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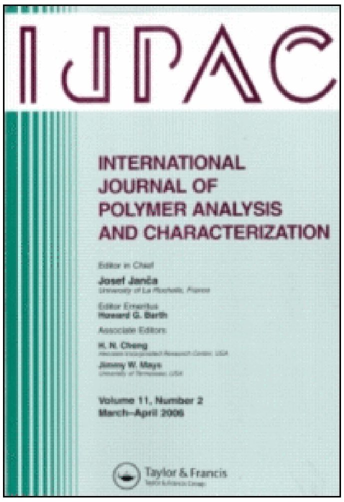

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
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Solution Properties of Poly(Methyl Methacrylate) in Dimethylsulfoxide

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To cite this Article Moyses, Stephan(2008) 'Solution Properties of Poly(Methyl Methacrylate) in Dimethylsulfoxide', International Journal of Polymer Analysis and Characterization, 13: 6, 413 — 427
To link to this Article: DOI: 10.1080/10236660802396354
URL: http://dx.doi.org/10.1080/10236660802396354

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International Journal of Polymer Anal. Charact., 13: 413–427, 2008
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ISSN: 1023-666X print
DOI: 10.1080/10236660802396354

Solution Properties of Poly(Methyl Methacrylate) in Dimethylsulfoxide

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Abstract: The solution properties of polymethylmethacrylate in dimethylsulfoxide were studied using multi-angle light scattering and an online viscometer coupled to size exclusion chromatography. The data demonstrate that DMSO is a suitable eluent for the determination of the molecular weight of PMMA by SEC. The Mark-Houwink coefficients K and α were determined as a function of temperature. At 35°C, DMSO is a theta solvent for PMMA, and it becomes a good solvent as the temperature increases. The unperturbed dimension K_θ was calculated using three different procedures. The data do not show evidence of a conformational transition controlled by the temperature such as the one reported in benzene and confirm the existence of a general relationship between the ratio K/K_θ and α. In the case of PMMA, the comparison of the dipole moment of the side group to that of the solvent can be used to predict the existence of a conformational transition.

Keywords: Intrinsic viscosity; Polymethylmethacrylate; Unperturbed dimension

INTRODUCTION

Dimethylsulfoxide (DMSO) is used as an eluent for the size exclusion chromatography (SEC) of polysaccharides.[1,2] DMSO is also well suited as a chromatographic solvent for poly(vinylidene fluoride).[3] When SEC is used in conjunction with online detectors such as multi-angle light

Submitted 15 July 2008; revised 7 August 2008; accepted 8 August 2008.
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scattering (MALS) and viscometers, a detailed characterization of the solution properties of these polymers is possible.

The properties of polymethylmethacrylate (PMMA) in solution have been the subject of numerous studies. Búrdalo et al.[4] determined the unperturbed dimensions of PMMA in tetrahydrofuran (THF). Kawai and Ueyama[5] found a maximum in the intrinsic viscosity versus temperature curve of PMMA in acetone. Katime and coworkers reported the existence of a conformational transition controlled by temperature in toluene, benzene,[6] and methyl isobutyl ketone[7] but not in 2-heptanone[6] or dimethylformamide (DMF).[8]

The mechanism proposed to explain these observations[9] is as follows: at lower temperature, a conformational order exists that is stabilized by the interactions between the side groups (dipole-dipole). As the temperature is increased, these intramolecular interactions are weaker and the ordered sequences disappear, resulting in a statistical conformation of the chain and an increase in flexibility. In polar solvents, the intramolecular forces between side groups of the polymer chains are inhibited, and this prevents the stabilization of a conformational order. In this study we investigate the properties of PMMA in DMSO with an added electrolyte as a function of temperature. DMSO is of particular interest because it is a highly polar solvent (dipole moment $\mu = 3.96$D) and because it is a critical solvent for PMMA.[10] It is known that the solvent polarity in the liquid state will decrease with increasing temperature,[11] while the addition of an electrolyte will increase it.[12] We measured the unperturbed dimension and the characteristic ratio of PMMA in DMSO/0.1 M LiBr at different temperatures, and we tested the validity of a relationship between the Mark-Houwink coefficients K and α.

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EXPERIMENTAL SECTION

The PMMA standards were purchased from Polymer Laboratories Inc. (Amherst, Mass.) and were used without further purification. Polymer Labs determined their tacticity to be 80% syndiotactic and provided the following molecular weights and polydispersities: $M_P = 5{,}720$ $M_w/M_n = 1.06$, $M_P = 7{,}600$ $M_w/M_n = 1.07$, $M_P = 9{,}400$ $M_w/M_n = 1.10$, $M_P = 12{,}700$ $M_w/M_n = 1.08$, $M_P = 30{,}650$ $M_w/M_n = 1.02$, $M_P = 55{,}600$ $M_w/M_n = 1.02$, $M_P = 100{,}000$ $M_w/M_n = 1.04$, $M_P = 212{,}000$ $M_w/M_n = 1.05$, $M_P = 254{,}100$ $M_w/M_n = 1.04$, $M_P = 745{,}000$ $M_w/M_n = 1.05$, $M_P = 910{,}500$ $M_w/M_n = 1.06$, $M_P = 1{,}577{,}000$ $M_w/M_n = 1.07$. We confirmed these values with light scattering measurements carried out in tetrahydrofuran.

The chromatographic system consisted of an Alliance 2695 equipped with a 2414 differential refractometer (Waters, Milford, Mass.) and a DAWN EOS multi-angle light scattering detector (Wyatt Technology

Corporation, Santa Barbara, Calif.) with a vertically polarized 690 nm semiconductor diode laser. The viscometer was a η-1001 unit (Polymer Standard Services (PSS), Warwick, R.I.). Data acquisition and processing were carried out with the WinGPC software from PSS. We used one modified silica column with 7 µm particle size (Polymer Standard Services, PFG linear XL).

Dimethylsulfoxide and lithium bromide were purchased from Fisher and were used without further purification. The 0.1 M LiBr solution in DMSO used as the eluent was prepared by sonication. The polymer solutions were prepared at concentrations between 0.5 and 4.0 mg/mL depending on the molecular weight. In addition to low-temperature measurements (35°–65°C), we also collected data at 95°C. The high-temperature gel permeation chromatography (GPC) instrument used for this is not tolerant towards salt. For this reason, pure DMSO was used at this temperature. The chromatographic system consisted of a Waters GPCV 2000 with a temperature controlled column/detector compartment that holds a three-capillary viscometer and a differential refractometer. The temperature in the column/detector compartment was 95°C. The light scattering measurements were made using the same MALS detector as for the low temperature measurements. The flow cell and the lines connecting the light scattering detector to the columns and the differential refractometer were held at 95°C. The flow rate was 1.0 mL/min. The data were acquired using the ASTRA software from Wyatt and the Millennium software from Waters. A PLgel mixed B column (Varian) with 10 µm particle size was used at this temperature. The injection volumes were 200 µL and 213 µL for the measurements done at 35°–65°C and 95°C respectively.

The molecular weight M and the root-mean-square radius of gyration R_G were calculated from the light scattering data for each elution time using the relationship established by Zimm:

$$\frac{Kc}{I(q)} = \frac{1}{M}\left(1 + \frac{R_G^2 q^2}{3}\right) + 2A_2 c \tag{1}$$

where

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \tag{2}$$

and q is the scattering vector's amplitude:

$$q = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2} \tag{3}$$

λ is the wavelength of the incident light, n is the refractive index of the solvent, θ is the scattering angle, A_2 is the second virial coefficient, and c is the polymer concentration.

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The determination of the radius of gyration has proven difficult because of the small coil size and the small scattering contrast between PMMA and DMSO. The scattering contrast is provided quantitatively by the refractive index increment dn/dc given by the Gladstone-Dale relation:

$$dn/dc = v_{sp}(n_{pol} - n_{sol}) \tag{4}$$

where v_{sp} is the partial specific volume of the polymer in the solvent, and n_{pol} and n_{sol} are the refractive indices of the polymer and solvent, respectively.

Thus, knowledge of the refractive index increments for PMMA in several solvents of known refractive indices will provide a way to determine dn/dc for any given solvent of known refractive index. Huglin[13] used the data from 19 solvents to determine the Gladstone-Dale relation for PMMA at 546 nm and 20°C:

$$dn/dc_{PMMA/DMSO,546\ nm,20^\circ C} = 0.885 \times (1.500 - n_{sol}) \tag{5}$$

It must be noted that in this case as well as in the case of polyethylene,[14] the reciprocal melt density is a good approximation for the specific volume. Using Equation (5) and the reported value of the refractive index of DMSO at 20°C, n = 1.4795, we get $dn/dc_{PMMA/DMSO,546\ nm,20^\circ C} = 0.018\ ml/g$. In order to obtain the value of the refractive index increment under our experimental conditions, we determined the refractive index increment of PMMA in DMSO at 35°C by injecting different concentrations of a PMMA standard. The differential refractometer peak area was plotted as a function of injected mass. The data were fitted with a linear function the slope of which is directly proportional to the refractive index increment. We obtained $dn/dc_{PMMA/DMSO,690\ nm,35^\circ C} = 0.021\ ml/g$ (690 nm is the wavelength of the light-emitting diode in the refractometer). At 95°C, the refractive index increment of PMMA in DMSO was determined to be $dn/dc_{PMMA/DMSO,880\ nm,95^\circ C} = 0.031\ ml/g$ (880 nm is the wavelength of the light-emitting diode in the refractometer of the GPCV 2000).

Another important parameter for the light scattering experiment is the refractive index of the solvent. Using the data of Tsierkezos et al.,[15] the temperature coefficient dn/dT of the refractive index of DMSO is $-4.75 \times 10^{-4}\,K^{-1}$ at 589 nm. This gives us $n_{DMSO}, 65^\circ C = 1.4583$. There is a 1.5% decrease from the value measured at 20°C. In another article from the same group,[16] the densities of DMSO/LiBr solutions at various molarities were measured at 20°C. At $0.1083\,mol{\cdot}L^{-1}$, they report a density of $1.10831\,g{\cdot}cm^{-3}$ (compare to 1.10041 for pure DMSO). Thus the change in density is small across the salt concentration range under consideration (+0.7%) and we used the values determined in DMSO for processing the data.

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The intrinsic viscosity, $[\eta]$, is obtained from the equation

$$\frac{\eta - \eta_S}{\eta_S c} = [\eta] \times (1 + k_H[\eta]c + \cdots) \qquad (6)$$

where η and η_S are the solution and solvent viscosities respectively and k_H is the Huggins coefficient. For dilute solutions, such as in the case with SEC, the left-hand side of Equation (1) is a good approximation of $[\eta]$.

RESULTS

Viscosity

Figure 1 shows the differential pressure recorded at 50°C as a function of elution time for the various PMMA standards in DMSO/0.1 M LiBr. The values of the intrinsic viscosities are reported in Table I, and Figure 2 shows $[\eta]$ as a function of molecular weight measured at different temperatures for the PMMA standards. The changes in intrinsic

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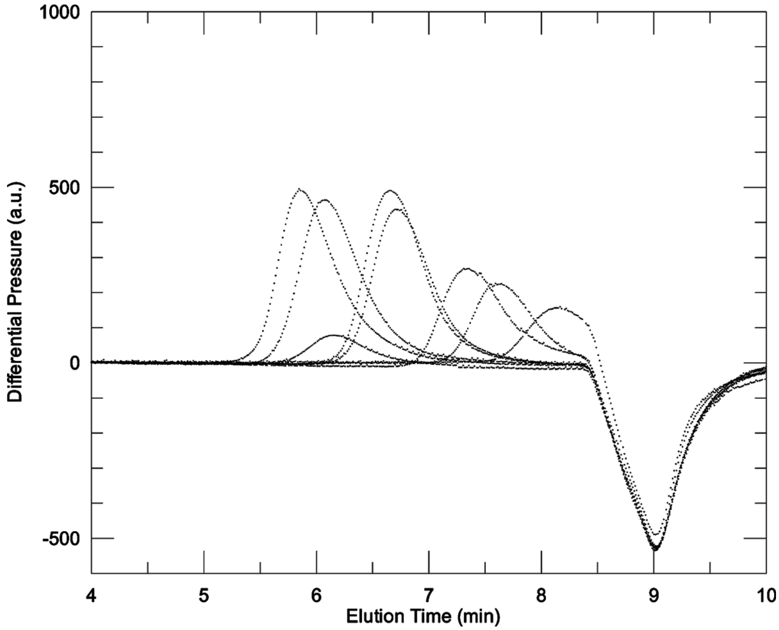

Figure 1. Differential pressure as a function of elution time for the PMMA standards measured at 50°C. The pressure drop at $t = 9$ min is due to the fact that the solvent used to prepare the samples is DMSO while the eluent is DMSO 0.1 M LiBr.

Table I. Intrinsic viscosities [η] (mL/g) for the PMMA standards measured at different temperatures

M kg/mol T°C	5.7	7.6	9.4	12.7	30.7	55.6	100.0	212.0	254.0	745.0	910.0	1,577.0
35	[a]	[a]	[a]	[a]	8.2	11.3	[b]	22.2	24.1	[b]	48.7	56.4
50	[a]	[a]	[a]	6.1	8.9	13.8	[b]	27.6	30.9	54.4	61.2	84.3
65	[a]	[a]	[a]	6.6	9.6	13.9	[b]	30.9	35.2	[b]	81.0	104.0
95	4.5	5.2	6.3	[b]	12.96	18.7	30.6	51.1	56.1	128.1	138.1	189.8

All the measurements were made in DMSO/0.1 M LiBr except the 95°C data, which were acquired in pure DMSO (see text).

[a] At these temperatures, the peak co-eluted with the solvent peaks, and it was not possible to determine [η].

[b] Not measured.

viscosity are significant over the temperature range under study. For example, the intrinsic viscosity of the 212 000 g/mol standard at 95°C nearly equals that of the 910 000 g/mol standard at 35°C. At any of the investigated temperatures, a power function can be used to fit the intrinsic viscosity versus molar mass data ($[\eta] = KM^{\alpha}$). In Figure 2, the

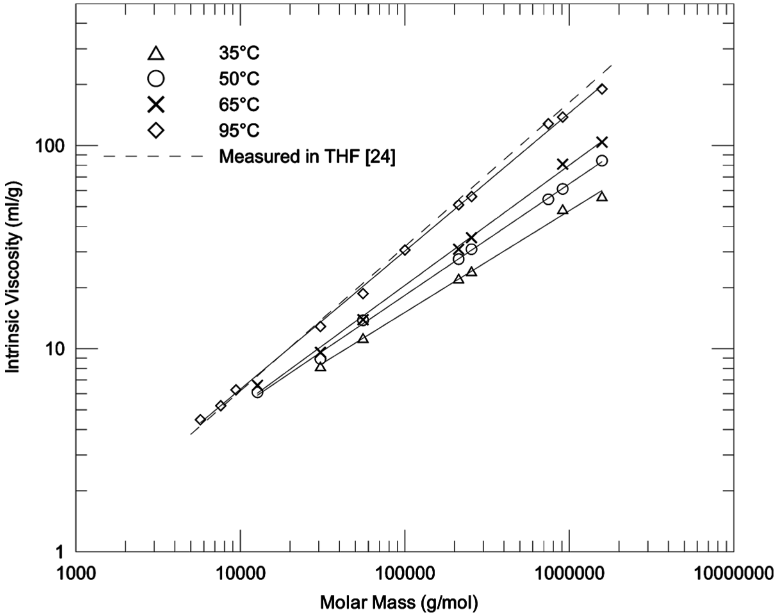

Figure 2. Mark-Houwink plots for the PMMA standards at various temperatures.

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Table II. Mark-Houwink Coefficients for PMMA in DMSO determined at different temperatures

T°C	α	K ($\times 10^3$) mL/g
35	0.50	47.4
50	0.55	33.1
65	0.59	23.5
95	0.68	12.0
25 THF[a]	0.72	7.5

[a] From *Polymer Handbook*.[25]

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dashed line represents the curve expected from the data reported in the literature[17] in tetrahydrofuran. As can be seen at 95°C and in DMSO, the curve approaches that measured in THF at 25°C. The values of the Mark-Houwink coefficients are reported in Table II. At 35°C, $\alpha = 0.50$ and α increases with the temperature indicating that at 35°C, DMSO is a theta solvent for PMMA and that at higher temperatures it becomes a good solvent. For comparison, the α exponent in DMF, another polar solvent, is 0.70 at 15°C and 0.73 at 55°C.[8]

In a previous article,[10] we showed that DMSO is a critical solvent for PMMA at approximately 41°C. It is interesting to point out that this temperature is very close to the θ temperature reported here. This was noted by Berek,[18] who commented that many known critical eluents for a given polymer are also poor solvents or theta solvents. Experimental evidence shows that the addition of a salt to a critical solvent will displace the critical condition. Phillips et al.[19] showed that in the case of PAA in a 53 water/47 acetonitrile v/v % eluent, the critical condition was reached with 17 mM phosphate buffer concentration. Below 17 mM, the system is in the size exclusion mode and above 17 mM the adsorption mode dominates. A study of the effect of salt concentration on the critical conditions of PMMA will be the subject of a separate article.

Unperturbed Dimension

The entanglement molecular weight M_e is an important parameter for the melt properties of polymers. Fetters et al.[20] showed that there is a relationship between M_e, calculated from the plateau modulus, and the unperturbed dimension. Thus M_e can be obtained from dilute solution viscosity measurements. The unperturbed dimension can be obtained directly from the Mark-Houwink coefficient K_θ measured at 35°C since

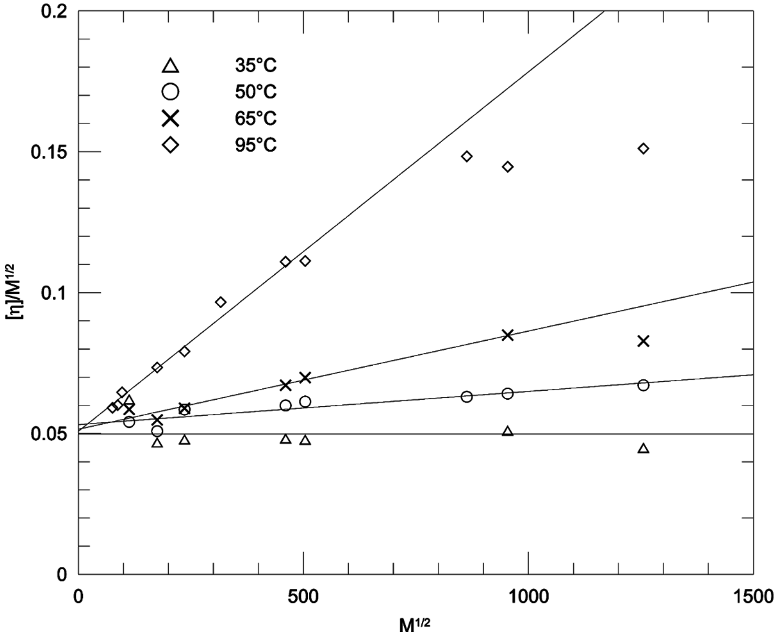

Figure 3. Stockmayer-Fixman plot for the PMMA standards obtained in DMSO and at different temperatures.

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this temperature corresponds to the θ condition. Several procedures were developed to determine the unperturbed dimension in good solvents from the viscosity measurements. We used three of these procedures to determine the unperturbed dimension of PMMA from the measurements of $[\eta]$ in DMSO carried out at different temperatures. The Stockmayer-Fixman equation[21] was used first:

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi_0 B M^{1/2} \tag{7}$$

B is the polymer-solvent interaction free energy parameter and $\Phi_0 = 2.5 \times 10^{23}\text{mol}^{-1}$ is Flory's universal viscosity constant.

Figure 3 shows the plots of $[\eta]/M^{1/2}$ as a function of $M^{1/2}$ for PMMA at the four temperatures. As the temperature increases, a curvature appears in the data and Equation (7) above does not hold for the entire molecular weight range available.[22] Tanaka[23] proposed a different equation:

$$([\eta]/M^{1/2})^{5/3} = K_\theta^{5/3} + 0.51\Phi_0 B M^{1/2} \tag{8}$$

It provides a linear range expanding beyond that of Equation (7). Figure 4 shows the result of plotting $([\eta]/M^{1/2})^{5/3}$ as a function of

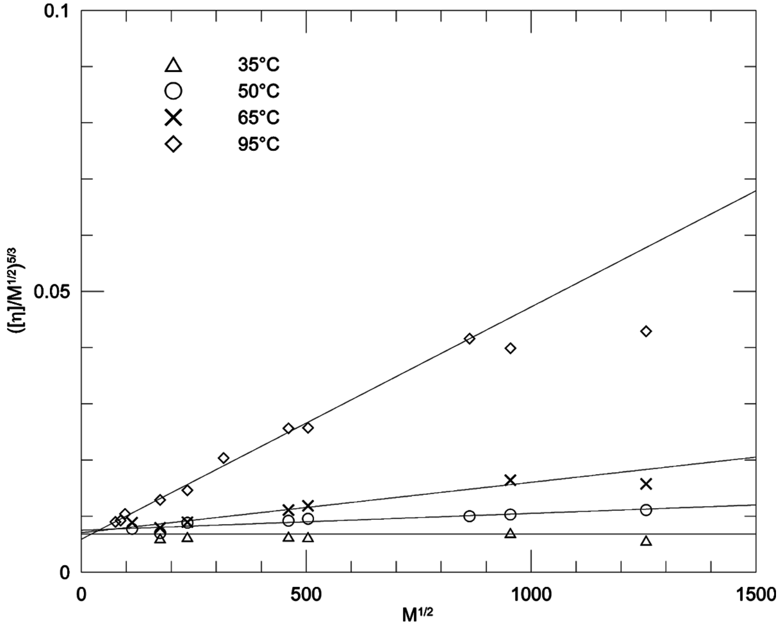

Figure 4. Tanaka plots for the PMMA standards obtained in DMSO and at different temperatures.

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$M^{\frac{1}{2}}$. While there is some improvement, the data collected at 95°C still show some curvature.

Another method for determining the unperturbed dimension is provided by the Dondos-Benoît equation[24]:

$$\frac{1}{[\eta]} = -A_2 + K_\theta^{-1} M^{-1/2} \tag{9}$$

In Figure 5, we plotted $1/[\eta]$ as a function of $M^{-1/2}$. In this plot, linearity is observed because the high molecular weight data points become crowded near the origin.

Table III shows the K_θ values obtained with the three methods above. There is good agreement between the three methods, and K_θ remains constant as the temperature increases. The unperturbed end-to-end distance $\frac{\langle \bar{r}_0^2 \rangle^{1/2}}{M^{1/2}}$ is calculated from K_θ using

$$K_\theta = \Phi_0 \left(\frac{\langle \bar{r}_0^2 \rangle^{1/2}}{M^{1/2}} \right)^3 \tag{10}$$

The values for the unperturbed dimension determined with the three methods are also given in Table III.

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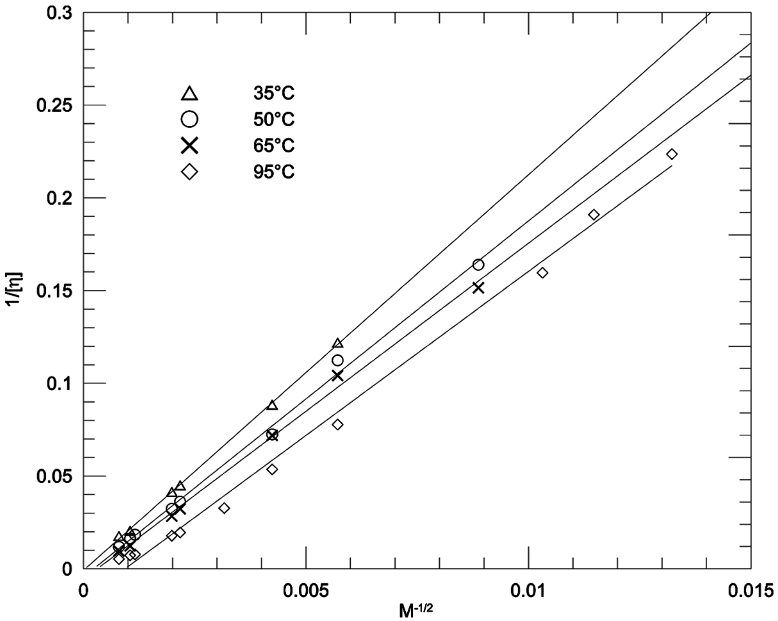

Figure 5. Dondos-Benoît plot for the PMMA standards obtained in DMSO and at fur temperatures.

The characteristic ratio C_∞ is the ratio of the mean square unperturbed end-to-end distance to the mean square end-to-end distance of the freely joined chain:

$$C_\infty = \frac{\langle \bar{r}_0^2 \rangle}{NL^2} = \left(\frac{K_\theta}{\Phi_0}\right)^{2/3} \frac{M_0}{2L^2} \tag{11}$$

Table III. K_θ, unperturbed dimension, and characteristic ratio C_∞ (from SF) for PMMA in DMSO

	K_θ (cm^3 g$^{-3/2}$ mol$^{1/2}$)				
Temperature (°C)	SF	TK	DB	$\frac{\langle \bar{r}_0^2 \rangle^{1/2}}{M^{1/2}} \times 10^9$ (cm g$^{-1/2}$ mol$^{1/2}$)	C_∞
35	0.050	0.050	0.047	5.84	7.2
50	0.053	0.053	0.052	5.96	7.5
65	0.052	0.051	0.055	5.92	7.5
95[a]	0.051	0.046	0.057	5.89	7.3
in THF				6.48[4]	

SF: stockmayer-Fixman, TK: Tanka, DB: Dondos-Benoit.
[a] The measurement at 95°C was carried out in pure DMSO.

Table IV. Radii of gyration and molar masses measured by light scattering for the different PMMA standards in DMSO at 95°C

$M_{NOMINAL}$ kg/mol	5.7	7.6	9.4	12.7	30.7	55.6	100.0	212.0	254.0	745.0	910.0	1,577.0
RG nm	^{a}	^{a}	^{a}	^{a}	^{a}	^{a}	^{a}	12.9	14.1	30.2	34.5	49.8
M_{MALS} kg/mol	5.6	8.0	8.8	^{b}	30.3	54.0	97.0	195.0	240.0	640.0	854.0	1,530

[a] Too small to be determined by MALS.
[b] Not measured.

M_0 is the molecular weight of the repeating unit ($M_0 = 100$ g/mol for PMMA), $L = 1.54$ Å, and N is the number of carbon-carbon bonds. The values measured for the characteristic ratio are reported in Table III. They are in good agreement with the values reported in the literature.[25]

Light Scattering

The angular dependence due to destructive interference is small, indicating that the coil size is small when compared to the wavelength of the

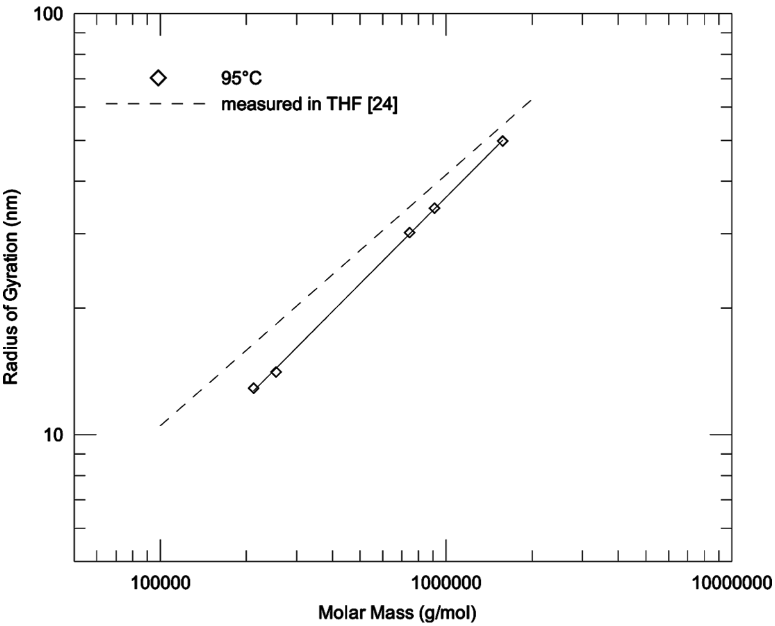

Figure 6. Radius of gyration as a function of molecular weight measured for the PMMA standards in DMSO at 95°C.

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incident light. Because of this and the low refractive index value of PMMA in DMSO, it was difficult to obtain the scaling law for the radius of gyration, and only the values at 95°C are reported in this article (Table IV). Figure 6 shows the radius of gyration as a function of molecular weight. The following relationship is established for PMMA in DMSO at 95°C:

$$R_G^{95C}(\mathrm{nm}) = 0.0029 \times M^{0.68}$$

The first two points are at the limit of detection (small angular dependence) and should be considered with judgment. It is interesting to note that the high molecular weight points approach the values expected in tetrahydrofuran in the same manner as the intrinsic viscosity data in THF at 35°C approached the values in DMSO at 95°C.

The molecular weights obtained in DMSO were in good agreement with the nominal values as shown in Table IV. This shows that DMSO is a suitable solvent for the characterization of PMMA by SEC.

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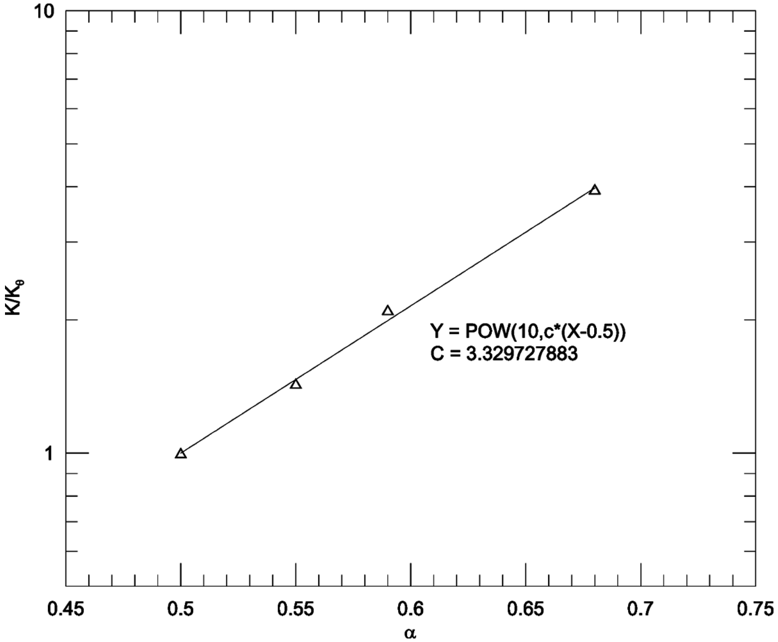

Figure 7. K_θ/K as a function of the Mark-Houwink exponent for PMMA in DMSO.

Relationship between the Mark-Houwink Coefficients

There is an accumulation of experimental evidence[26] showing that for a given polymer, a relationship exists between the two Mark-Houwink coefficients in the form

$$-\log\frac{K}{K_\theta} = C\left(\alpha - \frac{1}{2}\right) \tag{12}$$

where C is a constant. Using data compiled in the *Polymer Handbook*[25] and obtained with different solvents and temperatures Rai and Rosen[26] report $C = -3.67$ for atactic PMMA.

Figure 7 shows the k/k_θ versus α. A fit through the data gives us $C = -3.33$, within 9% of the value reported in the literature.[26]

DISCUSSION

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It was observed that solvents with larger dipole moment yield smaller unperturbed dimensions.[27] Our data confirm this trend since DMSO has a larger dipole moment than THF (3.96 and 1.75D respectively) and the unperturbed dimension reported in THF is $\langle \bar{r}_0^2 \rangle^{1/2}/M^{1/2} = 6.48 \times 10^{-9}$ cmg$^{-1/2}$ mol$^{1/2}$,[4] while we found 5.87 to 5.96 $\times 10^{-9}$ cmg$^{-1/2}$ mol$^{1/2}$ in DMSO 0.1 M LiBr and 5.89×10^{-9} cmg$^{-1/2}$ mol$^{1/2}$ in pure DMSO at 95°C.

In DMF ($\mu = 3.82$D), the values for $\langle \bar{r}_0^2 \rangle^{1/2}/M^{1/2}$ calculated from the intrinsic viscosities reported in the literature[8] are in the range 5.97 to 6.13 $\times 10^{-9}$ cmg$^{-1/2}$ mol$^{1/2}$, slightly higher than the value we measured in DMSO. In 2-heptanone ($\mu = 2.60$D), we calculated $\langle \bar{r}_0^2 \rangle^{1/2}/M^{1/2} = 6.35 - 6.38 \times 10^{-9}$ cmg$^{-1/2}$ mol$^{1/2}$ using the K_θ values determined by Katime et al.[6]

The data in the present study show that no conformational transition is observed for PMMA in DMSO. This adds to the existing evidence showing that conformational order is inhibited in polar solvents. When it is compared to the dipole moment of the solvent, the dipole moment of the methyl ester group on the PMMA chain $\mu_0 = 1.73D$[28] seems to be a good indicator of the ability of the solvent to inhibit conformational order in PMMA. For example, in toluene and benzene, two solvents with dipole moments below that of the methyl ester group of PMMA, a conformational transition was observed. Similarly, it was observed that for solvents with a dielectric constant smaller than that of the side group of poly-p-bromostyrene, a gauche conformation was more likely.[9] The importance of the solvent polarity on the chain conformation was also evidenced by Berghmans,[29] who showed that in PMMA with 90% syndiotacticity, the interaction between pendant methyl ester groups and the solvent yields a specific chain conformation (TT) that is the first step to gelation in concentrated toluene (0.38D) solutions. In dilute solutions, gelation does not occur, but the conformational change was observed using fluorescence spectroscopy.

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