Apparent specific volumes of polymers in dilute solutions

D. Sarazin and J. Francois

Centre de Recherches sur les macromolecules, C.N.R.S., 6 rue Boussingault, 67083 Strasbourg Cedex, France

New results obtained on various polymers in solvents of differing molecular size and polarity confirm the dependence of their apparent specific volume ϕ_2 on polymer molecular weight and solvent molar volume. Existing models are discussed and a new model is proposed which assumes that ϕ_2 essentially depends on α, the expansion coefficient of the macromolecular coil, through the variation of the conformer sequence length in the chain. Some technical problems encountered with the vibrating tube densimeter are discussed.

INTRODUCTION

In the course of an investigation of the density of polystyrene in solution, an unexpected molecular weight dependence of the apparent specific volume φ_2 was found[1]. Further experiments led us to explain this phenomenon by the variation of the intramolecular segment density, g, inside the coil[2,3]. Other hypotheses, already suggested[4], are the molecular weight dependence of local order in polymer solutions or the variation of the number of rotational isomers in a sequence with the expansion factor α of the coil[5]. Experimental data have been obtained only for polystyrene and are not sufficient for a good understanding of the phenomenon.

The purpose of this paper is to provide further experimental information on the behaviour of the apparent specific volume of various polymers in solution. We have focused our attention on the influence of the molar volume of the solvent and the tacticity of the samples.

Our previous experiments were carried out on an automatic digital densimeter[6] operating on the vibrating tube principle. Some recent studies led to the conclusion that this type of densimeter provides erroneous density values in the case of viscous samples. Bernhardt *et al.*[7] show that the densimeter over-estimates the density, but Groves[8] claims the opposite effect. The viscosity of polymer solutions is very sensitive to molecular weight and concentration, so it is important to determine the sense and magnitude of this viscosity effect. Since this is feasible with our improved densimeter, the experimental part of this paper is particularly detailed and included a comparison of our apparatus and method with other density measurement techniques.

EXPERIMENTAL

Samples

The values of the weight average molecular weight, M_w, of our samples, and their distributions (when available) are given in *Table 1*. The poly(methyl methacrylate) (PMMA) samples were obtained by anionic polymerization at 60°C, with diphenylmethyl sodium as initiator. It is generally assumed that this type of polymerization leads to samples of similar microstructure regardless of the molecular weight. However, since tacticity variation would induce some specific volume variation for low molecular weight, we have determined the composition in iso-, syndio- and hetero-sequences by means of C_{13} n.m.r. (We shall see later that in our case the tacticity effect is very small.) The results in *Table 1* show that the tacticity of our samples does not depend on molecular weight.

The isotactic polystyrene (PSI) samples, provided by J. M. Guenet, were synthesized according to the Natta method by using titanium tetrachloride and aluminium triethyl as polymerization initiators in heptane. The product is purified in hot heptane and methyl ethyl ketone in order to remove atactic material from the sample and then is fractionated in a mixture of toluene and ethanol at 50°C. The tacticity of similar samples has been found to be higher than 95%[9]. Samples of polyethylene oxide (PEO) with molecular weight lower than 30 000 Daltons were industrial material (from Hoechst). The higher molecular weight PEO was synthesized in our laboratory.

The preparation and characterization of the fractions F_{1a}, F_{1b}, F_{1c}, F_3 and F_5 of polyacrylamide (PAM) are described in another paper in which we show that this polymer has a swollen coil conformation in aqueous solution[10]. The fractions of lower molecular weight were obtained after fractionation from polyacrylamide samples prepared by radical polymerization using pure nitric acid at 70°C as the initiator[11].

Density method

This method relies on the difference in vibrating tube frequency between the solution and water acting as a reference. The study was carried out on a densimeter of the DMA 02 type (Anton Paar) improved in our

Table 1 Characteristics of polymer samples

Poly(methyl methacrylate):

Batch	M_W	M_W/M_n	% Iso-	% Hetero-	% Syndio
5	9 750	1.4	43	48	9
7	22 000	1.1	–	–	–
20	34 000	–	–	–	–
10	45 000	1.6	–	–	–
18	180 000	1.1	51	41	8
13	275 000	–	–	–	–
14	280 000	–	–	–	–
22	400 000	–	39	55	6

Isotactic polystyrene:			Polyacrylamide:		
$3F_{13}$	10 200	–	F_{1a}	8.2 10^6	–
$7F_{11}$	10 500	–	F_{1b}	6.1 10^6	–
$7F_{10}$	13 100	–	F_{1C}	2.55 10^6	1.3
$8F_{12}$	25 400	–	F_3	920 000	1.35
$9F_3$	27 200	1.4	F_2	290 000	1.3
$7F_9$	39 700	1.43	PASD 2	300 000	–
$7F_8$	70 000	1.67	PASD-Z_1	260 000	–
$8F_4$	400 000	–	PASD-Z_7	56 000	–
			PASD-Z_{99}	33 000	–
			PASD-Z_{10}	12 000	–

Polyethyleneoxide:

Batch	M_W	M_W/M_n	Batch	M_W	M_W/M_n
1	1.25 10^6	–	5	6 000	1.1
2	530 000	–	6	2 000	1.1
3	30 000	1.1	7	1 500	1.1
4	18 000	1.1	8	1 000	1.1

Figure 1 Diagram of the Mohr Balance. S=glass sinter; C=cover; J=thermostatted jacket

laboratory by the design of a new cell[6] which leads to a precision of 5 10^{-6} g ml^{-1} in density measurements.

A significant comparison between density values obtained with two different methods is very difficult. One must take into account objectively the errors occurring for the two different types of experimental conditions. For instance, either the temperature should be the same, or, if this is not the case, the effects of temperature shift must be well evaluated.

Bernhardt et al.[7] have compared densimetric and pycnometric measurements, assuming that the second method gives the better results. In fact, the filling up of a classical pycnometer is not easy with highly viscous samples and the degassing is also difficult. Retained bubbles would lead to an underestimation of the density as was observed by the authors. It was thus helpful to us to compare these results with those from a third method such as the buoyancy method.

We used a Mettler balance giving a relative accuracy of 10^{-2}% and a glass sinker with a volume approximately equal to 10 cm^3 and available with the Prolabo Mohr balance. We expected a precision 10^{-3}% for density measurements, which is certainly good enough when compared with the discrepancy of 10^{-1}% found by Bernhardt et al.[7] for densimetric measurements. The sample was contained in a thermostatically controlled reservoir closed by a cover with a hole for the passage of the platinium suspension wire of the sinker. A silica gel reservoir was used inside the balance jacket to prevent water absorption. Corrections due to the air buoyancy and density were taken into account. The temperature was controlled with two coupled probes of a quartz vibrating thermometer inside the densimeter cell and the liquid of the Mohr vessel (*Figure 1*).
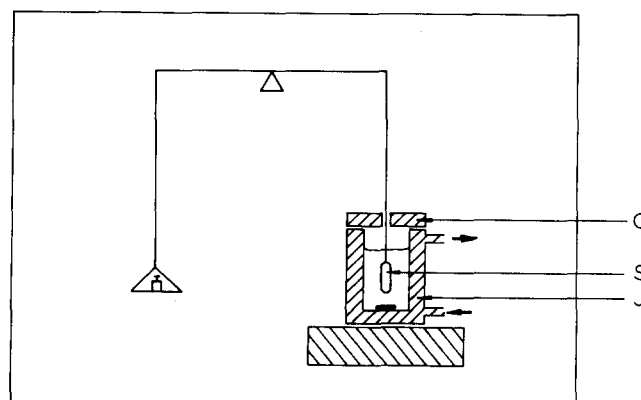
We chose five liquids of increasing viscosity and set a temperature difference of 0.2°C between the two apparatus 25.010°C for the densimeter and 24.810°C for the Mohr balance. The relative discrepancy $\Delta V/V$ between the two methods with the above mentioned conditions seems to decrease with the viscosity of the samples as seen in the penultimate line of *Table 2*:

$$\Delta V/V = (V_d - V_b)/V_d \quad (1)$$

Here, V_d is the specific volume determined with the densimeter, and V_b is the specific volume determined with the buoyancy method. In the last line of *Table 2* are reported the expected values of $\Delta V/V$ calculated from literature data[12,13] taking into account the temperature difference between the two apparatus. These values correspond exactly to the experimental quantity for such liquids from hexane to hexadecane. For glycerol, there is a relative discrepancy of 2.10^{-4}. So far we may say that our apparatus probably underestimates the specific volume of samples with viscosities up to 1000 cP as was pointed out by Bernhardt et al.[7] Nevertheless this shift is less for our densimetric cell than for that used by Bernhardt et al. In fact, the authors also found that these effects depend very much on the cell type. In our case and for liquid viscosities lower than 5 cP the densimeter has given certainly correct values of densities and one cannot be absolutely sure that the discrepancy observed with glycerol is not due to errors induced by the buoyancy method with very high viscous samples. A definitive answer to this problem will require many more careful measurements. If such a viscous effect exists, its origin and why it depends on the cell used remains to be explained. Our vibrating tube is longer than the one of the commercial cell and its vibrating period higher. If we assume, as suggested by Kim and Kauzmann[14], that a greater quantity of liquid participates in the vibration when the viscosity increases, this effect could be expected to vanish with a long tube.

For polymer solutions in the dilute range, errors are expected to be small, especially for polystyrenes with molecular weight lower than 10^6 and solution concentrations less than 2%, because the viscosities involved in these cases do not exceed 2 cP[15]. The high molecular weight dependence of the apparent specific volume φ_2 cannot be due to an experimental artifact. Moreover, this effect has been confirmed by refractive index increment measurements[16]. Another indication that the observed molecular weight dependence is not an

Table 2   Comparison between densities values obtained with the densimeter and the buoyancy balance

Liquid	Hexane	Decane	Dodecane	Hexadecane	Glycerol
Viscosity (cP)	0.294	0.92	1.35	3.34	9.54
Density g cm^{-3} (other works[15])	0.654726	0.726399	0.745732	0.770776	1.258310
Density from densimeter (g cm^{-3})	0.655142	0.726093	0.745132	0.770250	1.258555
Density from buoyancy bal.(g cm^{-3})	0.65567	0.726369	0.745393	0.7705	1.258410
$(\Delta V/V).10^4$ relation (1)	4.9	3.8	3.5	3.2	−1.11
$(\Delta V/V).10^4$ calculated from refs.12, 13, and					
15	4.6	4	3.6	3.11	1

artifact is the variation of φ_2 *versus* concentration for samples of PMMA as shown in *Figure 2*. For all molecular weights, φ_2 increases slowly with concentration without any tendency for the values corresponding to a high molecular weight to reach those of the lower molecular weight samples, with φ_2 given as:

$$\varphi_2 = V_s + (V - V_s)/C_w \qquad (2)$$

Here, V_s is the specific volume of the solvent; V is the specific volume of the polymer solution; C_w is the weight fraction of the polymer.

If an effect of viscosity modified the values of φ_2, one would expect the same value for very low concentrations and a departure when C_w increases. Also for polymer in aqueous solutions, the molecular weight dependence of φ_2 disappears while the same viscosity difference is observed between solutions of high and low molecular weight samples.

RESULTS

The variation of φ_2 with the reciprocal molecular weight for different polymers in various solvents departs by up to 2.10^4 from the linear behaviour observed for low molecular weight and shown in *Figure 3*. Our previous results of polystyrene in benzene and cyclohexane show this same type of departure for up to 2.10^4 from Flory's law[35], from the straight line defined by:

$$\varphi_2 = \varphi_{20} + A/M \qquad (3)$$

where A depends on the nature of the chain ends and φ_{20} is the extrapolation of the straight line from the low molecular weights to an infinite molecular weight.

This molecular weight effect has been found to be much higher for a swollen coil than for a non-perturbed coil for
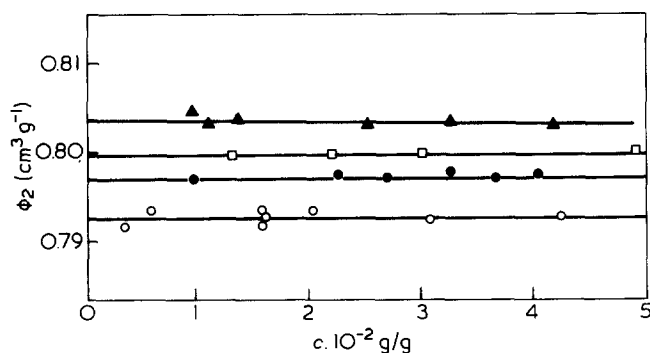
polystyrenes and for poly(methyl methacrylate). Moreover this effect is amplified by the molar volume V_M of the solvent and φ_2 increases with V_M as well. In order to verify this result we have studied the water soluble polymers, PAM and POE, in solution in water, which has a very low molar volume, and in other solvents of higher molar volumes. The φ_2 values obtained for these two polymers are in good agreement with other results found by other workers.

Roy, Chowdhury *et al.*[17] have measured 0.717 cm^3 g^{-1} for PAM in water and Lepori *et al.*[18] 0.837 cm^3 g^{-1} for PEO samples of low molecular weight in water as shown in *Figure 3b*. It is obvious from *Figure 3* that in water, the high molecular weight effect becomes unimportant although water is a good solvent for these two polymers. To make sure that this behaviour is not a consequence of the polar nature of these systems because of strong interactions such as hydrogen bonds, we have studied the
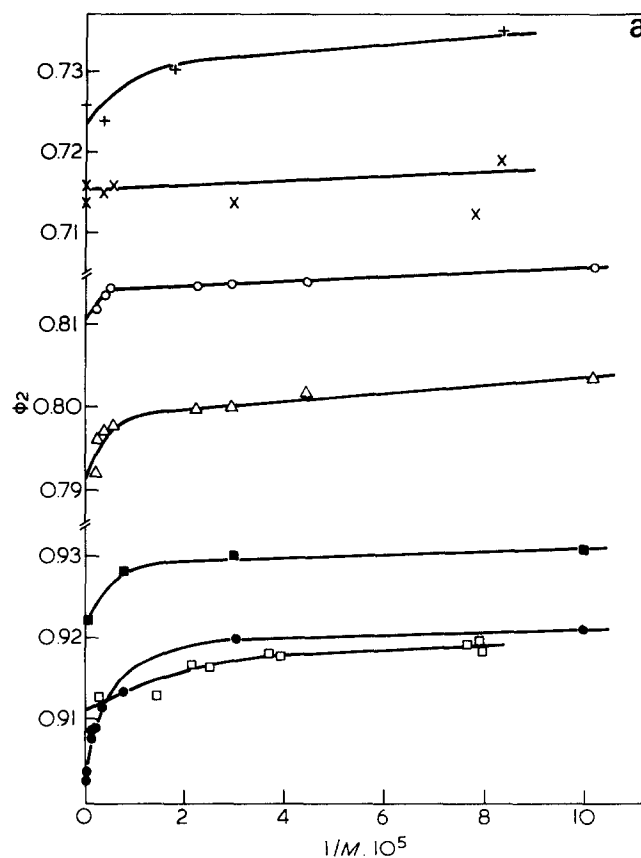

Figure 3a   Plots of ϕ_2 *versus* reciprocal molecular weight $1/M$ for different polymers: (●) PS in benzene (25°C); (■) PS in cyclohexane (θ temperature 34.5°C). (□) Isotactic PS in benzene (25°C). (△) PMMA in chloroform (25°C); (○) PMMA in p-xylene (θ temperature 23°C). (x) PAM in water (25°C); (+) PAM in formamide (25°C)

Figure 2   Variation of apparent specific volume ϕ_2 *versus* concentration C_w, for polymethylmethacrylate in chloroform at 25°C: (△) $M_w = 9\,750$; (□) $M_w = 45\,000$; (●) $M_w = 275\,000$; (○) $M_w = 400\,000$

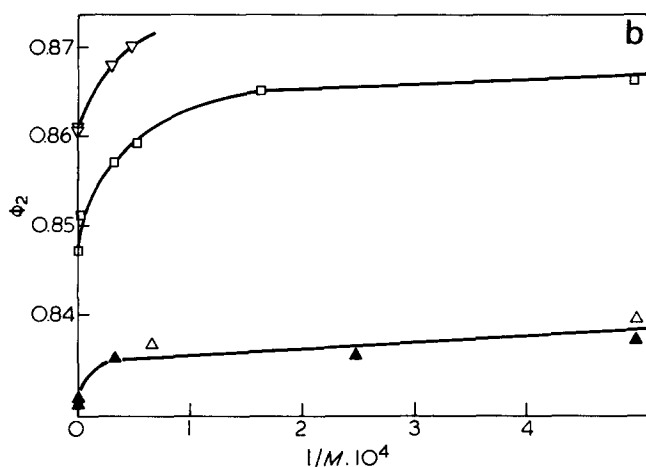*Figure 3b* Plots of ϕ_2 versus $1/M$ for PEO: ($\blacktriangle$) Our results in water; ($\triangle$) data ref.18; ($\square$) in benzene; (∇) in formamide

corresponds to an extended coil, is less dependent on V_M than is φ_{20} which corresponds to the specific volume of an unperturbed coil, i.e., (Gaussian distribution). For a solvent of very low molar volume (V_M), the φ_{20} and φ_∞ values are identical. This correlation between the extreme values of φ_2 has been predicted already by Heller[19] and observed by Edward et al.[20] in their study of alkanes, and alcohols in solvents such as benzene, ethanol and cyclohexane. These last authors consider that the partial molar volume of a flexible chain results from an additive relationship according to the following equation:

$$V_0 = V_c + \sum_1^m n^k I^k + \sum_1^n Z_g^1 \delta^1 \qquad (4)$$

where V_c is a constant covolume, and n^k and I^k are the number and the volume increment respectively of the
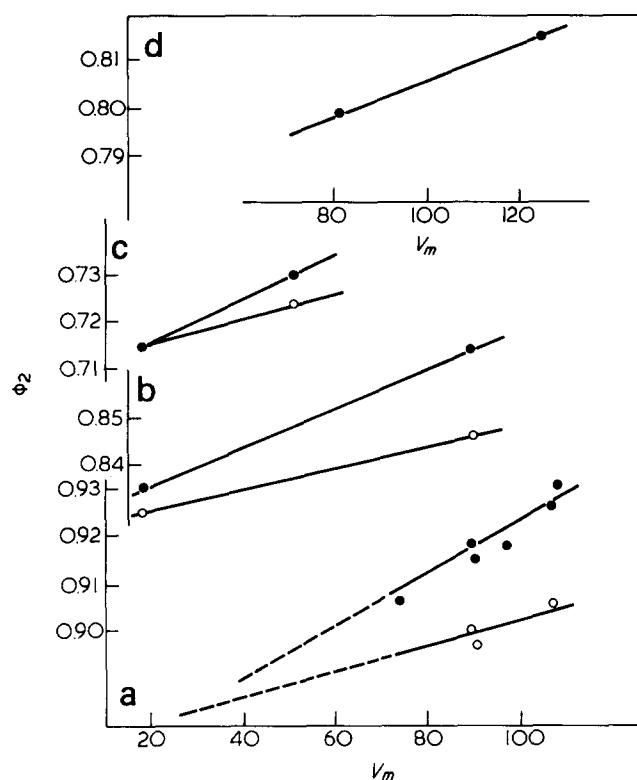
same polymers in another polar solvent, formamide, which has the higher molar volume and dielectric constant and is able to form hydrogen bonds with PAM and POE. These results, plotted in *Figure 3*, reveal the feature previously described, i.e., a high molecular weight dependence of φ_2 (up to 2.10^4) which is less pronounced in formamide than in benzene which has a higher molar volume (*Table 3*).

Anomalous behaviour is also observed for the system formamide–polyethyleneoxide (PEO) in which φ_2 has a value higher than in the system benzene–PEO, (see *Figure 3b*). Nevertheless the φ_2 value of polyacrylamide in the system formamide–PAM has the value expected from the molar volume of the solvent.

For isotactic polystyrene the molecular weight effect on φ_2 is lower than for the atactic polymers, as benzene is not a good solvent for these polymers. Moreover the φ_2 values are slightly lower than for the same system of atactic samples. These results confirm the relationship between the partial specific volume of a polymer and its conformation in solution. Also they show that this relationship is strongly related to the molar volume of the solvent. The variation of φ_{20} and φ_∞ is plotted in *Figure 4* against the molar volume of the solvent V_M for different polymers, φ_{20} is defined in relation (3) and φ_∞ is the extrapolated specific volume for an infinite molecular weight sample. As shown in *Figure 4*, φ_∞, which

Figure 4 Variation of ϕ_{20} ($\bullet$) and ϕ_{00} ($\bigcirc$) for PS (a): PEO (b). PAM (c). PMMA (d) *versus* the molar volume of the diluent

Table 3 Density and molar volume of the diluent

	M	Density (g cm^{-3})	V_m (cm^3 mol^{-1})
Water (25°C)	H$_2$O	18	0.97075	18.05
Formamide	HCONH$_2$	45	1.129269	39.85
Acetone	(CH$_3$)$_2$CO	58	0.785264	73.86
Chloroform	CHCl$_3$	119.5	1.471403	81.22
Benzene	C$_6$H$_6$	78	0.873366	89.31
Butanone	C$_4$H$_9$O	73	0.81003	90.12
Carbontetrachloride	CCl$_4$	154	1.584340	97.20
Toluene	C$_7$H$_8$	92	0.858690	107.14
Cyclohexane (25°C)	C$_6$H$_{12}$	84	0.774644	108.48
Cyclohexane (35°C)	—	—	0.764158	109.92
p-Xylene (25°C)	C$_8$H$_{10}$	106	0.856493	123.76
p-Xylene (28°C)	—	—	0.853818	124.15

constitutive groups k. The third factor gives the contribution due to the *gauche* arrangements of type 1 along the chain. This covolume V_c was introduced by Traube[21] and is required to obtain an additive scheme for the molar volumes of alkanes. It may be identified with Bondi's fluctuation volume[22].

Edward *et al.*[20] have determined a variation of $1.1 \text{ cm}^3 \text{ mol}^{-1}$ for V_c for an increase of $22 \, A^3$ in the van der Waals volume V_w. In our case, as shown in *Figure 3*, we obtained a similar slope for the molar volume of polystyrene *versus* the molar volume V_M of the solvent. Thus, for an increase of V_M of $22 \, A^3$ we find a variation of the molar volume V_x of $0.7 \text{ cm}^3 \text{ mol}^{-1}$ for an infinite swollen coil and 1.3 cm^3 for V_{20} for a Gaussian statistic $(M_w < 10^4)$ coil. The influence of the size of the solvent molecules seems to be of the same order of magnitude for polymers as for organic compounds of low molecular weight and may be related to the packing density of solvents molecules around the solute chains.

In summary, it appears that for polymers, regardless of their properties, that this dependence is more pronounced when the molar volume of the solvent molecules is large. We shall now consider why this is so.

DISCUSSION

In our earlier work[1-3], we suggested a direct relation between φ_2 and g, the average segment density inside the coil, and the existence of a free volume at each polymer–polymer contact which may disturb the packing of the solvent molecules around the polymer. Recently Khokhlov[23] introduced the 'quasi-monomer' concept and showed that the contact probability W, instead of being equal to $g \sim N/R^3_G$, must be written as:

$$W = W^* - K''/(N^{0.5})(\alpha^3) \qquad (5)$$

This increases with N. (K'' is a constant, N is the degree of polymerization, W^* is the contact probability of an infinite chain). This conclusion is in agreement with a recent renormalization calculation of Des Cloizeaux[24] which leads to the following relation for W:

$$W = A + B/(N^{\nu(3 + \theta_2)^{-1}})) + C/N \qquad (6)$$

where A, B, C are constants only dependent on ν and θ_2, ν is the excluded volume exponent, θ_2 is equal to 0.71 for high molecular weights. It is then obvious that the contact probability W has a finite limit A for an infinite chain and does not vary very much up to 10^4 daltons. An explanation in terms of intramolecular contacts is inappropriate here just as it was for the φ_2 variation measured[25] *versus* the polymer concentration c_w. Therefore we have to consider another possibility. In a recent paper, Khokhlov[5] proposed that the partial specific volume be expressed in terms of the relative number of *trans* and *gauche* isomers along the chain using the idea that the swelling of the macromolecular coil induces an increase in the persistence length of the chain and the number of *gauche* isomers varies as α^{-1}. An additive volume dV is associated with the *trans–gauche* transition. This led the author to the relation:

$$\varphi_2 = \varphi_{20} + (A/M) + (K/\alpha) = \varphi_{20} + (A/M) + (K/M^{0.1}) \qquad (7)$$

However, no attempt was made to quantify such an effect

or to compare it with the experimental data. Nevertheless it is well known that the average population of various rotational states is altered by deformation arising from the effects of excluded volume or coulombic repulsions of charges (as for polyelectrolytes) or by an applied stress. This general problem of rotational isomerization change with stretching has been extensively studied by various authors[26,27].

Abe and Flory[27] have shown that an increase of one unit in α^2, the square of the coil expansion coefficient, should alter the conformation population of a given state (η_g) by more than one bond per chain. Then the variation of number of *gauche* isomers per monomers $\langle \Delta\eta_g \rangle$ is expected to vary in a good solvent as:

$$\langle \Delta\eta_g \rangle/M \sim (M^{0.2} - 1)/M \qquad (8)$$

which shows that $\langle \Delta\eta_g \rangle$ is lower for higher molecular weights, as observed experimentally[28,29].

This result does not agree with the hypothesis of Khokhlov. So far it has been difficult to relate the molecular weight dependence of φ_2 to variations in the isomer population, because this does not explain the large change in the volume of about 2% per monomer in the chain. This explanation was used by Edward *et al.*[30] for the case of low molecular weight compounds, (alkanes and their derivatives). In this case a decrement of volume was attributed to the *trans–gauche* transition, the authors assuming an interpenetration of the hydrogen atom volumes for the *gauche* conformers. These hypotheses are not consistent with our observations on polymers.

In a more recent paper, Mattice and Santiago[31] observed that the earlier Abe and Flory calculations[27] did not take into account the connectivity of chain atoms. They proposed a matrix method which changes the statistical weight matrix by keeping constant the *a priori* probability, $p\eta$, that a bond is in state η. They were able to compute the average number of bonds in a sequence of *trans* placements $\langle \eta_t \rangle$ and the change of this number with the chain expansion coefficient α. The calculation for a methylene chain containing 10^4 units shows a change in $\langle \eta_t \rangle$ from 2 to 40 as α increases from 1 to 4. Since the packing of solvent molecules along the polymer chain strongly depends on the length of the sequences, this result could equally well be explained by a decrease of 2% for the specific volume when the chain expansion increases *versus* its length or temperature as well. If we consider the excess volume theories, such as the one developed by Eichinger and Flory[32], this means that the number of contacts polymer–solvent varies with α: the fundamental parameter in the φ_2 variations should then be α.

CONCLUSION

Our assumption of relating this molecular weight effect with the expansion coefficient α is in agreement with several examples of experimental data for the variation of φ_2 in good solvents *versus* the molecular weight of linear chain molecules. In fact it is now well known[33,34] that down to a critical number of segments N_c required for the development of the excluded volume statistics, the polymer coil is Gaussian and if $\alpha = 1$ then no variation of φ_2 occurs. Up to this limit, α increase with $\langle \Delta\eta_t \rangle$ and φ_2 decreases as observed. Finally we have proposed that the experimentally observed changes in φ_2 may be explained in terms of long range effects on the structure of the

solvent surrounding the polymer chain magnifying the increase of the *trans* sequence length when α increases. This effect will induce a closest packing of the solvent along the chain where the shape of the solvent molecules plays the role of a defect or an isomerization probe.

REFERENCES

1 Francois, J., Candau, F. and Benoit, H. *Polymer* 1974, **15**, 618
2 Sarazin, D. and Francois, J. *Polymer* 1978, **19**, 699
3 Sarazin, D. and Francois, J. *Polymer* 1978, **19**, 694
4 Privalko, V. P., Lipatov, Y. S. and Lobodina, A. P. *Makromol. Chem.* 1974, **175**, 2765
5 Khokhlov, A. R. *Vestn. Mosk. Univ., Ser. 3, Fiz., Astrom.* 1979, **20**, 57
6 Sarazin, D., Le Moigne, J. and Francois, J. *J. Appl. Polym. Sci.* 1978, **22**, 1377
7 Bernhardt, J. and Pauly, H. *J. Phys. Chem.* 1980, **84**, 158
8 Groves, M. J. *Colloid Polym. Sci.* 1979, **257**, 81
9 Guenet, J. M., Gallot, Z., Picot, C. and Benoit, H. *J. Appl. Polym. Sci.* 1977, **21**, 2181
10 Francois, J., Schwartz, T., Sarazin, D. and Weill, G. *Polymer* 1979, **20**, 969
11 Bhadani, S. M. and Prasad, Y. K. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 493–500
12 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471
13 Timmernans, J. 'Physicochemical Constant of Pure Organic Compounds', Plenum Press, New York, 1950
14 Kim, K. and Kauzmann, W. *J. Phys. Chem.* 1980, **84**, 163
15 Brandrup, J., Immergut, E. H. (Eds.), 'Polymer Handbook', J. Wiley Intersci., London, 1975
16 Candau, F., Francois, J. and Benoit, H. *Polymer* 1974, **15**, 626
17 Roy-Chowdhury, P. and Kale, K. M. *J. Appl. Polym. Sci.* 1970, **14**, 2937
18 Lepori, L. and Molica, V. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1123
19 Heller, W. and Thompson, A. C. *J. Colloid Sci.* 1951, **6**, 57
20 Edward, J. T., Farrell, P. G. and Shahidi, F. *Can. J. Chem.* 1979, **57**, 2887
21 Traube, J. *Samml. Chem. Vortr.* 1899, **4**, 255
22 Bondi, A. *J. Phys. Chem.* 1954, **58**, 92
23 Khokhlov, A. R. *Polymer* 1978, **19**, 1387
24 Des Cloizeaux, J. *J. Phys.* 1980, **41**, 223
25 Francois, J., Candau, F. and Sarazin, D. *C.R. Acad. Sci. Paris, Ser. C* 1978, **286**, 325
26 Birshtein, T. M. and Ptitsyn, P. 'Conformations of Macromolecules', Interscience Publishers, Ind., New York, 1966
27 Abe, Y. and Flory, P. J. *J. Chem. Phys.* 1970, **52**, 2814
28 Speak, R. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 997
29 Speak, R. and Shepherd, I. W. *J. Polym. Sci., Polym. Symp.* 1974, **44**, 209
30 Edward, J. T., Farrell, P. G. and Shahidi, F. *J. Phys. Chem.* 1978, **82**, 2310
31 Mattice, W. L. and Santiago, G. *Macromolecules* 1980, **13**, 1560
32 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035
33 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca and London, 1979
34 Daoud, M., Cotton, J. P., Farnoux, B., Janninck, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C. and De Gennes, P. G. *Macromolecules* 1975, **8**, 804