, New Orleans 70148, USA

† Present address: Departamento de Quimica Fisica, Universidad del Pais Vasco, Apartado 644, Bilbao, Spain

EXPERIMENTAL MATERIALS AND METHODS

PPA was prepared and fractionated as before¹. The single fraction used for this study had $\bar{M} = 1.46 \times 10^6 \text{ g mol}^{-1}$ (via light scattering in methyl ethyl ketone at 303 K; wavelength *in vacuo* 436 nm, specific refractive index increment $dn/dc = 0.183 \text{ dm}^3 \text{ kg}^{-1}$) and number-average molar mass $\bar{M}_n = 0.90 \times 10^6 \text{ g mol}^{-1}$ (via osmometry in toluene at 303 K). EL was dried over anhydrous MgSO_4 and distilled at atmospheric pressure. Light scattering measurements on solutions in EL were made at 10 temperatures within the range 284.7–379.3 K, the lowest temperature being the θ temperature. A Sofica model 42000 photometer, calibrated as before⁷, was used at 436 nm, at which wavelength values of dn/dc were also measured on a Brice Phoenix differential refractometer at several temperatures within the interval 293–333 K.

EXPERIMENTAL RESULTS

Over the temperature range covered the following linear dependence was obtained between dn/dc ($\text{dm}^3 \text{ kg}^{-1}$) and T (K):

$$dn/dc = 0.213 - 2.75 \times 10^{-4} T \quad (2)$$

Equation (2) was used to interpolate values of dn/dc at lower and higher temperatures. Some justification for this procedure was afforded by the constant ($\pm 4\%$) values of \bar{M}_w obtained thereby at all the 10 temperatures used in light scattering. Values of $\langle S^2 \rangle$ in conjunction with the mean-square radius of gyration at $T = 284.7 \text{ K}$ yielded values of α via equation (1). These experimentally determined values are denoted by α_s in Table 1, which also lists the experimental values of $\langle S^2 \rangle$ and the second virial coefficient A_2 .

The interpenetration function ψ is defined fundamentally as a theoretical quantity expressed in terms of the excluded-volume function (see later). The interpenetration function can also be defined in terms of

quantities that are all accessible experimentally. On this basis it will be denoted by ψ_e , which is given⁸ by equation (3) in which N_A is the Avogadro number:

$$\psi = A_2 \bar{M}_w^2 / (4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}) \quad (3)$$

The values of ψ_e at each of the 10 temperatures are listed in Table 1.

THEORETICAL PROCEDURE AND DISCUSSION

The interpenetration function is defined by the following expression⁸ in which z and $h(\bar{z})$ are the excluded-volume variable and the excluded-volume function, respectively:

$$\psi = zh(\bar{z}) \quad (4)$$

$$\bar{z} = z/\alpha^3 \quad (5)$$

Different excluded-volume theories have been proposed to predict values of ψ as a function of the variable \bar{z} . If the relevant expressions are combined with the proposed expressions for z as a function of α , they afford consequently theoretical values of ψ (denoted by ψ_t) as a function of α or, if preferred, as a function of α^3 , which is more tractable mathematically. As indicated before, the expansion factor can be obtained experimentally, and this quantity may be written as α_e . Hence the dependence of ψ_e on α_e^3 may be compared with the corresponding theoretical one, that is, the variation of ψ_t with α^3 , and conclusions may be drawn regarding the applicability of the excluded-volume theories to this particular system.

However, as noted by Yamakawa, only consistent pairs of theories can be used for the interpenetration function and the chain expansion factor, i.e. those based on the same model and assumptions. Three pairs of consistent theories are considered. From the smoothed Gaussian density model, there are

Combination 1: The original Flory–Krigbaum–Orofino (FKOo) theory⁹ for ψ as a function of z taken in conjunction with the original Flory (Fo) theory¹⁰ for z in terms of α , and

Table 1 Primary and derived quantities obtained via light scattering on solutions of PPA in EL at different temperatures

T (K)	A_2 ($10^{-5} \text{ m}^3 \text{ kg}^{-2} \text{ mol}$)	$\langle S^2 \rangle^{1/2}$ (nm)	α_e^3	ψ_e
284.7	0.00	30.5	1.00	0.000
286.8	0.60	31.8	1.12	0.030
289.8	2.92	34.1	1.40	0.117
295.9	5.17	36.0	1.64	0.176
304.8	6.87	37.7	1.91	0.203
318.6	9.40	39.4	2.15	0.244
332.6	11.7	41.0	2.41	0.270
347.6	12.5	42.3	2.69	0.262
363.0	14.1	43.4	2.86	0.274
379.3	15.0	43.8	2.99	0.284

Table 2 Form of interpenetration function and excluded-volume function for different theories and their combinations

	Combination 1	Combination 2	Combination 3
$\psi = h(\bar{z})$	$(1/2.30) \ln(1 + 2.30\bar{z})$ [FKOo]	$(1/5.73) \ln(1 + 5.73\bar{z})$ [FKOm]	$0.547[1 - (1 + 3.903\bar{z})^{-0.4683}]$ [KY]
$z = h(\alpha)$	$\alpha^5 - \alpha^3 = 2.60z$ [Fo]	$\alpha^5 - \alpha^3 = 1.276z$ [Fm]	$\alpha^2 = 0.541 + 0.459(1 + 6.04z)^{0.46}$ [YT]
$\psi_t = h(\alpha)$	$(1/2.30) \ln(0.115 + 0.885\alpha^2)$	$(1.573) \ln(4.491\alpha^2 - 3.491)$	$0.547 \left[1 - \left(1 + \frac{(2.179\alpha^2 - 1.179)^{2.17} - 1}{1.548\alpha^3} \right)^{-0.47} \right]$
z_e	$(1/2.30)[\exp(2.30\psi_e) - 1]$ [FKOo]	$(\alpha^3/5.73)\exp(5.73\psi_e) - 1$ [FKOm]	$(\alpha^3/3.903)(1 - 1.83\psi_e)^{-2.13} - 1$ [KY]

Combination 2: The modified Flory–Krigbaum–Orofino (FKOm) theory¹¹ for ψ as a function of z in conjunction with the modified Flory (Fm) theory¹² for z in terms of α .

From the hierarchy approach, there is

Combination 3: The Kurata–Yamakawa (KY) theory⁸ for ψ as a function of z in conjunction with the Yamakawa–Tanaka (YT) theory¹³ for z in terms of α .

For each of these three combinations there are two expressions, e.g. for combination 1, the FKOo formulation of $\psi = h(\bar{z})$ and the Fo formulation of $z = h(\alpha)$. All six expressions are given in Table 2. By elimination of z in each pair of expressions, i.e. within each combination, one obtains theoretical expressions for ψ as a function of α , which are also included as ψ_t in Table 2. Furthermore, the three expressions for $\psi = h(\bar{z})$ (FKOo, FKOm and KY) can be transposed to give \bar{z} as a function of ψ . When the experimental value of ψ is used, i.e. ψ_e , these transpositions afford the experimental \bar{z} , i.e. \bar{z}_e , as a function of ψ_e or, equivalently via (5), the expressions for z_e as a function of ψ_e , which are given in Table 2.

A graphical comparison of ψ as a function of α^3 is shown in Figure 1, where divergent behaviour is exhibited by the different theories employed. Although combinations 2 and 3 give rise to similar plots when $\alpha^3 < 1.4$, this no longer holds at larger values of α^3 where ψ_t is much higher for combination 2 than it is for combination 3. This is explicable on the basis of the limiting behaviour in both cases as $\alpha \rightarrow \infty$. In combination 2, ψ_t tends to

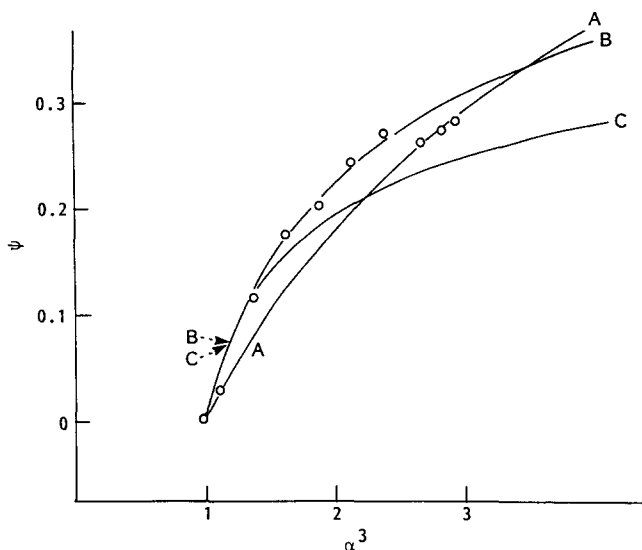


Figure 1 Theoretical dependence of ψ on α^3 calculated according to (A) combination 1, (B) combination 2 and (C) combination 3. The circles denote the experimental values of ψ_e obtained via equation (3) at different experimental values of α^3

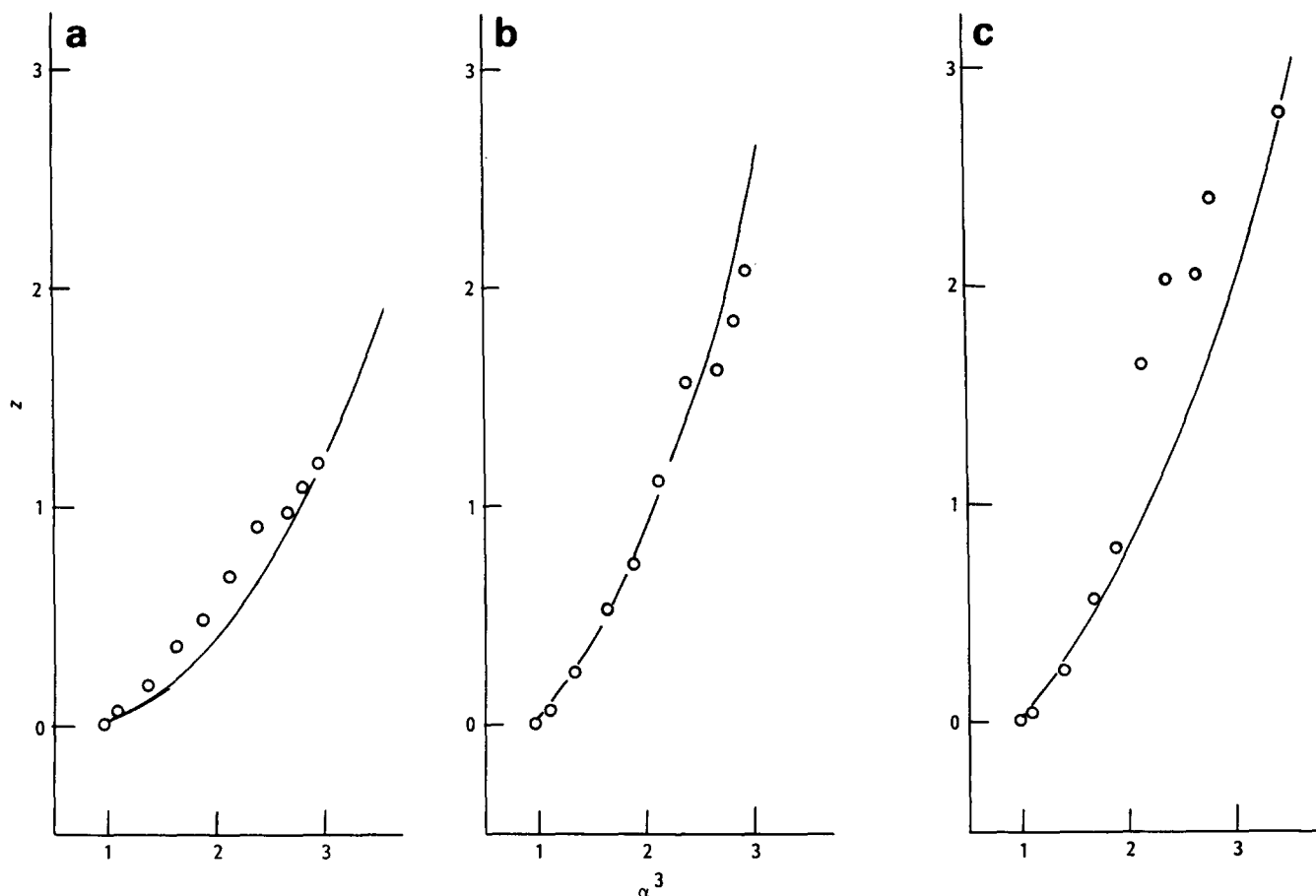


Figure 2 Dependence of z on α^3 according to the theories of (a) Fo, (b) Fm and (c) YT. The circles denote the experimental values of z_e obtained from ψ_e at different experimental values of α^3

infinity, whereas ψ_i tends to 0.547 for combination 3 (see Table 2). With regard to combination 1, this affords the lowest values of all for ψ_i when $\alpha^3 < 2.2$. However, for this combination ψ_i approaches infinity more rapidly at very high α than combination 2 does and, when $\alpha^3 \geq 3.6$, the values of ψ_i exceed those given by combination 2 (and, of course, as already indicated, those afforded by combination 3).

Figure 1 also includes the dependence of the experimental ψ_e with α_e^3 . It is immediately apparent that the following are true: (i) Accord with the curve for combination 1 (Figure 1, curve A) is very poor. (ii) There is good agreement with the curve for combination 2 (Figure 1, curve B) over the interval $2.4 > \alpha_e^3 > 1$, corresponding to the temperature range 284.7–332.6 K. On the other hand at higher temperatures, i.e. at larger values of α_e^3 , the increase in ψ_e becomes less pronounced and the values of ψ_e fall below the values predicted by combination 2. (iii) Accord with combination 3 occurs only at low values of α^3 (≤ 1.4) and thereafter the experimental magnitudes of the interpenetration function exceed those predicted by this combination. (iv) Hence none of the three combinations yields values of ψ_i which accord with ψ_e over the whole range of temperature. (v) At $T > 330$ K the rather slight increase in ψ_e with α^3 mirrors most closely the behaviour predicted by combination 3. Another mode of assessing graphically the different combinations in relation to experimental data consists of comparing the dependences of z on α^3 . Calculated plots are obtained for each pair of consistent theories. Thus the theoretical Fo, Fm and YT expressions yield the plots in

Figures 2a, 2b and 2c respectively. Within these the Fo expression affords the smallest value of z at any given α^3 . At small to medium values of α^3 the Fm theory gives a smaller value of z than is yielded by the YT expression, but this behaviour is reversed at high chain expansion. The corresponding consistent theories for ψ_i are those of FK00, and FK0m and KY and for these z_e was isolated from the corresponding expressions for ψ_e (see Table 2) as indicated before. In Figures 2a–c the variations of z_e with α_e^3 appear as data points. Again there is rather poor accord between theory and practice provided by combination 1 for which the theoretical values underestimate the experimentally determined z_e values over all the range of chain expansion covered. For values of α^3 up to ~ 2.3 and up to ~ 1.9 , combinations 2 and 3 respectively display excellent fits of experimental points with the theoretical curves. However, discord becomes apparent as z tends to infinity; at high α^3 the experimental quantities z_e are underestimated with respect to the theoretical curves for combination 2, but for combination 3 the experimental values exceed the theoretical ones.

Hence overall it is clear that the combination of the FK00 expression for ψ as a function of z with the Fo expression of z as a function of α does not lead to good agreement with experimental quantities obtained by light scattering. With regard to the other two combinations (i.e. FK0m with Fm and KY with YT) it is less easy to draw firm conclusions. Although neither combination affords excellent accord over the whole range of temperature studied, each exhibits its own region of α^3 over which agreement may be considered good when

assessed by both approaches (i.e. Figures 1 and 2). Overall, slight preference must be accorded to combination 2, because this provides acceptable agreement of both the experimental interpenetration and experimental excluded-volume function with the corresponding curves based on this combination over a reasonably wide interval of chain expansion. However, at very high α^3 it is observed experimentally that there is only a slight increase in ψ . This behaviour is mirrored by none of the theoretical curves but is closest to that for combination 3.

With regard to the experimental interpenetration function ψ_e , it is difficult to quantify exactly the errors or uncertainties in the values listed and plotted in Table 1 and Figure 1 respectively. From equation (3) it is seen that the relative error, $d\psi_e/\psi_e$, is given as follows in terms of the relative errors in the quantities from which ψ_e is obtained;

$$\frac{d\psi_e}{\psi_e} = \frac{dA_2}{A_2} + 2 \frac{d\bar{M}_w}{\bar{M}_w} - \frac{3 d\langle S^2 \rangle}{2 \langle S^2 \rangle} \quad (6)$$

Because errors can occur in both directions, it is necessary also to change the sign from negative to positive in the last term on the right-hand side of (6) in order to express the maximum relative error.

In the appropriate light scattering plot¹⁴, A_2 is obtained from the slope of ordinate data vs. concentration. The ordinate data depend on the optical constant via $(dn/dc)^2$. A typical value of dn/dc is that at the midpoint of the temperature range here, i.e. $0.124 \text{ dm}^3 \text{ kg}^{-1}$ at 323 K. Taking an uncertainty of $0.001 \text{ dm}^3 \text{ kg}^{-1}$ one obtains a relative error in dn/dc of $0.001/0.124 = 0.008 \sim 0.01$ and $d(dn/dc)^2/(dn/dc)^2 = 0.016 \sim 0.02$, which is thus equal to dA_2/A_2 . Similar considerations apply to \bar{M}_w , which is obtained from the intercept of a light scattering plot, and hence $2 d\bar{M}_w/\bar{M}_w \sim 0.04$. The optical constant and dn/dc are not relevant to $\langle S^2 \rangle$, when this is determined from the ratio of the slope to the intercept of light scattering plots, and hence no estimate of $d\langle S^2 \rangle/\langle S^2 \rangle$ is made. Consequently, on the basis of dn/dc alone, $d\psi_e/\psi_e \sim 0.06$.

In principle, there are other possible factors capable of affecting the accuracy of the values of A_2 , \bar{M}_w and $\langle S^2 \rangle$. These include calibration constant, extrapolation of plots to conditions of zero angle and/or zero concentration, assignment of a slope and an intercept to plotted data.

Regarding the latter two of these factors, the plots in the present experiments appeared to be extremely regular. However, it is realized that any small error in slopes, from which A_2 and $\langle S^2 \rangle$ are derived, represents a rather larger relative error in these quantities when A_2 and $\langle S^2 \rangle$ are small, i.e. in the region of low temperature.

Realistically, therefore, the values of ψ_e should be taken to be subject to a *minimum* uncertainty of $\pm 6\%$ with a larger uncertainty probably prevailing for the values at low temperature.

Because we are unable to quote total errors from all sources, no error bars have been indicated on the data points of Figure 1. The value of $d\psi_e/\psi_e = \pm 0.06$ corresponds to uncertainties in ψ_e of 0.002, 0.007 and 0.017 at low (286.8 K), intermediate (295.9 K) and high (379.3 K) temperatures respectively. The discussion on the relative fits of different combinations to experimental data remains qualitatively unchanged.

ACKNOWLEDGEMENT

One of us (PMS) thanks the Basque Government for generous financial support.

REFERENCES

- 1 Hooshmand-Mozafar, F., Hosseinalizadeh-Khorasani, M.-K. and Huglin, M. B. *Polymer* 1980, **21**, 413
- 2 Gregory, P., Huglin, M. B., Khorasani, M. K. H. and Sasia, P. M. *Br. Polym. J.* 1988, **20**, 1
- 3 Berry, G. C. *J. Chem. Phys.* 1966, **44**, 4550
- 4 Norisuye, T., Kawahara, K., Teramoto, A. and Fujita, H. *J. Chem. Phys.* 1968, **49**, 4330
- 5 Kawahara, K., Norisuye, T. and Fujita, H. *J. Chem. Phys.* 1968, **49**, 4339
- 6 Tanaka, G., Imai, S. and Yamakawa, H. *J. Chem. Phys.* 1970, **52**, 2639
- 7 Abdel-Azim, A.-A. and Huglin, M. B. *Polymer* 1984, **25**, 803
- 8 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971, p. 373
- 9 Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, **26**, 1067
- 10 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, Ch. 12
- 11 Stockmayer, W. H. *Makromol. Chem.* 1960, **35**, 54
- 12 Stockmayer, W. H. *J. Polym. Sci.* 1955, **15**, 595
- 13 Yamakawa, H. and Tanaka, G. *J. Chem. Phys.* 1967, **47**, 3991
- 14 Huglin, M. B. *Topics Current Chem.* 1978, **77**, 143