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Solution properties and characteristic ratio of near-monodisperse poly(tert-butyl methacrylate)

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Summary

The dilute solution properties of six near-monodisperse samples of poly(tert-butyl methacrylate) covering the molecular weight range $3 \times 10^4 \leq \bar{M}_w \leq 1.1 \times 10^6$ are reported. Unperturbed chain dimensions were derived from a combination of light scattering and intrinsic viscosity data. A characteristic ratio (C_∞) of 12.0 was obtained in the theta solvent cyclohexane at 10°C. This C_∞ value is considerably larger than the value of 8.8 reported previously for poly(n-butyl methacrylate) and reflects the greater bulkiness of the tert-butyl substituent and also, possibly, tacticity effects.

Introduction

In this paper, we report dilute solution properties and the characteristic ratio (C_∞) for poly(tert-butyl methacrylate) (PtBMA). Samples of extremely narrow molecular weight distribution, prepared by anionic polymerization, are utilized. The results obtained are compared with those previously reported for other poly(alkyl methacrylate)s. This comparison provides insight into the effect of the nature of the side group of polymethacrylates on properties in dilute solution.

Experimental

The narrow molecular weight distribution PtBMA samples were purchased from Pressure Chemical Company. These polymers were prepared by "living" anionic polymerization in order to limit polydispersity.

Polydispersities were examined by size exclusion chromatography (SEC) in tetrahydrofuran at 25°C. A Waters Model 510 pump and Model 410 differential refractometer were used. Two mixed-bed ultrastyragel columns were connected in series; a flow rate of 1.0 mL min^{-1} was employed. Calibration of the SEC unit was based on weight-average molecular weights ($\bar{M}_w$) determined for these same well-defined PtBMA samples using low-angle laser light scattering (LALLS). The LALLS experiments were conducted in purified (by distillation) butanone using the Chromatix KMX-6 unit at 25°C and at a wavelength of 633 nm. The refractive index increment was measured as 0.096 mL g^{-1} under the same conditions.

Theta conditions were established by phase equilibria studies involving PtBMA and several solvents. Intrinsic viscosities $[\eta]$ were measured in cyclohexane (Aldrich, HPLC grade) at 10°C, the measured theta condition,

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Table 1: Molecular Characteristics of Poly(tert-butyl methacrylates)

		cyclohexane, 10°C		THF, 30°C			
$\bar{M}_w \times 10^{-4}$ ($g\ mol^{-1}$)	$A_2 \times 10^4$ ($mL \cdot mol \cdot g^{-2}$)	$[\eta]$ ($dL\ g^{-1}$)	k_H	$[\eta]$ ($dL\ g^{-1}$)	k_H	$\frac{\bar{M}_w}{\bar{M}_n}$	$\frac{\bar{M}_z}{\bar{M}_w}$
2.77	3.81	0.106	1.23	0.130	0.51	1.03	1.02
6.60	3.55	0.155	1.10	0.240	0.33	1.03	1.03
19.0	3.14	0.254	0.96	0.484	0.36	1.03	1.03
41.4	2.73	0.393	0.79	0.847	0.27	1.07	1.06
83.5	2.61	0.567	0.78	1.18	0.27	1.12	1.12
107	2.56	0.646	0.82	1.53	0.29	1.07	1.05

and in THF (Aldrich, 99+%) at 30°C. Ubbelohde dilution viscometers yielding flow times in excess of 120s were used. Huggins equation (1) was used to treat data obtained for four concentrations of polymer, where relative viscosities ranged between 1.1 and 1.5.

Tacticity was evaluated by ^{13}C-NMR from examination of the carbonyl region using methods previously described (2). The fractions of isotactic, heterotactic, and syndiotactic triads are, respectively, 8, 47, and 45%.

Results and Discussion

Molecular characteristics of PtBMA samples are presented in Table 1. The second virial coefficient and $\bar{M}_w$ data (Figure 1) lead to the following equation:

$$A_2\ (mL \cdot mol \cdot g^{-2}) = 1.25 \times 10^{-3}\ \bar{M}_w^{\,-0.115} \qquad (1)$$

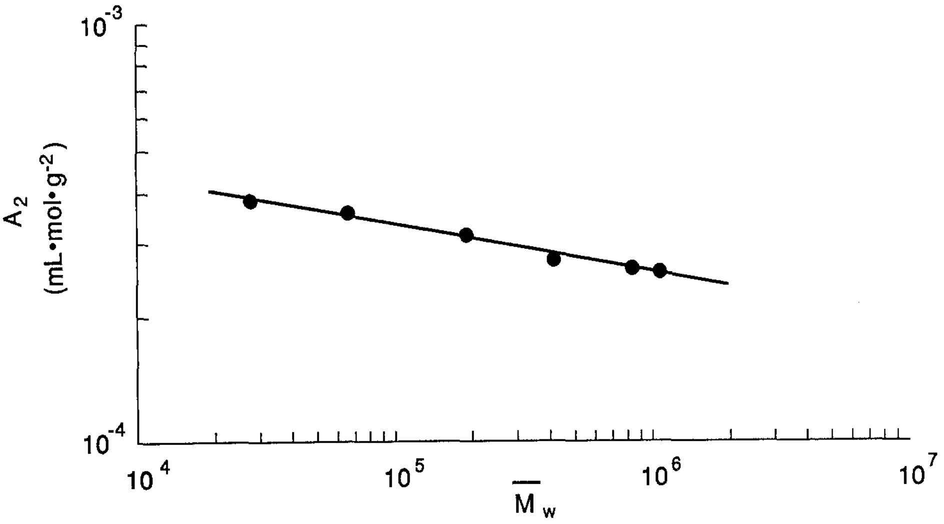

Figure 1: Second virial coefficient as a function of molecular weight for PtBMA in butanone at 25°C.

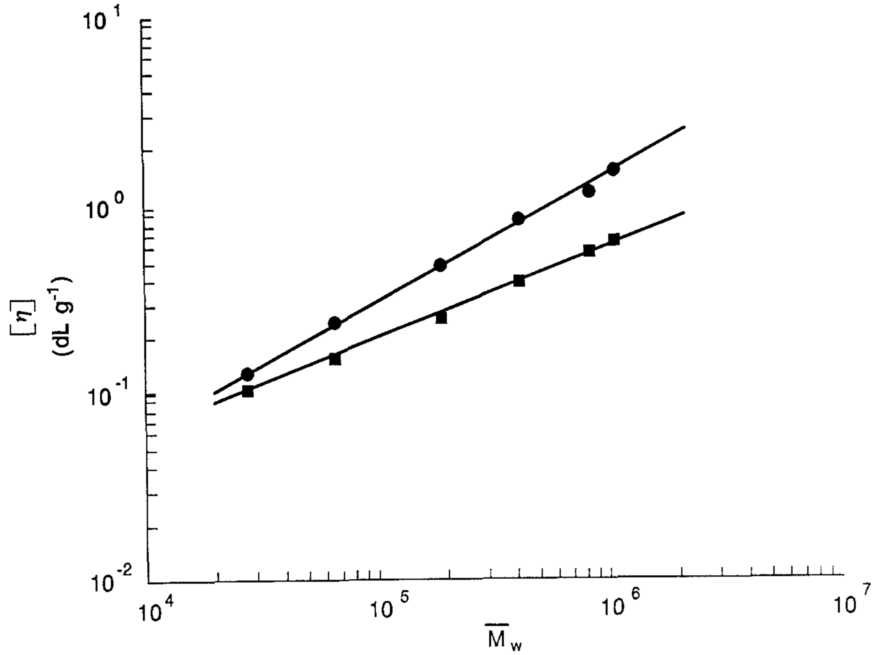

Figure 2: MHS plots for PtBMA in THF (●) and under theta conditions, cyclohexane at 10°C (■).

The small magnitude of the exponent in Equation 1, along with the rather small A_2 values (Table 1), suggests that butanone is a moderate solvent for PtBMA at 25°C.

From the $[\eta]$ and $\bar{M}_w$ data of Table 1 and Figure 2 we obtain the following Mark-Houwink-Sakurada (MHS) equations:

$$[\eta] = 1.52 \times 10^{-4}\ \bar{M}_w^{0.66} \quad \text{(THF, 30°C)} \qquad (2)$$

$$[\eta] = 6.19 \times 10^{-4}\ \bar{M}_w^{0.50} \quad \text{(cyclohexane, 10°C)} \qquad (3)$$

The MHS exponent of 0.66 indicates that THF is also a moderate solvent for PtBMA, while the exponent of 0.50 in cyclohexane confirms 10°C as the theta temperature for this polymer-solvent system.

The preexponential term of Equation 3 ($K_\Theta = 6.19 \times 10^{-4}$) allows determination of the unperturbed mean-square end-to-end distance ($\langle r^2\rangle_o$) via (3,4)

$$K_\Theta = \Phi_o\ (\langle r^2\rangle_o/M)^{3/2} \qquad (4)$$

where Φ_o is a hydrodynamic constant for linear unperturbed flexible chains equal to 2.5×10^{21} (5,6) and M is molecular weight. From $\langle r^2\rangle_o$ the characteristic ratio is calculated as

$$C_\infty = \frac{\langle r^2\rangle_o}{n\ell^2} \qquad (5)$$

where n is the number of main chain bonds of length ℓ. $C_\infty = 12.0$ is obtained.

This value of C_∞ can be compared with those available in the literature for polymethacrylates with related side groups. Poly(n-butyl methacrylate), poly(cyclobutyl methacrylate), and poly(2-ethyl-butyl methacrylate) have C_∞ values of 8.8 (7-9), 10.0 (9,10), and 9.8 (11), respectively. It should be noted, however, that these last three polymers were prepared by free radical polymerization and all probably have somewhat different tacticities. The PtBMA samples used in this work (products of anionic polymerization) have lower syndiotactic content and higher heterotactic and isotactic contents than do alkyl methacrylate polymers made by a radical mechanism (9). If these tacticity differences can be neglected, it is clear that the bulky and approximately spherical tert-butyl group imparts the lowest chain flexibility.

Finally, we note that the Huggins coefficients of Table 1 are similar to those reported for other polymethacrylates under comparable thermodynamic conditions (10,12). In future work, we plan to investigate the solution properties of free radically polymerized tert-butyl methacrylate to explore possible tacticity effects on dilute solution behavior.

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