Third Virial Coefficients of Polystyrene in Different Θ Solvents

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ABSTRACT: Third virial coefficients (A_3) are reported for a series of high molecular weight, narrow molecular weight distribution polystyrenes (PS) in benzene, a good solvent, and three Θ solvents: cyclohexane (CH), 1-chloroundecane (CUD), and diethyl malonate (DEM). A_3 values measured in benzene and cyclohexane are in good agreement with previously reported results for these polymer/solvent systems. A_3 values measured in CUD and DEM are consistently much smaller than values measured in CH for the same sample. This specific solvent effect is also reflected in larger Θ condition intrinsic viscosity ($[\eta]$) values for PS in CH, as compared to PS in CUD or DEM. These results demonstrate a correlation between larger repulsive three-body interactions under Θ conditions and larger Θ condition $[\eta]$ values. However, the radii of gyration of PS samples in these three Θ solvents were identical within experimental error. These results suggest that hydrodynamic properties are more sensitive to residual ternary interactions than are thermodynamic properties. Furthermore, our results indicate that the Flory hydrodynamic parameter ϕ can have different values in different Θ solvents. Similar results were reported recently by Yamakawa and co-workers for poly(methyl methacrylate) in two different Θ solvents.

Introduction

For a linear flexible polymer in solution, the osmotic pressure π can be expressed as a virial series:

$$\pi/(RTc) = 1/M_n + A_2c + A_3c^2 + \ldots \quad (1)$$

where R is the gas constant, T the absolute temperature, M_n the number-average molecular weight of the polymer, and c the concentration of the polymer solution in units of grams per milliliter. The quantities A_2 and A_3 are the second and third virial coefficients of the polymer solution, respectively. A_2 and A_3 are thermodynamic parameters which reflect interactions among polymer segments and the solvent. An understanding of these coefficients is essential to the thorough understanding of the fundamental behavior of polymer solutions. In addition, a practical understanding of the viral coefficients will allow for more accurate measurement of polymer molecular weight by light scattering and colligative properties methods.

A great deal of research has been conducted on A_2 since the early days of the development of polymer solution theories, owing to its relatively easy access by experiment. Even though some problems still prevail,[1] our understanding of A_2 has become reasonably satisfactory. On the other hand, information about A_3 is fragmentary, and available experimental results are extremely limited. The accurate measurement of A_3 requires great care and hence poses a major challenge to experimentalists. Recent attempts to measure A_3 in good solvents began in 1980 when Appelt and Meyerhoff reported A_3 data for polystyrene (PS) in toluene.[2] Independently, Kniewske and Kulicke measured A_3 of the same polymer/solvent system, extending to a much wider range of molecular weight.[3] They basically confirmed the earlier results of PS in toluene at 25 °C with the following relationship: A_3 (mol mL^6 g^{-3}) = 9.12 × $10^{-6}M_w^{0.58}$; here, M_w is the weight-average molecular weight. The good solvent exponent 0.58 was further confirmed for three PS fractions in benzene at 25 °C by Sato et al.,[4] who evaluated A_2 and A_3, respectively, from the intercept and initial slope of the Bawn plot[5] applied to light scattering data. Adopting the same method, Nakamura et al.[6] explored the same PS/benzene system, yielding the exponent of the $A_3 - M_w$ power law of 0.6, which is the asymptotic value predicted by two-parameter theory.[7] The same research group later applied the same method to the polyisobutylene (PIB) in cyclohexane system,[8] and they observed a similar slope for this linear flexible polymer/good solvent system.

The above-mentioned experimental results on A_3 were all obtained in good solvent conditions. For linear flexible polymers, our understanding of A_3 under theta (Θ) conditions is even less developed due to increasing experimental difficulties in handling moderately concentrated Θ solutions, which are on the verge of phase separation. Yet, as pointed out by Fujita,[9] this information of is great importance in understanding the fundamentals of polymer solutions. According to the two-parameter theory,[7] A_3 should vanish at the Θ temperature, as A_2 does. However, experimental evidence has appeared[10–15] which contradicts this prediction. Flory and Daoust[10] analyzed their osmotic pressure data for a PIB in benzene at the Θ temperature, and their results gave a small but positive A_3 value. In 1974, analyzing his osmotic pressure data on PS in cyclohexane using the Stockmayer–Casassa (SC) plot,[16] Vink obtained A_3 values on the order of (3–7) × 10^{-4} mol g^{-3} mL^6 at the Θ temperature.[11] One year later, Murakami et al.[12] estimated A_3 at Θ for a polychloroprene sample in methyl ethyl ketone to be 6 × 10^{-4} mol g^{-3} mL^6 by applying the same SC plot method to their sedimentation equilibrium data. Berry and co-workers[13,14] studied PS in cyclohexane and cyclopentane at their Θ temperatures by light scattering and estimated A_3 to be 6.4 × 10^{-4} mol g^{-3} mL^6 for cyclohexane and 1.2 × 10^{-3} mol g^{-3} mL^6 for cyclopentane, respectively. Recently, Nakamura et al.[15] carried out extensive light scattering experiments to measure A_3 of PS in cyclohexane at the Θ temperature via the Bawn plot method.[5] They

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obtained positive A_3 values and an interesting A_3 versus molecular weight relationship. Since a nonvanishing A_3 at Θ implies that the many-body interaction is nonzero, unambiguous determination of A_3 will give us greater insight into the fundamentals of polymer physics. Yamakawa and co-workers[17] extended work on the PS/cyclohexane system to include oligomeric PS samples. They observed a large systematic increase in A_3 as molecular weight was decreased, due to enhancement of chain end effects at low molecular weight.

Yamakawa[18] showed theoretically in 1966 that A_3 would not necessarily vanish when $A_2 = 0$. This concept had also been put forth in earlier work.[19] A theoretical breakthrough came when de Gennes[20,21] indicated that the infinite polymer Θ point is a tricritical point in terms of phase transitions. This laid the theoretical foundation for the existence of ternary interactions at Θ. As shown later by Cherayil et al.,[22] the ternary cluster integral β_3 for the three-body interactions is related to A_3 at Θ by

$$A_3 = (N_A^2/3)(4\pi R_g^2/M)^3(z_3 + ...) \quad (2)$$

with

$$z_3 = [3/(2\pi b^2)]^3\beta_3 \quad (3)$$

where N_A is the Avogadro constant, R_g the radius of gyration, b the effective segment length, and z_3 the excluded-volume parameter due to three-body interactions.

Another motivation for carrying out the present research is to study the effect of the third virial coefficient on other polymer solution properties such as the Flory hydrodynamic parameter (ϕ) and specific solvent effects on "unperturbed" dimensions. According to Flory,[23] the hydrodynamic factor ϕ should be a universal constant. Recently, this universality has been seriously challenged and it seems that ϕ is dependent on the particular polymer/solvent system used.[24,25] This discrepancy arises because theories of the hydrodynamic factors referred to above all use the binary cluster approximation. However, as recommended by Fujita,[9] when dealing with polymer solutions at Θ conditions, the many-body interactions must be considered. Specific solvent effects upon the unperturbed dimensions have generated much interest among polymer researchers. Through a series of viscometric studies of PS in different solvents, Orofino and co-workers[26-28] found a larger unperturbed dimension for PS in cyclohexane (CH) than in other "linear" solvents such as diethyl malonate (DEM) and 1-chloroundecane (CUD). This difference is apparently not due to the differences in temperature because these three systems all have Θ temperatures around 34 °C. Mays et al.[29] extended the above work by choosing a much wider range of solvents, and they confirmed the earlier results. Mays et al.[29] proposed that the hindrance of certain solvents upon internal rotation in polymers leads to more extended conformations and that these conformational differences reflect the differences in the interactions within various solvents. It should be noted that the unperturbed dimensions mentioned above were all estimated through intrinsic viscosity [η] measurements at or near Θ conditions using the Burchard-Stockmayer-Fixman (BSF) method.[30] Even though this method provides a convenient and fairly accurate route to estimate the unperturbed chain parameter (K_Θ), the parameter that really defines the unperturbed chain dimension is the Θ condition end-to-end distance d_0 or radius of gyration $R_{g,\Theta}$, which are related to K_Θ through the Flory-Fox equation:[31]

$$K_\Theta = \phi(d_0^2/M_w)^{3/2} = \phi(6R_{g,\Theta}^2/M_w)^{3/2} \quad (4)$$

It can be seen that the potentially rather controversial ϕ parameter is involved in this relationship. Thus, it is necessary to measure R_g directly in order to clarify this issue.

In this paper, results are reported from light scattering experiments on PS in three Θ solvents: CH, DEM and CUD. The third virial coefficients of PS in benzene at 25 °C are also obtained for comparison with the available results.[6] Third virial coefficients and radii of gyration are directly measured at the respective Θ solvent conditions.

Experimental Section

Polystyrenes prepared by anionic polymerization were purchased from Pressure Chemical Co. and Toya Soda Co. and have been repeatedly characterized in our laboratory by a combination of low-angle laser light scattering (LALLS), membrane osmometry, and size-exclusion chromatography (SEC). Details of our characterization procedures have been previously reported,[29,32,33] so we only summarize pertinent details below.

Light scattering measurements were conducted using a Chromatix KMX-6 unit (modified to allow control of temperature to ±0.1 °C) with a 2-mW vertically polarized He-Ne laser source operating at 633 nm or a Brookhaven BI2030AT light scattering unit with an Ar^+ laser operating at 488 nm. For most light scattering measurements, a custom-designed, temperature-controlled closed-loop filtration system was employed for sample clarification, using 0.2-μm PTFE filters purchased from Gelman. Details of this clarification system have been reported previously.[33] The refractive index increment dn/dc was measured as a function of temperature and wavelength using an Otsuka Electronics DRM-1020 double-beam differential refractometer.

A BI-ZP4.0 Zimm plot software program, purchased from Brookhaven Instrument Corporation (BIC), was utilized to analyze light scattering results taken at 10 angles from 30-142.5°. Toluene was used as the calibration standard with its Rayleigh ratio (R_Θ) taken as 39.6×10^{-6} cm^{-1} at 488 nm and 25 °C.[34] Rayleigh ratios of toluene at temperatures other than 25 °C were obtained through the following equation:[35]

$$R_\Theta^t/R_\Theta^{25} = (I_t/I_{25})\exp(2\gamma rc)(n_t/n_{25})^x \quad (5)$$

where γ is the absorption coefficient of the scattering solution, r the distance of the BIC detector from the center of the sample cell, I the scattering light intensity, n the refractive index, c the concentration of scattering solution, and x the slit/pinhole combination number for the BIC detector.

For toluene, it is easy to see that the term $\exp(2\gamma rc) = 1$, because the concentration for pure toluene is zero. With $x = 1$ for the BIC detector, eq 5 can be simplified to

$$R_\Theta^t/R_\Theta^{25} = (I_t/I_{25})(n_t/n_{25}) \quad (6)$$

where $n^{25} = 1.4927$ for toluene. Thus, by measuring the scattered light intensities at the respective temperatures, we were able to obtain the Rayleigh ratios of toluene at 30 and 36.2 °C to be 40.6×10^{-6} and 41.4×10^{-6} cm^{-1}, respectively. Rayleigh ratios of toluene at other temperatures were obtained through interpolation or extrapolation.

From the light scattering data, M_w, R_g, and A_2 were all obtained using BIC software and the classical Zimm analysis:[36]

$$Kc/\Delta R_\Theta = (1/M_w)[1 + 16\pi^2R_g^2\sin^2(\theta/2)/3\lambda_0^2] + 2A_2c + 3A_3c^2 + ... \quad (7)$$

where the optical constant K is equal to $(2\pi n)^2(dn/dc)^2(N_A\lambda_0^4)^{-1}$, ΔR_Θ is the excess Rayleigh ratio (difference of Rayleigh ratios

Table 1. Molecular Characteristics of PS Samples

sample	$M_w \times 10^{-4}$ [b]	$M_w \times 10^{-4}$ [c]	M_w/M_n [d]
PC233K	23.3	26.0	1.06
PC590K	59.0	59.0	1.06
PC900K	90.0	90.0	1.10
TS1.3M	130	126	1.05
TS2.9M	289	285	1.09
TS3.8M	384	384	1.04
TS4.5M	448	448	1.14
TS6.7M	677	667	1.14

[a] PC: Pressure Chemicals Co. TS: Toya Soda Co. [b] Nominal values from manufacturers. [c] Via LALLS. [d] Maximum values as derived from SEC measurements in our laboratory. No corrections were made for peak broadening.

Table 2. Values of d*n*/d*c* (mL/g) for PS in Three Solvents at Different Temperatures and Wavelengths

	633 nm		488 nm	
solvent	35 °C	40 °C	35 °C	40 °C
cyclohexane	0.165	0.168	0.178	0.181
1-chloroundecane	0.147	0.149	0.160	0.161
diethyl malonate	0.171	0.174	0.182	0.189

between solution and solvent), θ is the scattering angle, and λ_0 is the wavelength of the laser light in vacuum. Here, molecular weight heterogeneity is an important consideration, since use of eq 7 for a polydisperse material will give a weight-average molecular weight and a z-average size $\langle R_g \rangle_z$. Thus, in working with our PS standards, even though they have very narrow molecular weight distributions, it is important to correct for polydispersity. The most common approach is to compute the weight-average mean-square radius of gyration $\langle R_g \rangle_w$ using the equation:[37]

$$\langle R_g \rangle_w = [(u + 1)/(2u + 1)]\langle R_g \rangle_z \quad (8)$$

where u is the polydispersity parameter equal to $M_w/M_n - 1$.

In the case of low-angle laser light scattering (LALLS), eq 7 can be simplified to

$$Kc/\Delta R_\Theta = 1/M_w + 2A_2c + 3A_3c^2 + \ldots \quad (9)$$

with the sacrifice of information about polymer size.

Nowadays, light scattering experiments are the dominant method used to measure the third virial coefficient due to their enhanced sensitivity, as compared to osmotic pressure measurements. The Bawn plot[5] method is utilized to derive A_3 from light scattering data, even though this method was originally developed for treating data from osmotic pressure experiments. The Bawn plot method for light scattering data treatment can be briefly described as[15]

$$S(c_i,c_j) \equiv (Kc_i/\Delta R_{\Theta i} - Kc_j/\Delta R_{\Theta j})/(c_i - c_j) = 2A_2 + 3A_3(c_i + c_j) \quad (10)$$

where c_i and c_j are any two concentrations in a series of measurements. If we make a plot of $S(c_i,c_j)$ versus $c_i + c_j$, the slope and intercept of this plot will give information about A_2 and A_3, respectively. While treating light scattering data using the Bawn plot method, we found that appropriate ranges of concentration are vital for the successful measurement of A_3. The concentrations have to be high enough for significant A_3 effects to be observed while avoiding the contribution of A_4 and higher order virial coefficients. When too high a concentration is used, the Bawn plot exhibits a downward deviation from the initial linear slope, which indicates that A_4 is apparently negative, at least for the PS/benzene system. Sato et al. also observed similar behavior for their PS/benzene systems.[4] It appears to us that the concentration used in the Bawn plot analysis should be in the range of $0.3c^*-0.7c^*$, where c^* is the overlap concentration given by $3M_w/(4\pi N_A R_g^3)$.[9] Fitting of data obtained in this concentration range by polynomial regressions gave A_3 values that were generally in excellent agreement with A_3 values from Bawn plots (see below). We note that while Nakamura et al.[15] adopted a simlar range of concentrations in their A_3 measurements for PS in cyclohexane Θ solvent, Berry and co-workers[13,14] extended the concentration to about $4c^*$ to obtain A_3 for their PS in cyclohexane and cyclopentane at Θ temperatures.

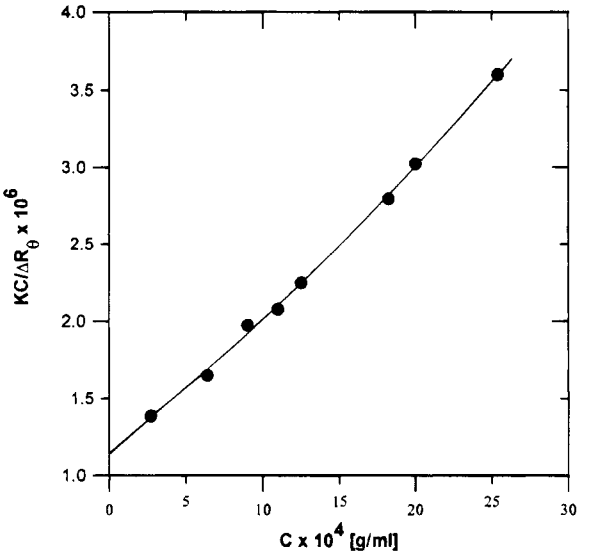

Figure 1. Representative light scattering plot for PS 900K in benzene.

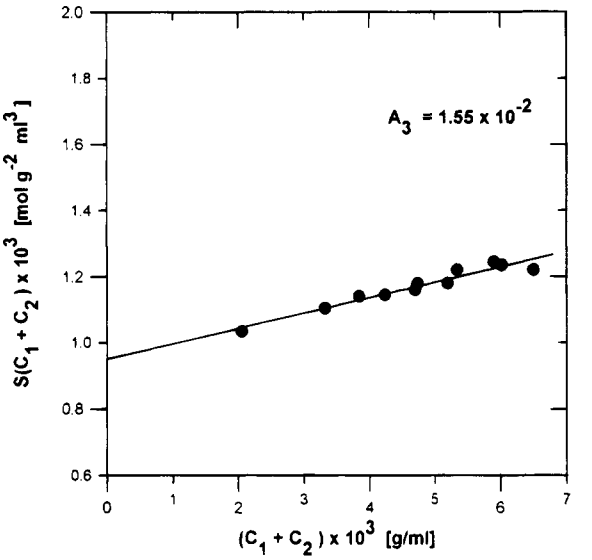

Figure 2. Representative Bawn plot for PS 233K in benzene.

Θ temperatures for PS are 34.5 °C in CH, 33.0 °C in CUD, and 35.0 °C in DEM. The accuracy of these Θ temperatures was confirmed by previous dilute solution measurements in our laboratory and other literature results.[15,17,26-29] In addition, as noted below, A_2 values derived from the Bawn plots under these conditions were vanishingly small.

The solvents used in the present work were HPLC-grade CH (Aldrich, 99.9+% by gas chromatography), DEM (Aldrich, 99+% by GC), and CUD (Tokyo Kasei Kogyo, 99+% by GC). Literature values[38] for the physical constants of these solvents were employed; the refractive index and density are 1.4194 and 0.7640 g/mL for CH at 34.5 °C, 1.4327 and 0.8562 g/mL for CUD at 33.0 °C, and 1.4082 and 1.0393 g/mL for DEM at 35.0 °C, respectively.

Results and Discussion

Molecular weights and polydispersities of the PS samples are presented in Table 1. The samples employed cover a broad range of molecular weights and exhibit narrow and symmetrical molecular weight distributions.

The dn/dc values obtained for PS in CH, CUD, and DEM at 488 and 633 nm wavelength and at tempera-

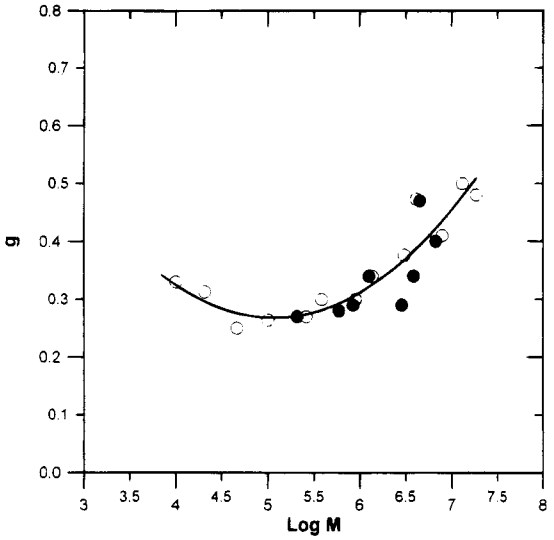

Figure 3. Plot of reduced third virial coefficient g parameter versus molecular weight: (●) from these experiments; (○) from ref 6.

Table 3. Results from Light Scattering Measurements on Polystyrene Standards in Benzene at 25 °C

sample	$M_w \times 10^{-5}$	$A_2 \times 10^4$ (mol g^{-2} mL^3)	$A_3 \times 10^2$ (mol g^{-3} mL^6)	g
PC233K	2.60	4.73	1.55	0.27
PC590K	5.90	3.87	2.44	0.28
PC900K	9.00	3.50	3.32	0.30
TS1.3M	12.6	3.11	4.19	0.34
TS2.9M	28.5	2.66	5.75	0.29
TS3.8M	38.4	2.26	6.70	0.34
TS4.5M	44.8	2.07	9.16	0.47
TS6.7M	66.7	2.00	10.76	0.40

tures of 35 and 40 °C are listed in Table 2. The dn/dc values at other temperatures were obtained through extrapolation at the respective wavelength. The literature dn/dc value of 1.066 mL g^{-1} at 633 nm for PS in benzene at 25 °C was used in the current experiments.[6]

Representative light scattering and Bawn plots for PS in benzene are shown in Figures 1 and 2. Values of A_2, A_3 and g ($g \equiv A_3/A_2^2M$) obtained for PS in benzene at 25 °C are presented in Table 3. These values give the following relationships:

$$A_2 = 1.50 \times 10^{-2} M_w^{-0.276} \quad (11)$$

$$A_3 = 1.08 \times 10^{-5} M_w^{0.586} \quad (12)$$

which are in good agreement with those of Nakamura et al.[6] The g values are also shown in Figure 3, along with values of Nakamura et al.[6] From this figure, it can be seen that g exhibits values near 0.3 up to $M = 3 \times 10^5$ and then increases toward 0.5 with increasing M. Nakamura et al.[8] also observed similar g behavior for polyisobutylene in cyclohexane by light scattering.

Representative light scattering plots are given in Figures 4 and 5, whereas the representative Bawn plots are presented in Figures 6–8. Values of A_3 for PS in the three Θ solvents, obtained by Bawn plots and polynomial regressions, are tabulated in Table 4 and shown in Figure 9, along with the data of Nakamura and co-workers[15] and Yamakawa et al.[17] for PS in cyclohexane at 34.5 °C. Experimental errors were estimated to be ±4%. It is found that A_3 values in CH are consistently larger than those in CUD and in DEM. This is consistent with the trend observed for K_Θ of PS in the three solvents through viscometry (i.e., there is

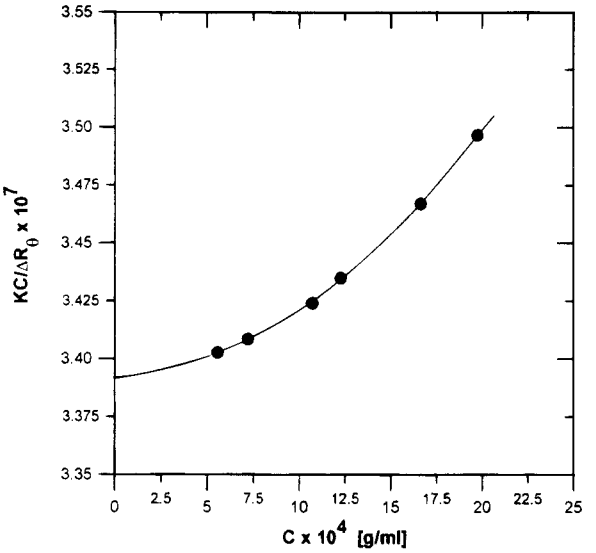

Figure 4. Light scattering plot for PS 2.9M in cyclohexane.

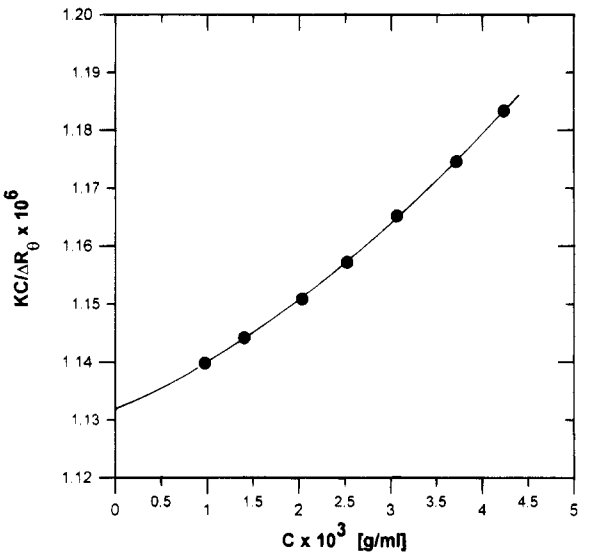

Figure 5. Light scattering plot for PS 900K in 1-chloroundecane.

perhaps a correlation between the magnitude of A_3 and K_Θ values[22]). It is worth noting that we observed an apparent minimum A_3 around a molecular weight of 6 × 10^5 for PS in all three Θ solvents. This minimum also is seen in the data of Nakamura et al.,[15] who attributed this behavior to possible experimental errors involving the highest molecular weight samples. Our data support their earlier findings and extend the molecular weight range to higher molecular weight. We believe that at the current stage, even though there appears to be no theory which can explain this phenomenon, a rather strong A_3–M dependence for PS in these Θ solvents can be safely stated. Yamakawa et al.[17] have showed clearly that increases observed in A_3 for low M_w PS in CH are due to chain end effects.

Values of radii of gyration for two PS samples in the three Θ solvents are listed in Table 5. The unperturbed dimensions for PS in these three solvens are almost constant, with average $\langle R_g^2\rangle_w/M_w$ values of 8.93 × 10^{-18}, 8.78 × 10^{-18}, and 8.77 × 10^{-18} cm^2 mol/g for PS in cyclohexane, 1-chloroundecane, and DEM, respectively. The value obtained in cyclohexane is in agreement with the value of 8.88 × 10^{-18} cm^2 mol/g reported by Miyaki et al.[39,40] The $\langle R_g^2\rangle_w/M_w$ value in cyclohexane is larger

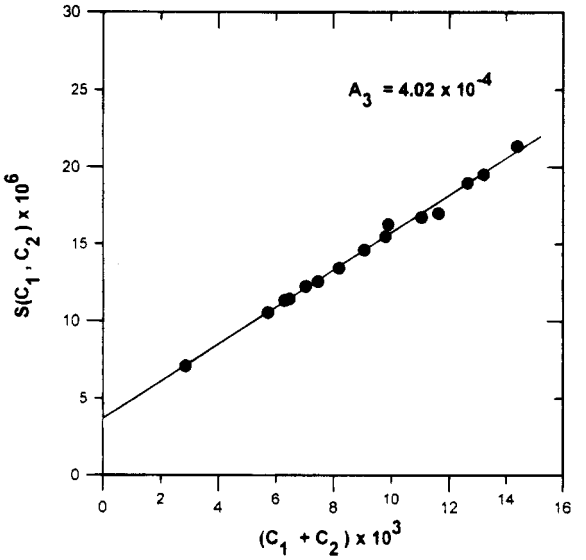

Figure 6. Representative Bawn plot for PS 590K in cyclohexane.

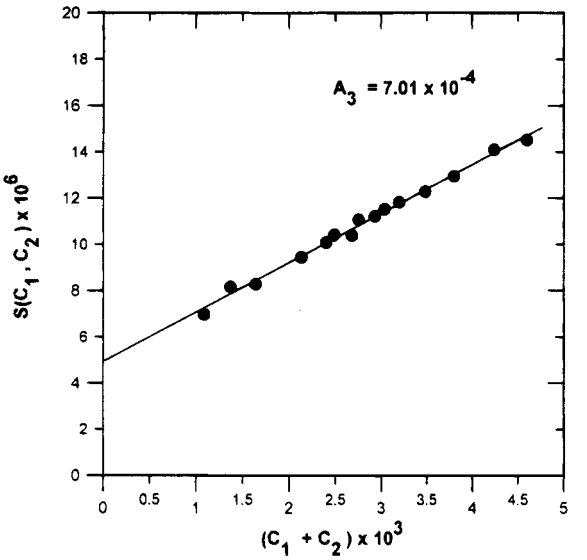

Figure 7. Representative Bawn plot for PS 3.8M in 1-chloroundecane.

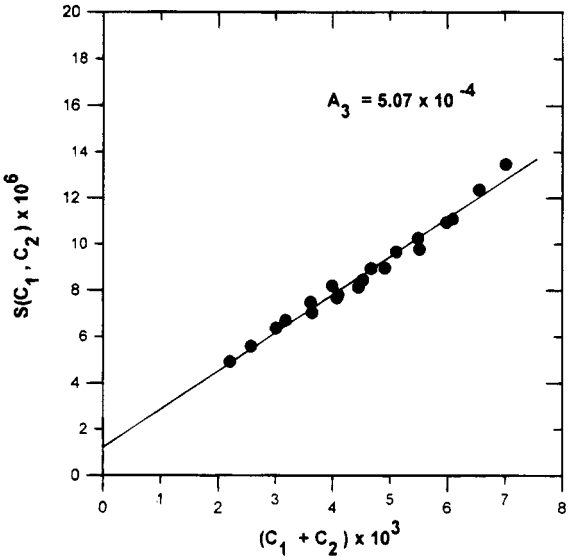

Figure 8. Representative Bawn plot for PS 1.3M in DEM.

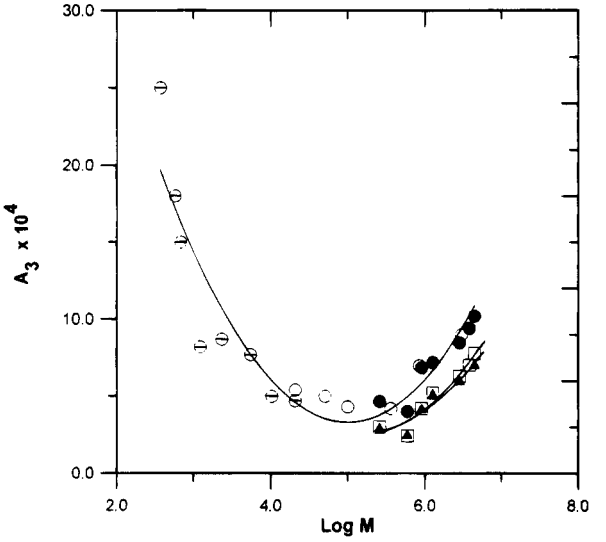

Figure 9. Plot of A_3 versus molecular weight for PS in different Θ solvents: (●) PS/cyclohexane; (□) PS/1-chloroundecane; (▲) PS/diethylmalonate; (○) PS/cyclohexane data of ref 15; (⊖) PS/cyclohexane data of ref 17.

than the values measured in the other solvents but only by about 2%. These values are probably indistinguishable if experimental errors are taken in account. In contrast, the reported K_Θ value is around 10% larger in cyclohexane than in the other two solvents.[29] Thus, the differences among K_Θ values cannot be entirely due to the parameter R_g^2/M but must also result from the differences in ϕ. Similar findings have been reported by Fujii and co-workers[24] for poly(methyl methacrylate) (PMMA) in two Θ solvents, acetonitrile and butyl chloride, where ϕ is reported to be solvent dependent. Based on our experiments, the value of ϕ in cyclohexane must be larger than those in 1-chloroundecane and DEM.

In conclusion, we have observed positive third virial coefficients, which are dependent on the particular Θ solvents used. An interesting A_3 versus M relationship was obtained, which awaits theoretical explanation. The differences in "unperturbed dimensions" for PS in various solvents obtained through viscometric measurements appears to be mainly due to the differences in hydrodynamic constants of the different polymer–solvent systems. Measured R_g values are only marginally larger in CH than in CUD or DEM.

Table 4. $A_3 \times 10^4$ (mol g^{-3} cm^6) Measured for PS in Three Θ Solvents

	CH, 34.5 °C		CUD, 33.0 °C		DEM, 35.0 °C	
sample	Bawn	polynomial	Bawn	polynomial	Bawn	polynomial
PC233K	4.67	5.27	3.01	2.99	2.89	2.08
PC590K	4.02	4.02	2.43	2.42	2.45	2.60
PC900K	6.84	7.04	4.20	3.95	4.11	4.33
TS1.3M	7.21	7.21	5.23	5.39	5.07	5.53
TS2.9M	8.47	8.58	6.31	7.01	5.96	5.78
TS3.8M	9.41	9.08	7.01	6.91		
TS4.5M	10.2	10.2	7.79	7.72	6.99	6.60

The strong solvent dependence of A_3 values is similar to that reported previously by Berry and co-workers[13,14] for PS in cyclohexane and cyclopentane. Since A_3 at Θ reflects repulsive three-body interactions,[41] it might be expected that systems exhibiting larger A_3 values might also exhibit larger unperturbed dimensions. The large differences in A_3 for PS in the various Θ solvents are not reflected in corresponding larger unperturbed radii of gyration. Theoretical work by Cherayil et al.[22]

Table 5. Radii of Gyration of Two PS Samples in Three Θ Solvents

system	$\langle R_g \rangle_w$[a]	$\langle R_g^2 \rangle_w / M$[b]
TS2.9M/CH	50.3	8.89
TS4.5M/CH	63.4	8.97
TS2.9M/CUD	50.0	8.76
TS4.5M/CUD	62.8	8.80
TS2.9M/DEM	49.7	8.86
TS4.5M/DEM	63.1	8.87

[a] In units of nm. [b] In units of 10^{-18} cm^2 mol/g.

predicts an impact of ternary interactions of hydrodynamic properties but little impact on R_g.

We hope that the data reported in this paper will stimulate more theoretical and experimental work in this area. We are presently conducting A_3 measurements on PS stars in both good and Θ solvents.

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Note added in proof: The nonzero A_2 values in the Θ solvents should have negligible impact on the reported A_3 values since $(A_2M)^2$ is not large in comparison with A_3M.

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