# Hydrodynamic and Thermodynamic Properties of Poly($\alpha$-methylstyrene) in Dilute *n*-Butyl Chloride Solution

**Jimmy W. Mays,*,† Shouyan Nan,† and Michael E. Lewis‡**

*Departments of Chemistry and Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294*

*Received January 29, 1991; Revised Manuscript Received April 9, 1991*

ABSTRACT: Solution properties of near-monodisperse poly($\alpha$-methylstyrene) chains in the moderate solvent *n*-butyl chloride were investigated by a combination of static and dynamic light scattering and intrinsic viscosity measurements. These data allow the determination of the radii of gyration ($R_G$) as well as equivalent sphere radii: the hydrodynamic radius ($R_H$), the viscometric radius ($R_V$), and the thermodynamic radius ($R_T$) (defined below). Ratios of these various radii allow a comparison between solution properties of poly($\alpha$-methylstyrene) in *n*-butyl chloride and those of other polymer/solvent systems, as well as with theoretical predictions. Whereas $R_G/R_H$ values are intermediate, as expected, between those normally found in good solvents or at the $\Theta$ state, the average value of $R_V/R_H = 1.18_5$ is substantially larger than that commonly found for other chains in solvents of varying thermodynamic quality. Unusually large values of $R_V/R_H$ were also recently reported for the related system, polystyrene/*n*-butyl chloride. Such a dependence of $R_V/R_H$ on solvent quality (larger values in thermodynamically moderate solvents) has not been previously noted or predicted by theory.

## Introduction

Numerous experimental studies of hydrodynamic and thermodynamic properties of linear polymers in dilute solution have been conducted over the last several decades. The vast majority of these studies have involved polymers in thermodynamically good solvents (large positive second virial coefficients, $A_2 \gg 0$) or in $\Theta$ media ($A_2 = 0$). In contrast, rigorous studies involving measurement of all of the primary chain parameters (molecular weight ($M$), radius of gyration ($R_G$), intrinsic viscosity ($[\eta]$), translational diffusion coefficient ($D_0$), and $A_2$) for chains in moderate solvents ($A_2 > 0$) are extremely rare.

In this work, the thermodynamic and hydrodynamic properties of poly($\alpha$-methylstyrene) (P$\alpha$MS) in the moderate solvent *n*-butyl chloride are reported. The data were obtained by a combination of photon correlation spectroscopy (PCS), low-angle laser light scattering (LALLS), multiangle laser light scattering (MALLS), and viscometry. The results are compared to available experimental and theoretical results.

## Experimental Section

P$\alpha$MS samples used in this study were the near-monodisperse products of controlled anionic polymerizations. They were either purchased as polymer standards (Pressure Chemical Co. and Polymer Laboratories) or prepared by using standard high-vacuum techniques.

Size-exclusion chromatography (SEC) experiments were conducted by using a Waters Model 510 pump and Waters Model 410 differential refractometer. Tetrahydrofuran (Aldrich, 99+%, used as received) was the mobile phase at 30 °C and at a flow rate of 1 mL min$^{-1}$. The column set consisted of two Waters "Linear Ultrastyragel" columns having continuous porosities of $10^2$–$10^6$ Å. Twenty microliters of ca. 0.2% (w/v) polymer solutions was injected (Rheodyne injector). Polydispersities were calculated based on a direct calibration obtained using, in part, the near-monodisperse polymers of this work, where absolute weight-average molecular weights ($M_w$) were determined by LALLS or MALLS (see below).

LALLS experiments were conducted by using a Chromatix KMX-6 unit at 25 °C. This instrument was operated at an angle of 6–7° and at a wavelength of 633 nm. Solutions were filtered directly into the scattering cell through 0.2- or 0.45-$\mu$m poly(tetrafluoroethylene) filters. Specific refractive index increments ($dn/dc$) at 633 nm and 25 °C were measured with a Chromatix KMX-16 unit, which was calibrated with aqueous KCl solutions. $dn/dc$ values of 0.2094 and 0.122 mL g$^{-1}$ were measured for P$\alpha$MS/*n*-butyl chloride and P$\alpha$MS/toluene, respectively. The lowest molecular weight P$\alpha$MS sample (PC-3) exhibited lower $dn/dc$ values of 0.107 and 0.2056 in toluene and *n*-butyl chloride. The *n*-butyl chloride solvent was purchased from Fluka or Aldrich (HPLC grade) and was 99.9% pure by gas chromatography. Toluene was obtained from Burdick & Jackson (distilled-in-glass grade) and was used as received. Data were analyzed by conventional plots of $Kc/R_\theta$ versus $C$, where $K$ is the optical constant, $c$ is the concentration, and $R_\theta$ is the excess Rayleigh factor. For static and dynamic light scattering experiments, the concentrations ranged from about $5 \times 10^{-3}$ to $2 \times 10^{-2}$ g mL$^{-1}$ at the lowest molecular weights and from about $2 \times 10^{-5}$ to $1 \times 10^{-3}$ g mL$^{-1}$ at the highest molecular weights.

MALLS experiments were conducted on the four highest molecular weight P$\alpha$MS samples in *n*-butyl chloride at 25 °C. A Brookhaven Instruments Company goniometer was used in conjuction with a Spectra Physics Series 2000 argon-ion laser operating at a wavelength ($\lambda$) of 488 nm and a power of ca. 25 mW. The alignment was confirmed by measuring the scattering envelope for carefully purified toluene; $I$ sin $\Theta$ values were identical (±1%) between 30 and 120° ($I$ = intensity, $\Theta$ = scattering angle). Calibration was based on the scattering of pure toluene.[1] Conventional Zimm plots were used to treat the experimental data.

All solvents and solutions were freed of particulates by using the closed-loop filtration system[2] with 0.2- or 0.45-$\mu$m pore size poly(tetrafluoroethylene) filters. MALLS data were analyzed via conventional Zimm plots. The $dn/dc$ value for P$\alpha$MS/*n*-butyl chloride under these conditions was measured by using a C. N. Wood Model 6000 unit with the RF-500 attachment. A value of 0.2185 mL g$^{-1}$ was obtained. In addition, a value of 0.2239 mL g$^{-1}$ was measured at 436 nm. The combined $dn/dc$ data at the three wavelengths for this polymer/solvent system are shown in Figure 1.

PCS experiments also involved the Brookhaven goniometer at an angle of 25° and the Spectra Physics Series 2000 argon-ion laser at 488 nm. Laser power was varied from 25 to 100 mW depending on scattering efficiencies. Temperature was controlled to 25 ± 0.1 °C. A Brookhaven Model BI2030 correlator was used; data were analyzed to second order by the method of cumulants.[3,4] Second moment values were always less than 0.1, and calculated and measured baselines differed by less than 0.02%.

† Department of Chemistry.
‡ Department of Physics.

0024-9297/91/2224-4857$02.50/0 

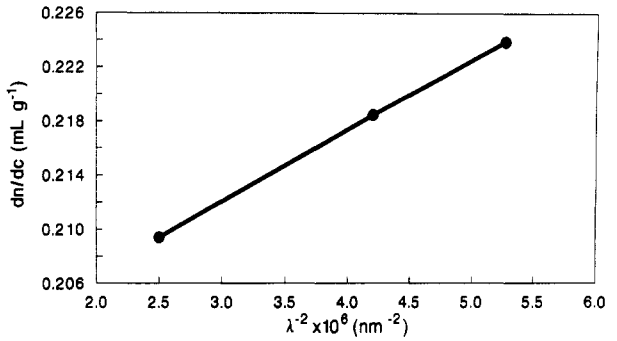


**Figure 1.** Cauchy plot for d$n$/dc of P$\alpha$MS/$n$-butyl chloride as a function of wavelength.

**Table I**
**Molecular Characteristics of P$\alpha$MS Samples**

| sample | $10^{-4}M_w$,[a] g mol$^{-1}$ | $10^4A_2$,[b] mL mol g$^{-2}$ | $R_G$,[b] nm | $M_w/M_n$[c] | $M_z/M_w$[c] |
|---|---|---|---|---|---|
| JL-4 | 354 | 0.60 | 57.9 | 1.15 | 1.13 |
| PC-16 | 107 | 0.98 | 32.2 | 1.11 | 1.08 |
| PL-770 | 88.1 | 1.06 | 27.7 | 1.05 | 1.04 |
| PC-17 | 66.6 | 1.19 | 23.9 | 1.09 | 1.06 |
| PC-10 | 51.5 | 1.07 | | 1.06 | 1.06 |
| PL-285 | 31.5 | 1.04 | | 1.04 | 1.03 |
| PC-6 | 30.3 | 1.19 | | 1.07 | 1.06 |
| PL-150 | 17.1 | 1.41 | | 1.05 | 1.05 |
| PC-4 | 11.6 | 1.48 | | 1.03 | 1.03 |
| PC-2 | 7.43 | 1.72 | | 1.03 | 1.02 |
| PL-55 | 5.97 | 2.01 | | 1.13 | 1.11 |
| PC-8 | 5.38 | 1.86 | | 1.06 | 1.05 |
| PC-1 | 2.49 | 2.66 | | 1.14 | 1.12 |
| PL-19 | 2.02 | 2.71 | | 1.03 | 1.03 |
| PC-3 | 0.69 | 2.97 | | 1.33 | 1.25 |

[a] Average of LALLS and MALLS (where available) values. [b] In $n$-butyl chloride at 25 °C. [c] Via SEC.

Viscometry experiments were conducted by using Ubbelohde dilution viscometers requiring negligible kinetic energy corrections. Temperature control to ±0.02 °C was achieved with a water bath and Fisher heater/circulator. Solution concentrations were chosen to give relative viscosities between 1.7 and 1.1. [$\eta$] values and Huggins coefficients $k_H$ were derived from Huggins plots; [$\eta$] values were reproducible to ±1%.

## Results and Discussion

Molecular characteristics of the P$\alpha$MS samples are given in Table I. The very narrow molecular weight distributions exhibited by these samples eliminate the need for polydispersity corrections. In subsequent analysis, these samples are considered to be monodisperse.

The $A_2$ and $M_w$ data of Table I lead to the following power law

$$A_2 = 3.11 \times 10^{-3} M_w^{-0.255} \quad (\text{mL mol g}^{-2}) \qquad (1)$$

which is valid over the entire range of molecular weights (6900–3540 000; correlation coefficient of 0.977). These data are also plotted in Figure 2. Although the exponent of −0.255 is in agreement with theoretical predictions corresponding to thermodynamically good solvents,[5] the absolute magnitudes of the $A_2$ values are much smaller than those reported earlier for P$\alpha$MS in the self-avoiding limit.[6-8] Interestingly, an exponent of −0.23 was recently reported by Cotts and Selser[8] for P$\alpha$MS in the moderate solvent cyclohexane at 50 °C.

The $R_G$ and $M_w$ data of Table I lead to the expression

$$R_G = 2.10 \times 10^{-2} M_w^{0.526} \quad (\text{nm}) \qquad (2)$$

with a correlation coefficient of 0.9982 (see also Figure 3). This exponent of 0.526 fortifies the $A_2$ data in that $n$-butyl chloride at 25 °C is a moderate solvent for P$\alpha$MS, since theory and experiment support exponents of 1/2 at the Θ condition and of ca. 0.588[9] at the self-avoiding (good solvent) limit.

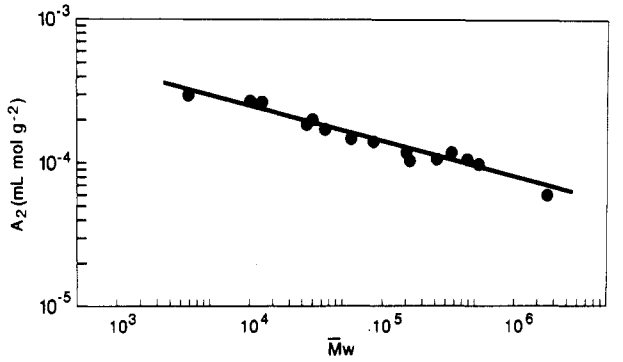


**Figure 2.** Dependence of $A_2$ on $M_w$ for P$\alpha$MS/$n$-butyl chloride.

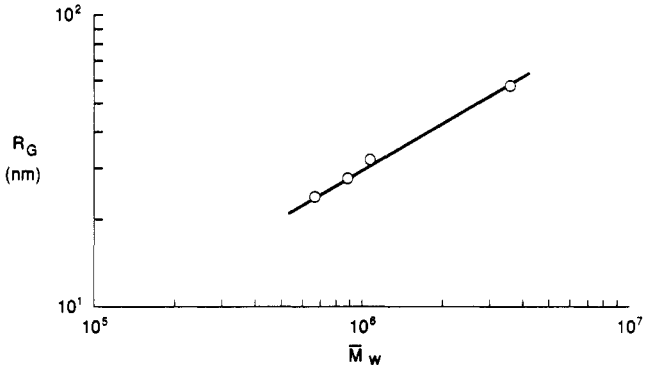


**Figure 3.** Power law dependence of $R_G$ on $M_w$.

**Table II**
**Hydrodynamic Properties of P$\alpha$MS in $n$-Butyl Chloride at 25 °C**

| sample | $10^{-4}M_w$, g mol$^{-1}$ | [$\eta$], mL g$^{-1}$ | $k_H$ | $10^7D_0$, cm$^2$ s$^{-1}$ | $k_d$, mL g$^{-1}$ |
|---|---|---|---|---|---|
| JL-4 | 354 | 198 | 0.74 | 1.26 | −21.9 |
| PC-16 | 107 | 98.5 | 0.50 | 2.38 | −25.6 |
| PL-770 | 88.1 | 86.2 | 0.56 | 2.67 | −25.4 |
| PC-17 | 66.6 | 74.1 | 0.50 | 3.04 | −26.1 |
| PC-10 | 51.5 | 62.6 | 0.59 | | |
| PL-285 | 31.5 | 46.7 | 0.64 | | |
| PC-6 | 30.3 | 46.4 | 0.59 | 4.56 | −23.2 |
| PL-150 | 17.1 | 32.5 | 0.68 | 6.38 | −24.3 |
| PC-4 | 11.6 | 26.1 | 0.68 | | |
| PC-2 | 7.43 | 20.5 | 0.58 | 10.1 | −22.3 |
| PL-55 | 5.97 | 17.5 | 0.79 | | |
| PC-8 | 5.38 | 17.0 | 0.82 | 11.4 | −24.8 |
| PC-1 | 2.49 | 11.5 | 0.77 | | |
| PL-19 | 2.02 | 10.1 | 0.90 | | |
| PC-3 | 0.69 | 6.1 | 0.86 | | |

Hydrodynamic properties of P$\alpha$MS in $n$-butyl chloride are summarized in Table II. The Mark–Houwink–Sakurada (MHS) equation, valid over the molecular weight range of 53 800–3540 000 is

$$[\eta] = 2.70 \times 10^{-2} M_w^{0.590} \quad (\text{mL g}^{-1}) \qquad (3)$$

with a correlation coefficient of 0.9999 (see Figure 4). The MHS exponent also suggests a condition of moderate solvent quality for this polymer/solvent/temperature combination. The $k_H$ values are also typical of a moderate solvent, since values of ca. 0.4[7] and ca. 1.0[10] have been found for P$\alpha$MS in good and Θ solvents, respectively.

Values of $D_0$ and $k_d$, the diffusion virial coefficient, are calculated from $D_{app}$ values as a function of concentration from $D_{app} = D_0(1 + k_dc + ...)$. The $D_0$ values of Table II lead to the expression (see also Figure 5)

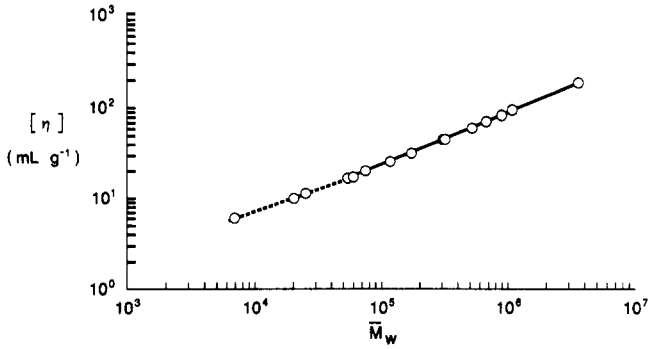


**Figure 4.** MHS plot for PαMS/*n*-butyl chloride.

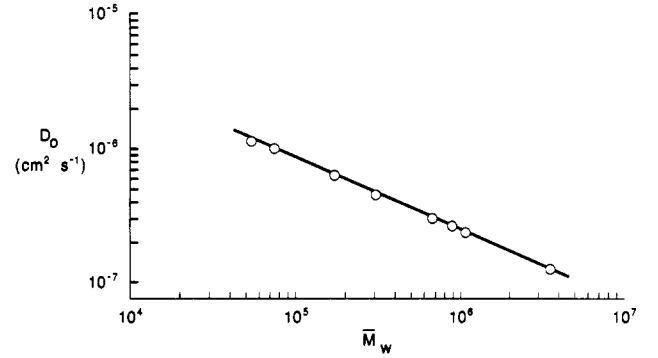


**Figure 5.** Variation of $D_0$ with $M_w$ for PαMS/*n*-butyl chloride.

$$D_0 = 3.81 \times 10^{-4} M_w^{0.531} \quad (\mathrm{cm^2\ s^{-1}}) \tag{4}$$

This equation is valid (correlation coefficient = 0.9997) over the molecular weight range of 53 800–3540 000.

The $k_d$ values are of interest. Generally, positive values are found in good solvents and negative values are found in Θ solvents, with both systems exhibiting larger absolute values with increasing molecular weight (see, for example, refs 7, 8, 11, and 12). Both negative and positive values are reported in marginal solvents[8,12,13] depending on absolute solvent quality and $M_w$. In this work, constant negative values of $k_d$ (within experimental error ca. ±10%) are found over nearly 2 orders of magnitude in molecular weight. The $k_d$ values reported by Cotts and Selser[8] for the moderate solvent system PαMS/cyclohexane at 50 °C were also negative and showed only a weak dependence on $M_w$.

Values of $k_f$, the frictional virial coefficient, may be calculated from $k_d$ as

$$k_f = 2A_2M - v_2 - k_d \tag{5}$$

where $v_2$ is the partial specific volume of the polymer.

The reduced frictional virial coefficient, $k_f^*$, may then be derived from

$$k_f^* = k_f(M/V_H N_A) \tag{6}$$

where $V_H = {}^4/_3\pi R_H^3$ and $R_H$, the hydrodynamic radius, equals $kT/(6\pi\eta_0 D_0)$ where $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $\eta_0$ is the solvent viscosity. Values of $k_f$ and $k_f^*$ are presented in Table III. The $k_f^*$ values, like the $k_H$ values of Table II, are independent of molecular weight. The average value of 9.8 is in fair agreement with the theoretical value of 7.2 suggested by Pyun and Fixman[14] for spheres and the experimental value of 7.0 reported for the PαMS/toluene (good solvent) system.[7]

Besides the physical radius ($R_G$) values of Table I, equivalent sphere radii can also be derived from the $A_2$, $[\eta]$, and $D_0$ data of Tables I and II. The thermodynamic

**Table III**
**Frictional Virial Coefficients of the PαMS/*n*-Butyl Chloride System**

| sample | $10^{-4}M_w$, g mol$^{-1}$ | $k_f$, mL g$^{-1}$ | $k_f^*$ |
|---|---|---|---|
| JL-4 | 354 | 446 | 9.3 |
| PC-16 | 107 | 234 | 10.0 |
| P-770 | 88.1 | 211 | 10.4 |
| PC-17 | 66.6 | 184 | 10.1 |
| PC-6 | 30.3 | 94.4 | 8.1 |
| PL-150 | 17.1 | 71.6 | 9.3 |
| PC-2 | 7.43 | 47.0 | 10.6 |
| PC-8 | 5.38 | 43.9 | 10.3 |

**Table IV**
**Equivalent Sphere Radii[a] and Size Ratios for PαMS in *n*-Butyl Chloride**

| sample | $10^{-4}M_w$, g mol$^{-1}$ | $R_T$ | $R_V$ | $R_H$ | $R_G/R_H$ | $R_T/R_H$ | $R_V/R_H$ |
|---|---|---|---|---|---|---|---|
| JL-4 | 354 | 42.1 | 48.1 | 40.7 | 1.42 | 1.03 | 1.18 |
| PC-16 | 107 | 22.3 | 25.6 | 21.5 | 1.50 | 1.04 | 1.19 |
| PL-770 | 88.1 | 20.1 | 22.9 | 19.2 | 1.44 | 1.05 | 1.19 |
| PC-17 | 66.6 | 17.4 | 19.8 | 16.9 | 1.41 | 1.03 | 1.17 |
| PC-10 | 51.5 | 14.1 | 17.2 | 14.6[b] | | 0.97 | 1.18 |
| PL-285 | 31.5 | 10.1 | 13.3 | 11.2[b] | | 0.90 | 1.19 |
| PC-6 | 30.3 | 10.3 | 13.1 | 11.2 | | 0.92 | 1.17 |
| PL-150 | 17.1 | 7.42 | 9.58 | 8.04 | | 0.92 | 1.19 |
| PC-4 | 11.6 | 5.83 | 7.83 | 6.60[b] | | 0.88 | 1.19 |
| PC-2 | 7.43 | 4.55 | 6.22 | 5.08 | | 0.90 | 1.22 |
| PL-55 | 5.97 | 4.14 | 5.49 | 4.64[b] | | 0.89 | 1.18 |
| PC-8 | 5.38 | 3.77 | 5.25 | 4.50 | | 0.84 | 1.17 |
| PC-1 | 2.39 | 2.54 | 3.57 | | | | |
| PL-19 | 2.02 | 2.22 | 3.18 | | | | |
| PC-3 | 6.9 | 1.12 | 1.88 | | | | |

[a] Radii are in nm. [b] Calculated from the power law.

radius, $R_T$, is defined as[15]

$$R_T = [(3M^2A_2)/(16\pi N_A)]^{1/3} \tag{7}$$

while the viscometric radius, $R_V$, is derived from the expression[16]

$$R_V = ([\eta]M)^{1/3}(10/3\pi N_A)^{-1/3} \tag{8}$$

The hydrodynamic radius, $R_H$, was defined above; values of these three radii and various ratios of the radii are collected in Table IV.

The average value of $R_G/R_H$ of 1.44 is, as expected, slightly smaller than the good solvent PαMS/toluene value of 1.54.[7] It is substantially larger, however, than the experimental value for the Θ system, PS/cyclohexane ($R_G/R_H$ = 1.28[17]). Theory predicts values between 1.50[18] and 1.29[19] in the nondraining good solvent limit.

The $R_T/R_H$ values of Table IV initially increase with molecular weight and then level off at a value of ca. 1.04 at high molecular weights. This limiting value is in excellent agreement with the theoretical estimate of 1.04 predicted by Oono[20] for self-avoiding coils and also agrees with the value of unity, corresponding to hard spheres. This asymptote is, however, considerably larger than the value of 0.914 suggested by Douglas et al.[19] The lower values of $R_T/R_H$ at low molecular weights are indicative of the diminishing excluded volume effect in this regime ($R_T$ = 0 for unperturbed coils).

The $R_V/R_H$ values are of special interest. No molecular weight dependence is observed; the average value for this parameter is $1.18_5$. This value falls between the early theoretical values of 1.23 and 1.13[14,20,21] for unperturbed and self-avoiding coils, respectively, but is much larger than the values of 1.03 ± 0.05 reported previously[22] for PS chains of various architectures in both good and Θ solvents and the more recent theoretical values of 1.07 and 1.03 for Θ and nondraining good solvents, respectively.[19] The

Table V
Intrinsic Viscosities and Huggins Coefficients of PαMS in n-Butyl Chloride as a Function of Temperature

| | | at 5 °C | | at 50 °C | |
|---|---|---|---|---|---|
| sample | $M_w$, g mol$^{-1}$ | $[\eta]$, mL g$^{-1}$ | $k_H$ | $[\eta]$, mL g$^{-1}$ | $k_H$ |
| PL-55 | 60 300 | 17.6 | 0.81 | 18.2 | 0.54 |
| PC-2 | 72 700 | 20.0 | 0.74 | 20.7 | 0.47 |
| PC-4 | 116 000 | 25.9 | 0.67 | | |
| PL-150 | 166 000 | 31.9 | 0.68 | 33.5 | 0.52 |
| PC-6 | 301 000 | 45.1 | 0.61 | 46.8 | 0.55 |
| PL-285 | 315 000 | 46.1 | 0.60 | | |
| PC-17 | 656 000 | 70.0 | 0.55 | 75.3 | 0.46 |
| PC-16 | 1070 000 | 90.8 | 0.54 | 102 | 0.40 |

present result is, however, in excellent accord with the result $R_V/R_H = 1.16$ found previously[23] for the PS/n-butyl chloride system. Reasons for these differences in experimental $R_V/R_H$ ratios for different PS/solvent systems and in comparison to theory are not apparent, although $R_V$ does contain both static and dynamic contributions,[24] whereas $R_H$ is purely dynamic. At any rate, it appears that $R_V/R_H$ values may assume larger values for a given polymer chain in thermodynamically moderate solvents than in either good or Θ solvents. This finding, to our knowledge, is not predicted by theory. In future work, we plan to probe the behavior of PS in another moderate solvent, 2-butanone, to try and ascertain if large $R_V/R_H$ ratios are an inherent characteristic of moderate solvent systems.

Radii data of Table IV lead to the following power laws:

$$R_T = 6.77 \times 10^{-3} M_w^{0.582} \quad (9)$$

($6900 \le M_w \le 3.54 \times 10^6$, correlation coefficient = 0.9995)

$$R_V = 1.62 \times 10^{-2} M_w^{0.530} \quad (10)$$

($53\,800 \le M_w \le 3.54 \times 10^6$; correlation coefficient > 0.9999)

$$R_H = 1.35 \times 10^{-2} M_w^{0.531} \quad (11)$$

($53\,800 \le M_w \le 3.54 \times 10^6$; correlation coefficient = 0.9998)

The power law exponents of ca. 0.53 for $R_V$ and $R_H$ relationships are in very close agreement with that reported above (eq 2) for the radius of gyration. The larger exponent for the $R_T$-based equation, as noted above, reflects the approach toward unperturbed dimensions at low molecular weight.

Finally, in Table V we present data for $[\eta]$ and $k_H$ obtained at 5 and 50 °C. These data and the data of Table II show clearly that chain expansion changes negligibly on going from 50 to 25 °C, and only a small decrease in $[\eta]$ is observed on further reducing temperature to 5 °C. The data of Table V lead to the following MHS equations at 50 and 5 °C, respectively

$$[\eta] = 2.65 \times 10^{-2} M_w^{0.594} \ (\text{mL g}^{-1}) \quad (12)$$

$$[\eta] = 3.36 \times 10^{-2} M_w^{0.570} \ (\text{mL g}^{-1}) \quad (13)$$

A comparison of the exponents of eqs 3, 12, and 13 again suggests only a marginal change in solvent quality on going from 50 to 5 °C. Earlier work with the PS/n-butyl chloride moderate solvent system also noted only a very weak dependence of size on temperature.[23] This aspect of the behavior of these polymer/moderate solvent systems is not seen in other "moderate" systems such as PS in cyclohexane or decalin above the Θ temperature.[25]

In summary, the power law exponents for the dependence of various measures of polymer size as a function of molecular weight are intermediate between those reported in good and Θ solvents. $A_2$ and $k_H$ values are also intermediate in magnitude, as is the ratio $R_G/R_H$. In contrast, unusually large values of $R_V/R_H$ are found; the values are larger than those observed previously in both good and Θ solvents and larger than predicted by the most recent theory.[19] This finding, along with previous results for polystyrene in n-butyl chloride,[2] suggests that this ratio may assume a maximum in solvents of intermediate thermodynamic quality.

**Acknowledgment.** This work was supported in part by a NSF-EPSCoR award to J.W.M. J.W.M. also acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. We are also grateful to Professor W. W. Wilson (Mississippi State University) for the use of the C. N. Wood photometer.

## References and Notes

(1) Bender, T. M.; Lewis, R. J.; Pecora, R. *Macromolecules* **1986**, *19*, 244.
(2) For a brief description of the closed loop filtration system, see: Lewis, M. E.; Nan, S.; Mays, J. W. *Macromolecules* **1991**, *24*, 197.
(3) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(4) Pusey, P. N. In *Photon Correlation and Light Beating Spectroscopy*; Cummins, H. Z., Pike, E. R., Eds.; Plenum: New York, 1974; p 397.
(5) Berry, G.; Casassa, E. F. *J. Polym. Sci., Part D* **1970**, *4*. 1. de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(6) Kato, T.; Miyaso, K.; Noda, I.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 777.
(7) Lindner, J. S.; Wilson, W. W.; Mays, J. W. *Macromolecules* **1988**, *21*, 3304.
(8) Cotts, P. M.; Selser, J. C. *Macromolecules* **1990**, *23*, 2050.
(9) LeGuillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(10) Mays, J. W.; Hadjichristidis, N.; Graessley, W. W.; Fetters, L. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2553.
(11) King, T. A.; Knox, A.; Lee, W. I.; McAdam, J. D. G. *Polymer* **1973**, *14*, 151.
(12) Fetters, L. J.; Hadjichristidis, N.; Lindner, J. S.; Mays, J. W.; Wilson, W. W. *Macromolecules* **1991**, *24*, 3127.
(13) King, T. A.; Knox, A.; McAdam, J. D. G. *Polymer* **1973**, *14*, 293.
(14) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 937.
(15) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(17) Schmidt, M.; Burchard, W. *Macromolecules* **1980**, *13*, 657.
(18) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 2344; **1985**, *18*, 201.
(19) Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168. This reference gives theoretical values of 1.29 for $R_G/R_H$ in both Θ and nondraining good solvents. Fixman (Fixman, M. *J. Chem. Phys.* **1986**, *84*, 4085) has indicated that increases in the $R_G/R_H$ parameter in good solvents over that observed at the Θ state cannot be predicted without taking into account the effect of internal friction. In addition, $R_G/R_H$ has been shown to depend on chain conformation and stiffness (Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **1989**, *91*, 7900).
(20) Oono, Y. *J. Chem. Phys.* **1983**, *79*, 4629.
(21) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838.
(22) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(23) Lewis, M. E.; Nan, S.; Mays, J. W. *Macromolecules* **1991**, *24*, 197.
(24) Weill, G.; des Cloizeaux, J. *J. Phys.* **1979**, *40*, 99.
(25) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550; **1967**, *46*, 1338.

**Registry No.** PαMS, 25014-31-7; butyl chloride, 109-69-3.