On the Molecular Weight Dependence of the Second Virial Coefficient of Polystyrene in Toluene

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ABSTRACT: The molecular weight dependence of the second virial coefficient A_2 was measured osmometrically for polystyrene in toluene at 30°C in the molecular weight range of (6.6—445) × 10³ and compared with the results of our previous light scattering measurements. It was found that for M (molecular weight) > 4.5 × 10⁴, A_2^{osm} and A_2^{ls} agreed fairly well. However for $M < 3 \times 10^4$ the former was much larger than the latter and followed the relation $A_2 = 0.964 M^{-1/2} - 4.36 \times 10^{-3}$.

KEY WORDS   Polystyrene / Toluene / Second Virial Coefficient / Osmometry / Light Scattering /

The molecular weight (MW) dependence of the second virial coefficient (A_2) is of considerable interest in the theory of polymer solutions. One of the chief difficulties in the investigation of A_2 lies in the embarrasing incapability of using a single experimental technique to cover a wide range of MW, say from 10^3 to 10^6, although monodisperse polystyrene (PS) samples available since the sixties have made it possible to get around polydispersity effects. Recently, we have published the results of A_2 measurements on PS in toluene at 25°C by low angle laser light scattering over a range of MW from 4×10^3 to 2.6×10^6.[1] One of the present authors[2,3] has developed a semi-permeable membrane which can be used to measure MW by dynamic osmometry down to 10^3.

Therefore, we were interested in measuring A_2 of PS in toluene by osmometry in the MW range of 6×10^3—4.5×10^5 and comparing the results with A_2^{ls} obtained previously.

EXPERIMENTAL

Samples

Samples used here were ten monodisperse polystyrenes as shown in Table I. The samples No. 1 (A-5000), No. 2 (500-A), and No. 6 (F-4) were purchased from Japan, the sample No. 9 from England, and the samples No. 3 (7101), No. 4 (ND-4), No. 5 (JD-2), No. 7, No. 8 (ND-6) and No. 10 (ND-9) from China.

Solvents

Toluene, AR, $\rho^{30} = 0.8563 \text{ g cm}^{-3}$; N,N-dimethylformamide (DMF), AR; ethanol (EtOH), CP; acetone (Me₂CO), CP, all were used without further purification.

Osmometer and Semi-Permeable Membrane

A modified Bruss osmometer of small cell volume made of stainless steel was used for osmotic pressure measurements. A semi-permeable membrane was made from cellophane obtained from Tianjin No. 4 Paper Mill in China, first by soaking it in 20% EtOH for 20

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L. ZHANG, D. QIU, and R. QIAN

Table I. Molecular weight dependence of A_2 of PS in toluene
at 30.0°C by osmotic pressure measurements

Samples No.	Nominal values		Concentration range (in $10^{-3} \, \mathrm{g \, cm^{-1}}$)	$M_n^{\mathrm{osm}} \times 10^{-4}$	$A_2^{\mathrm{osm}} \times 10^4$ $\mathrm{mol \, cm^{-3} \, g^{-2}}$
	$M_w \times 10^{-4}$	M_w/M_n			
1	0.67	1.04	0.4—1.8	0.66	$74._9$
2	0.91	1.01	0.6—2.8	0.92	$58._0$
3	1.47	—	0.7—3.4	1.46	$38._1$
4	2.44	1.03	1.2—5.8	2.33	$18._1$
5	3.40	1.03	1.5—7.3	3.26	8.7_4
6	4.39	1.01	1.8—8.8	4.43	5.1_3
7	10.0	—	3.2—16	8.90	3.8_2
8	13.3	1.06	3.8—19	12.4^a (13.0^b)	$4.4_2{}^a$ $(4.6_7{}^b)$
9	20.0	—	5.2—13	17.9	4.3_8
10	53.3	1.17	6.9—17	44.5^a (43.6) (46.8^b)	3.04^a (2.98) $(3.0_2{}^b)$

[a] Determined by static osmometry.
[b] Determined by an automatic membrane osmometer of Wescan Inc.

days and then by transferring it to absolute EtOH, to EtOH–DMF (1:1) and finally to DMF, for 5 h in each bath. The cellophane membrane was then rinsed at least three times with fresh DMF and kept in DMF. For the determination of M_n (the number-average-molecular weight) and A_2 of PS in toluene, the membrane was first transferred from DMF to Me_2CO and further to Me_2CO–toluene and then mounted on the osmometer. It was conditioned in toluene before each osmotic pressure measurement. This gradual change of solvent from DMF to toluene via Me_2CO was found necessary, since otherwise the regenerated cellulose membrane would shrink drastically when it was transferred directly from DMF to toluene and thus lost its solvent permeability. The semi-permeable membrane thus prepared has a permeability constant of $0.26 \times 10^{-13} \, \mathrm{cm^3 \, s \, g^{-1}}$ in toluene when estimated according to Kuhn,[4] and hence it can be used to measure molecular weight down to 10^3.[3]

Osmometry

Dynamic osmometry was mainly employed to determine osmotic pressures since its measuring time is much shorter than that for static osmometry, and hence the leak of low

molecular weight components does not seriously affect the observed values of osmotic pressure. In the dynamic osmometry the external applied pressure difference across the semi-permeable membrane extrapolated to zero flow rate was taken as the osmotic pressure. The experimental relationships between applied pressure and flow rate were linear and the extrapolated values from the higher and lower external applied pressures than the expected osmotic pressure agreed with each other as shown in previous papers.[2,3] It was already reported[3] that molecular weights of polystyrenes having low molecular weights obtained from the dynamic osmometry are in good agreement with those obtained from static osmometry and vapor pressure osmometry. In this work, moreover, molecular weights and second virial coefficients of polystyrenes having higher molecular weight (No. 8 and No. 10) were determined by the static and dynamic osmometries, and also by using an automatic membrane osmometer of Wescan Inc. As shown in Table I they agree well with each other. These results indicate that reliable data of osmotic pressure can be obtained by the dynamic osmometry.

Number-average molecular weight M_n and

second virial coefficient A_2 were evaluated from the osmotic pressure π for a series of solution concentration c using the relation:

$$(\pi/c)^{1/2} = (RT/M_n)^{1/2}[1 + (1/2)A_2 M_n c] \quad (1)$$

The use of this equation implies that the third virial coefficient of the solution has been partially taken into account.[5]

RESULTS AND DISCUSSION

The results of osmotic pressure measurements on 10 monodisperse PS samples in toluene at 30°C are shown in Figure 1. The M_n and A_2 values obtained from these data are listed in Table I. The molecular weight dependence of $A_2^{osm}(M)$ is compared with that of $A_2^{ls}(M)$ in Figure 2. It is apparent that for $M > 4.5 \times 10^4$, $A_2^{osm}(M)$ and $A_2^{ls}(M)$ agree fairly well both in magnitude and in the slope of $\log A_2 - \log M$ plot. A value of -0.19 is obtained for the slope of $\log A_s^{osm} - \log M$ plot, in close agreement with the value of -0.189 from light scattering measurements at $25°C$.[1] Both are close to the value -0.20 predicted by scaling theory.[6]

For $M < 3 \times 10^4$, however, A_2^{osm} is very much larger than A_2^{ls}. Our use of nearly monodisperse PS samples precludes any possibility of interpreting this large difference as due to the polydisperse effect discussed by Tanaka and Solc.[7] The origin is not understood at the present moment. For $M < 3 \times 10^4$ both osmotic pressure and light scattering measurements were made in the same concentration range, while for $M > 3 \times 10^4$ the light scattering experiments were performed at concentrations at least one order of magnitude smaller than those in the osmotic pressure measurements. For samples of $M < 4 \times 10^4$, linear plots of π/c vs. c gave M_n and A_2 values which were in close agreement with those from square root plots.

It has been reported in literature[8–10] that in the MW region of $M < 2 \times 10^4$ the value of A_2 increased rapidly with decreasing MW. A
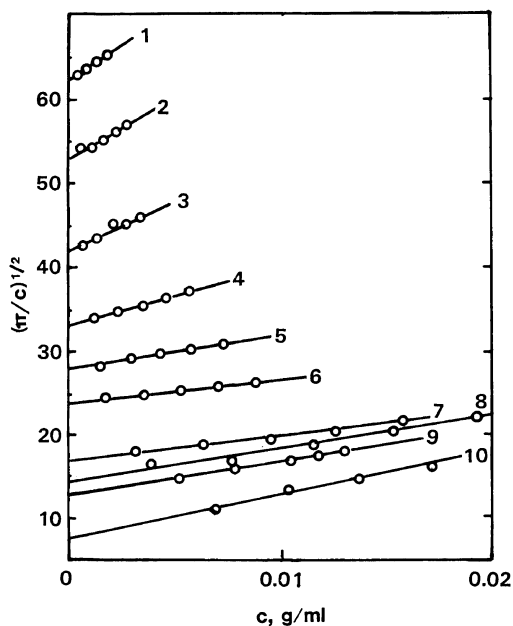

Figure 1. Osmotic pressure data for PS samples No. 1—10 in toluene at 30.0°C. π in g cm^{-2}, c in g ml^{-1}.
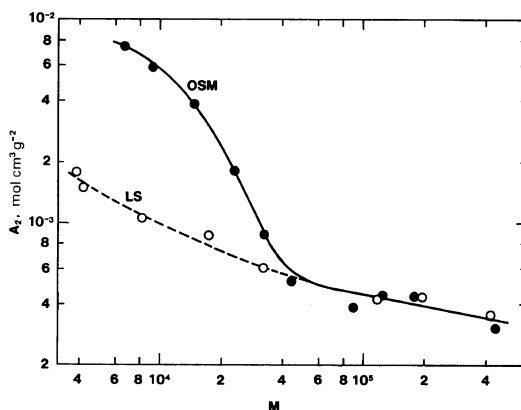

Figure 2. MW dependence of A_2 of PS–toluene system at 30.0°C: ●, A_2^{osm}; ○, A_2^{ls}.

linear relationship between A_2 and $M^{-1/2}$ has been found to fit the experimental data in this MW range.[1,9,11] The present data conform to this relation as well in the MW range (6—30) $\times 10^3$:

$$A_2 = 0.964 M^{-1/2} - 4.36 \times 10^{-3} \quad (2)$$

However, these values for the intercept and

L. Zhang, D. Qiu, and R. Qian

slope of the A_2 vs. $M^{-1/2}$ plot differ considerably from those obtained by light scattering experiments.[1]

Even from the rather scanty experimental studies on low MW flexible polymers in good solvents it seems clear cut that the behavior of $A_2(M)$ changes rather abruptly when MW is lowered below a certain value. This critical MW appears to coincide with the MW below which the polymer coil in a good solvent will no longer be expanded by solvent swelling.[9] Further studies in this MW region are certainly needed to attain a thorough understanding of the transition of dilute solution properties in moving from oligomers to high MW polymers.

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