Solution Properties and Unperturbed Dimensions of Stereoirregular Poly(*tert*-butyl methacrylates)

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ABSTRACT: A comparative study of the dilute-solution properties of poly(*tert*-butyl methacrylate) prepared by anionic and free-radical polymerization mechanisms is reported. The latter material has a substantially higher syndiotactic triad content than does the former (59% versus 45%). Significant differences are noted in both thermodynamic (second virial coefficient) and transport (intrinsic viscosity) properties, as well as in the characteristic ratios of these materials. The more highly syndiotactic free-radical polymer is substantially more flexible and exhibits a greater degree of polymer–solvent interaction as compared to the anionically polymerized material.

Introduction

Unperturbed dimensions for a broad range of polymethacrylates have been reported.[1] Only in the case of poly(methyl methacrylate) (PMMA), however, has the influence of tacticity on chain dimensions been elucidated.[2,3] A progressive increase in unperturbed dimensions of PMMA occurs as isotactic content is increased.[3]

We recently published a preliminary account[4] of the dilute-solution properties of anionically produced poly(*tert*-butyl methacrylate) (PtBMA). In the present work, we report the unperturbed dimensions and solution properties of PtBMA samples prepared by both anionic and free-radical polymerization. Tacticities of these materials and the influence of tacticity on their dilute-solution properties are also investigated.

Experimental Section

Six narrow molecular weight distribution PtBMA samples were purchased from Pressure Chemical Co. These materials, according to the supplier, were prepared by anionic polymerization at low temperatures in tetrahydrofuran (THF).

Four additional samples of PtBMA were prepared by free-radical polymerization in benzene at 50 °C by using recrystallized azobis(isobutyronitrile) (AIBN) as initiator. Prior to polymerization, the monomer (purchased from Polysciences) was dried and freed of inhibitor by distillation from calcium hydride on a high-vacuum (ca. 10^{-6} mmHg) line. Details of polymerization and polymer characteristics are given in Table I. The whole polymers were subjected to solvent–nonsolvent fractionation using toluene as solvent and methanol or methanol/water mixtures as nonsolvent. Seven fractions were selected for subsequent dilute-solution studies.

Size-exclusion chromatography (SEC) measurements were conducted with Waters Ultrastyragel columns in THF at a flow rate of 1.0 mL min^{-1}. Low-angle laser light scattering (LALLS) experiments were performed in purified (by distillation) butanone with the Chromatix KMX-6 photometer at 25 °C and at a wavelength of 633 nm for evaluation of weight-average molecular weight ($\bar{M}_W$) and second virial coefficient (A_2). Specific refractive index increments, dn/dc, were measured under the same conditions with the KMX-16 refractometer; values of 0.096 and 0.102 mL g^{-1} were obtained for the anionic and free-radical polymers, respectively.

The search for Θ solvents involved phase-equilibrium studies. *n*-Heptane was determined, via a Shultz–Flory plot,[5] to be a Θ solvent at 64 °C for the free-radically produced polymer. Although cyclohexane solutions of both types of PtBMA remained homogeneous down to the freezing point (ca. 5 °C), we suspected that this solvent might also serve as a Θ solvent at low temperatures.

Intrinsic viscosities [η] and Huggins coefficients k_H were measured with standard Cannon–Ubbelohde viscometers in the Θ solvents *n*-heptane (Fisher, HPLC grade) and cyclohexane (Aldrich, HPLC grade) and also in the good solvents butanone (Fisher, reagent grade) and THF (Aldrich, 99+%). All solvents for viscometric studies were used as received; temperature control was maintained to ±0.02 °C by using a water bath. The Huggins equation was used to extract [η] and k_H values from data for four concentrations of polymer chosen to give relative viscosities between 1.1 and 1.4 and flow times well in excess of 100 s. Values of [η] were accurate to within ±2%.

Tacticity was determined from the carbonyl intensities of ^{13}C NMR (Nicolet FT-300 instrument operating at 75.5 MHz). Five percent solutions of polymer in $CDCl_3$ were employed for this purpose, using methods previously described.[6]

Results and Discussion

Tacticity of the PtBMA samples is given in Table II. The free-radically produced polymers (FR-PtBMA) have considerably enhanced syndiotactic contents relative to their anionically produced counterparts (A-PtBMA) (59% and 45% rr triads, respectively). Consequently, it is of interest to determine how this difference in tacticity will affect the dilute-solution behavior of these macromolecules.

Molecular characteristics of the anionically produced PtBMA standards and the fractionated free-radical products are presented in Table III. The former materials are nearly monodisperse, as expected based on their preparation via a "living" polymerization technique. The fractionated polymers also exhibit narrow and symmetrical molecular weight distributions, with average $\bar{M}_W/\bar{M}_N$ and $\bar{M}_Z/\bar{M}_W$ ratios of 1.16 and 1.17, respectively. Thus, all polymers are adequately well-defined to allow for meaningful dilute-solution studies. It should also be noted that the conversions were intentionally limited during the free-radical polymerizations (see Table I) to prevent or limit potential chain transfer to polymer and the undesirable presence of branched macromolecules.

It should also be mentioned that the molecular weights reported in Table III for A-PtBMA are generally different from the values supplied by Pressure Chemical Co.; values of 38 500, 85 300, 187 000, 430 000, 650 000, and 900 000

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Table I
Polymerization of *tert*-Butyl Methacrylate

batch	[monomer],[a] % (w/w)	[initiator],[a] % (w/w)	duration, h	yield, %	$\bar{M}_W$[b] × 10^{-5}	$\bar{M}_W/\bar{M}_N$[b]	$\bar{M}_Z/\bar{M}_W$
A	10.0	7.7×10^{-2}	114	84	1.43	1.83	1.62
B	10.0	7.7×10^{-3}	139	63	3.63	1.68	1.58
C	9.6	3.1×10^{-3}	160	69	6.45	1.52	1.43
D	10.0	1.2×10^{-3}	160	56	10.5	1.64	1.48

[a] Based on solution weight. [b] Based on SEC calibration using polystyrene standards.

Table II
Tacticity of Poly(*tert*-butyl methacrylate)

	triads, %		
method of polymerizn	mm	mr + rm	rr
anionic	8	47	45
free radical	3	38	59

Table III
Molecular Characteristics of PtBMA Samples

$\bar{M}_W$ × 10^{-4}	A_2 × 10^4,[a] mL mol g^{-2}	$\bar{M}_W/\bar{M}_N$	$\bar{M}_Z/\bar{M}_W$
	Anionic Polymerization		
2.77	3.81	1.03	1.02
6.60	3.55	1.03	1.03
19.0	3.14	1.03	1.03
41.4	2.73	1.07	1.06
83.5	2.61	1.12	1.12
107	2.56	1.07	1.05
	Free-Radical Polymerization		
3.42	5.63	1.16	1.17
6.83	5.23	1.07	1.08
13.8	4.53	1.15	1.15
24.2	3.34	1.16	1.22
34.2	3.01	1.13	1.13
61.1	2.79	1.19	1.19
155	2.44	1.26	1.27

[a] In butanone at 25 °C.

were supplied on going from lowest to highest molecular weights. These values, however, were essentially identical with peak molecular weights obtained via SEC in our laboratory using a polystyrene calibration. It thus appears that the $\bar{M}_W$ values reported by Pressure Chemical Co. were obtained by SEC using polystyrene calibration and, consequently, are only relative values.

The A_2 and $\bar{M}_W$ data of Table III lead to the following power laws for A-PtBMA and FR-PtBMA, respectively:

$$A_2 = 1.25 \times 10^{-3} \bar{M}_W^{-0.115} \quad (1)$$

$$A_2 = 7.55 \times 10^{-3} \bar{M}_W^{-0.25} \quad (2)$$

The power law exponents and A_2 values in Table III suggest that butanone at 25 °C is a better solvent for FR-PtBMA than for A-PtBMA, since the value of −0.25 found for the former polymer is in accord with both theoretical predictions[7,8] and other experimental findings for polymethacrylates.[9,10]

$[\eta]$ and k_H values measured in THF, butanone, and the Θ solvents cyclohexane and *n*-heptane are presented in Table IV and Figures 1–4. The $[\eta]$ data in THF lead to the following Mark–Houwink–Sakurada (MHS) equations for A-PtBMA and FR-PtBMA, respectively:

$$[\eta] = 1.52 \times 10^{-4} \bar{M}_W^{0.66} \quad (3)$$

$$[\eta] = 5.84 \times 10^{-5} \bar{M}_W^{0.76} \quad (4)$$

The MHS exponents clearly show that the increase in syndiotactic content present in the FR-PtBMA renders THF a markedly better solvent in the thermodynamic sense for this polymer.

The following MHS equations represent, respectively, the A-PtBMA and FR-PtBMA viscosity data in butanone.

$$[\eta] = 1.20 \times 10^{-4} \bar{M}_W^{0.675} \quad (5)$$

$$[\eta] = 5.91 \times 10^{-5} \bar{M}_W^{0.73} \quad (6)$$

As with THF, the polymer–solvent interactions are enhanced for the free-radically produced polymer relative to the anionically polymerized material, based on the power law exponents of eqs 5 and 6. As Figure 4 shows, however, $[\eta]$ values in butanone are actually larger for A-PtBMA at low molecular weights ($< 2 \times 10^5$). This is a reflection of the larger unperturbed dimensions of A-PtBMA relative to FR-PtBMA (see below). At higher molecular weights, the greater thermodynamic interactions for FR-PtBMA dominate and $[\eta]$ values are larger for this material.

MHS parameters for A-PtBMA and FR-PtBMA at the measured Θ conditions are presented in Table V. Also given in Table V are values of the unperturbed parameter K_θ, which is related to the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ by[11,12]

$$K_\theta = \Phi_0 (\langle r^2 \rangle_0 / M)^{3/2} \quad (7)$$

where Φ_0 is a hydrodynamic constant for flexible linear chains at the Θ state (2.5×10^{21})[13–15] and M is molecular weight. The values of K_θ were obtained through use of the Burchard–Stockmayer–Fixman (BSF) procedure[16,17] to correct for deviations from the Θ state.

From $\langle r^2 \rangle_0$ the characteristic ratio C_∞ can be calculated[18]

$$C_\infty = \lim_{n \to \infty} \frac{\langle r^2 \rangle_0}{nl^2} \quad (8)$$

where n is the number of bonds in the main chain and l is the bond length. C_∞ values are also tabulated in Table V, and clearly A-PtBMA is a substantially less flexible chain than FR-PtBMA. A similar effect of tacticity on poly(methyl methacrylate) unperturbed dimensions has also been noted,[3] again with more syndiotactic materials being more flexible.

Since $[\eta]$ values were measured for FR-PtBMA in two different Θ solvents having substantially different Θ temperatures, some insight into effects of temperature on chain dimensions can also be realized. Although the influence of specific solvent effects[19] cannot be ruled out, virtually identical values of C_∞ are found at 10 and 64 °C, suggesting that $d \ln \langle r^2 \rangle_0 / dT = 0$ for this polymer. Negligible temperature effects have also been reported for poly(methyl methacrylate) prepared free radically;[20] on the other hand, a large positive value of $d \ln \langle r^2 \rangle_0 / dT$ has been reported[21] for poly(*n*-butyl methacrylate).

The C_∞ value of this work for FR-PtBMA (10.2) can also be compared with literature results for unperturbed dimensions of polymers prepared free radically, with related side groups. Poly(*n*-butyl methacrylate), poly(cyclobutyl methacrylate), and poly(2-ethylbutyl meth-

Table IV
Intrinsic Viscosities and Huggins Coefficients of PtBMA

	THF, 30 °C		butanone, 25 °C		cyclohexane, 10 °C		n-heptane, 64 °C	
$\bar{M}_W \times 10^{-4}$	$[\eta]$, dL g^{-1}	k_H	$[\eta]$, dL g^{-1}	k_H	$[\eta]$, dL g^{-1}	k_H	$[\eta]$, dL g^{-1}	k_H
				Anionic Polymerization				
2.77	0.130	0.51	0.124	0.30	0.106	1.23		
6.60	0.240	0.33	0.210	0.28	0.155	1.10		
19.0	0.484	0.36	0.432	0.24	0.254	0.96		
41.4	0.847	0.27	0.705	0.32	0.393	0.79		
83.5	1.18	0.27	1.22	0.29	0.567	0.78		
107	1.53	0.29	1.45	0.34	0.646	0.82		
				Free-Radical Polymerization				
3.42	0.177	0.64					0.088	0.81
6.83					0.127	2.5	0.125	0.84
13.8	0.485	0.42	0.332	0.24	0.175	1.5	0.169	0.48
24.2	0.725	0.40					0.235	0.76
34.2	0.985	0.23	0.700	0.27	0.298	1.2	0.263	0.64
61.1	1.58	0.33	1.06	0.23	0.392	1.4	0.368	0.70
155	3.22	0.32	1.96	0.33	0.597	1.6	0.528	0.80

Table V
MHS Parameters and Unperturbed Dimensions of PtBMA

polymerizn mode	solvent	temp, °C	$K \times 10^4$, dL g^{-1}	a	$K_\theta \times 10^4$,[a] dL g$^{-3/2}$ mol$^{1/2}$	C_∞[b]
anionic	cyclohexane	10.0	6.20	0.499	6.08	11.8
free radical	cyclohexane	10.0	4.60	0.505	4.89	10.2
free radical	n-heptane	64.0	6.21	0.476	4.86	10.2

[a] Via the BSF procedure.[16,17] [b] No polydispersity corrections were applied in view of the narrow distributions of these polymers.

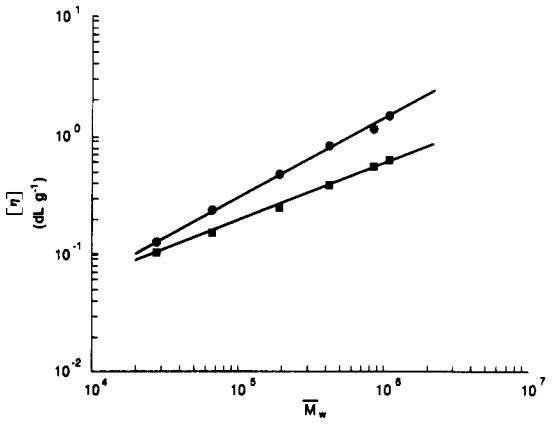

Figure 1. MHS plots for A-PtBMA in THF (●) and cyclohexane (■), a Θ solvent at 10 °C.

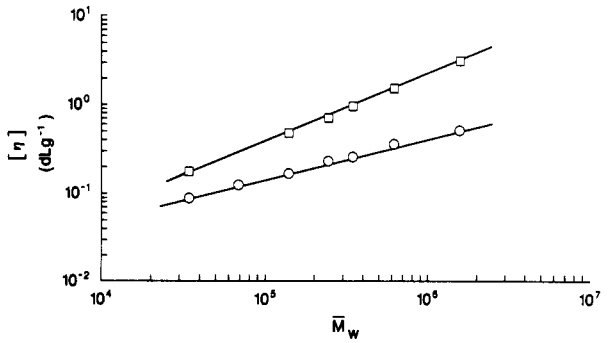

Figure 2. MHS plots for FR-PtBMA in THF (□) and n-heptane (○), a near-Θ solvent at 64 °C.

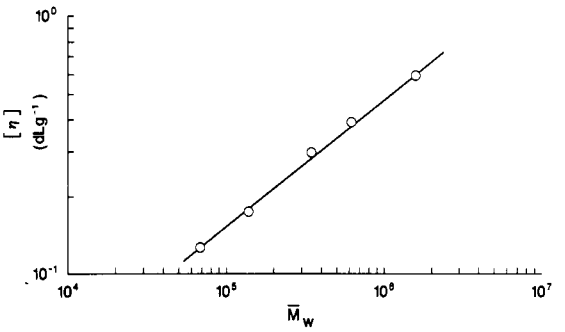

Figure 3. MHS plot for FR-PtBMA in cyclohexane, a Θ solvent at 10 °C.

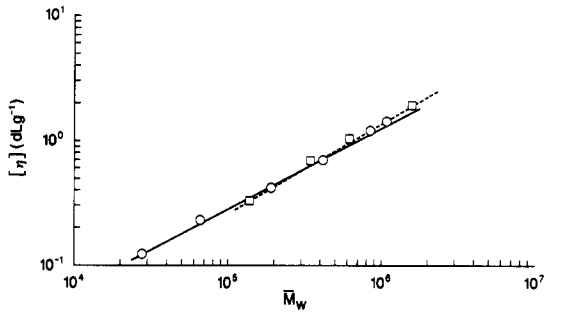

Figure 4. MHS plot for A-PtBMA (○) and FR-PtBMA (□) in butanone at 25 °C. $[\eta]$ values are larger for FR-PtBMA above ca. 2×10^5 in molecular weight.

acrylate) have C_∞ values, respectively, of 8.8 (21,22), 10.0 (23), and 9.8 (24). C_∞ for FR-PtBMA is identical within experimental error (±5%) to those found for the cyclobutyl and 2-ethylbutyl esters but larger than that for poly(n-butyl methacrylate), which has a flexible n-alkyl substituent. The tert-butyl group is rigid and roughly spherical, while the strained cyclobutyl ring is rigid but planar; both impart essentially identical flexibility to polymethacrylates. The larger size of the 2-ethylbutyl group accounts for the comparable influence on C_∞ of this flexible substituent.

Finally, we note that the Huggins coefficients found for both PtBMA series in THF are typical of those reported for other flexible chains in thermodynamically good solvents. Interestingly, the k_H values obtained for FR-PtBMA in cyclohexane at the Θ temperature are much larger than usual and, also, are considerably larger than those found for A-PtBMA under the same conditions. Conversely, "normal" values of k_H are found for FR-PtBMA in the Θ solvent n-heptane, even though these data were obtained slightly below the Θ temperature (MHS exponent of 0.476). We are unable to explain these

findings, although an influence of the nature of the Θ solvent on the magnitude of k_H has previously been reported.[25]

In summary, measurable differences exist in the dilute-solution behavior of PtBMA samples prepared by free-radical and anionic mechanisms. FR-PtBMA is more flexible and exhibits stronger polymer–solvent interactions than does its anionically polymerized counterpart. These observations can be attributed to tacticity differences between the two sets of samples; similar influences of tacticity on solution properties of PMMA have been noted.[2,3]

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Registry No. PtBMA (homopolymer), 25189-00-8.