

The Influence of Alkylene Spacers on Conformational and Thermal Properties of Poly(aryl Methacrylates)

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SYNOPSIS

The effect of introducing alkylene spacers on the thermal and conformational properties of poly(aryl methacrylates) has been studied. Poly(2-phenylethyl-1-methacrylate) (PPEMA) and poly(4-phenylbutyl-1-methacrylate) (PPBMA) samples of narrow polydispersities and covering a very broad range of molecular weights were produced by free radical solution polymerization, followed by fractionation. These materials were studied by a combination of differential scanning calorimetry, light scattering, and viscometry measurements to allow evaluation of their glass transition temperatures (T_g) and characteristic ratios (C_∞). These results are compared with literature data available for poly(phenyl methacrylate) (PPMA), which has no alkylene spacer, and poly(benzyl methacrylate) (PBMA), which has a methylene spacer. A progressive decrease in T_g is observed as the length of the alkylene spacer is increased, reflecting the enhancement of side group (local) flexibility. C_∞ decreases substantially on going from PPMA to PBMA but then increases on going to PPEMA and PPBMA. This behavior is attributed to the fact that while side group flexibility increases for the materials with longer alkylene spacers, and this would be expected to decrease C_∞ , the side group size is progressively increasing. Larger side groups generally increase C_∞ of polymethacrylates. Thus the observed C_∞ behavior for these polymers reflects both the size and flexibility of the substituents. © 1994 John Wiley & Sons, Inc.

Keywords: poly(aryl methacrylates) • chain flexibility • glass transition temperature • viscometry

INTRODUCTION

Polymethacrylates is one of the most important classes of polymers because they allow polymer properties to be easily tailored through appropriate choice of substituents. The conformational characteristics of a large number of polymethacrylates have been investigated.^{1,2} One area of strong current interest³ is the development and utilization of methacrylate-based side chain liquid crystal polymers. These polymers utilize flexible alkylene or oxyalkylene spacers to attach mesogens (frequently aromatic groups such as substituted biphenyls) to the polymer backbone. Given the high level of interest in such systems, we decided to investigate the influence of the varying the length of the flexible spacer on both the conformational and thermal

properties of polymethacrylates with phenyl substituents. Literature data are available which describe the relevant properties of poly(phenyl methacrylate) (PPMA) and poly(benzyl methacrylate) (PBMA). In this work, we describe the synthesis and characterization of poly(2-phenylethyl-1-methacrylate) (PPEMA) and poly(4-phenylbutyl-1-methacrylate) (PPBMA) and compare results obtained for these polymers with those available for PPMA and PBMA.

EXPERIMENTAL

Monomers

2-Phenylethyl-1-methacrylate was purchased from Polysciences. 4-Phenylbutyl-1-methacrylate was prepared by reacting 4-phenyl-1-butanol with methacrylic acid in toluene solution at reflux. The

Table I. Tacticity of Polymethacrylates

Polymer	% of Triads		
	<i>rr</i>	<i>mr + rm</i>	<i>mm</i>
PPBMA	63	29	8
PEMA	60	34	6

progress of the reaction was monitored by collecting the H₂O byproduct in a calibrated Dean-Stark trap. Methylene blue was employed as an inhibitor to avoid the formation of polymeric products. Both monomers were purified by distillation on a high vacuum (ca. 10⁻⁶ mmHg) line. The structure and purity of the 4-phenylbutyl-1-methacrylate was confirmed by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography/mass spectrometry.

Polymerization

Free radical solution polymerizations were conducted under high vacuum conditions in benzene at 50°C. The initiator used was 2,2'-azo-bis-isobutyronitrile (AIBN), which had been purified by recrystallization from methanol. Two polymerizations were conducted for the phenylethyl monomer, while three polymerizations were carried out for the phenylbutyl derivative. Monomer concentrations were maintained at about 10% (w/w) in all cases, and conversions were limited to < 70% to minimize the potential for branching. Initiator concentrations were varied between about 0.001 and 0.1% (w/w) to allow molecular weights to be varied. Fractionation was conducted by incrementally adding methanol (nonsolvent) to dilute (< 1% w/v) solutions of polymer in toluene.

Polymer Characterization

Tacticities of PPEMA were evaluated using 75 MHz ¹³C-NMR, as previously described.⁴ Differential

scanning calorimetry (DSC) was used to measure the glass transition temperatures (*T_g*) of the polymers. A Perkin-Elmer DSC-2 unit, calibrated with indium, was employed at a heating rate of 10°C/min under a nitrogen atmosphere. Sample sizes of about 15 mg were used. The *T_g* values of 10 and 56°C for PPBMA and PPEMA, respectively, correspond to the transition onset.

Size exclusion chromatography (SEC) experiments were done in tetrahydrofuran (THF) at 30°C and a flow rate of 1 mL/min through two Waters linear Ultrastaygel columns in series. Injections of 0.2% solutions of 20 μL were used. Reported polydispersities are based upon a polystyrene calibration curve. Data acquisition and manipulation involved the use of Viscotek hardware and software.

Low-angle laser light-scattering (LALLS) experiments were conducted using a Chromatix KMX-6 unit with a 2 mW vertically polarized He-Ne source operating at 633 nm. These experiments were conducted for PPEMA and PPBMA in, respectively, 1-chloroundecane and 1-chloroheptane. These solvents, which serve as theta solvents for the respective polymers, were found by gas chromatography to exhibit purity levels well in excess of 99%. Weight-average molecular weights (*M_w*), and second virial coefficients (*A₂*) were derived from conventional plots of *Kc*/*R₉₀* versus *c*, where *K* is a combination of known optical parameters, *c* is polymer concentration, and *R₉₀* is the excess Rayleigh ratio. In some preliminary LALLS experiments the variation of *A₂* with temperatures was studied to allow the theta temperature to be estimated. These results indicated theta temperatures of 27.5 and 23.0°C for PPEMA and PPBMA, respectively. LALLS measurements on the various fractions under these conditions yielded zero or near-zero *A₂* values for the various fractions, as expected.

The specific refractive index increments *dn/dc* were measured using the Otsuka Electronics DRM-1020 double-beam differential refractometer. At 633 nm values of 0.128 and 0.100 mL/g were measured

Table II. Molecular Characteristics of Poly(2-phenylethyl-1-Methacrylates)

Sample	10 ⁻⁴ <i>M_w</i>	[η] _θ (dL/g)	<i>k_{H,θ}</i>	[η] _{THF} (dL/g)	<i>k_{H,THF}</i>	<i>M_w/M_n</i>
IF-10	5.9	0.091	1.48	0.159	0.55	1.11
IF-8	12.5	0.121	1.40	0.262	0.32	1.12
IF-6	18.2	0.154	1.33	0.391	0.40	1.17
IF-4	33.1	0.214	1.22	0.565	0.43	1.25
IIF-5	52.6	0.252	1.37	0.886	0.33	1.26
IIF-4	74.4	0.303	1.14	1.12	0.28	1.41
IIF-3-1	118	0.404	1.02	1.55	0.25	1.25

Table III. Molecular Characteristics of Poly(4-phenyl-1-butyl Methacrylates)

Sample	$10^{-5}\bar{M}_w$	$[\eta]_\theta$ (dL/g)	$k_{H,\theta}$	$[\eta]_{\text{THF}}$ (dL/g)	$k_{H,\text{THF}}$	$\bar{M}_w/\bar{M}_n$
IF-7	1.43	0.129	0.95	0.285	0.39	1.29
IF-5	2.46	0.165	0.76	0.400	0.41	1.14
IF-3	3.45	0.189	0.82	0.522	0.37	1.15
IF-2	5.01	0.227	0.71	0.663	0.36	1.24
IIF-4	6.91	0.276	0.78	0.921	0.34	1.18
IIF-3	12.9	0.388	0.40	1.33	0.31	1.30
IIIF-5	16.7	0.422	0.69	1.60	0.28	1.28
IIIF-3	31.3	0.580	0.93	2.98	0.29	1.32
IIIF-1	47.2	0.726	0.62	3.72	0.35	1.31

for PPEMA in 1-chloroheptane at 27.5°C and for PPBMA in 1-chloroundecane at 23.0°C, respectively. Values of 0.134 and 0.105 mL/g were obtained at 488 nm for PPEMA and PPBMA, respectively.

Intrinsic viscosities $[\eta]$ and Huggins coefficients k_H were measured using Cannon-Ubbelohde dilution viscometers with negligible kinetic energy corrections. Solutions with relative viscosities between 1.1 and 1.7 were used. Temperature control was maintained to within $\pm 0.01^\circ\text{C}$ using thermostatted water baths. Solvents and solutions were filtered directly through 1.0 μm pore size Teflon membrane filters directly into the viscometers.

RESULTS AND DISCUSSION

Tacticity results for PPEMA and PPBMA are presented in Table I. The rather high syndiotactic contents of these materials are similar to those generally found for other polymethacrylates produced under similar conditions.¹ Since tacticity can influence thermal and conformational characteristics, in studying the influence of structure on properties it is important to compare materials with similar tacticities.

Molecular characteristics of selected fractions of PPEMA and PPBMA are presented in Tables II and III, respectively. The selected fractions exhibit

narrow, symmetrical molecular weight distributions and encompass a broad range of molecular weights.

Mark-Houwink-Sakurada (MHS) parameters for PPEMA and PBEMA, in both a good solvent (THF) and under theta conditions, are presented in Table IV. These data are also presented in graphical form in Figures 1 and 2. The observed exponents of virtually $\frac{1}{2}$ for the theta condition measurements fortify the theta temperature determinations using LALLS. The exponents obtained in THF are typical of those observed for other polymethacrylates in good solvents.^{5,6}

Based upon the data obtained under measured theta conditions, values of the unperturbed parameter K_θ were obtained using the method of Burchard⁷ and Stockmayer and Fixman.⁸ This approach corrects for slight deviations from the true theta state. Flory's characteristic ratio C_∞ was calculated using the equations⁹

$$K_\theta = \Phi_0 (\langle r^2 \rangle_0 / \bar{M}_w)^{3/2} \quad (1)$$

and

$$C_\infty = \lim_{n \rightarrow \infty} \langle r^2 \rangle_0 / nl^2 \quad (2)$$

where Φ_0 is the Flory "universal" hydrodynamic factor (assumed to equal 2.5×10^{21} with $[\eta]$ in dL/g), $\langle r^2 \rangle_0$ is the mean-square unperturbed end-to-

Table IV. Mark-Houwink-Sakurada Parameters for PPEMA and PPBMA

Polymer	Solvent	Temperature (°C)	$K(\text{dL/g})$	a
PPEMA	THF	30	3.17×10^{-5}	0.774
PPEMA	1-Chloroheptane	27.5	3.71×10^{-4}	0.498
PPBMA	THF	30	3.75×10^{-5}	0.748
PPBMA	1-Chloroundecane	23.0	3.35×10^{-4}	0.499

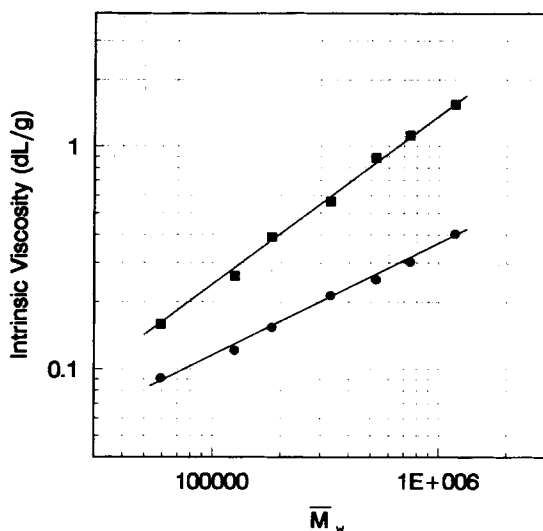


Figure 1. Mark-Houwink-Sakurada plots for PPEMA in THF (■) and 1-chloroheptane (●).

end distance, and n is the number of main chain bonds of length l . Results for K_θ , corrected for polydispersity effects¹⁰ and C_∞ are presented in Table V.

In Figure 3, T_g results for PPEMA and PPBMA are plotted along with literature results for free radically produced PPMA and PBMA.¹¹ The introduction of alkylene spacers of increasing length increases the flexibility of the side chain and leads to a progressive decrease in T_g . This clearly demonstrates the role of local (substituent) flexibility in determining T_g of these materials (i.e., T_g is influ-

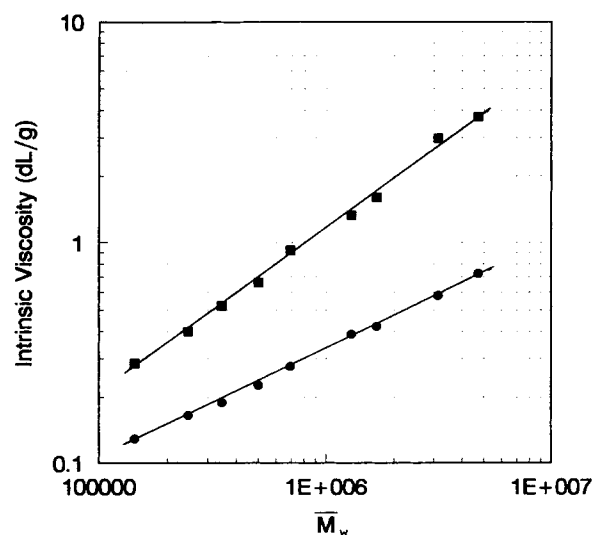


Figure 2. Mark-Houwink-Sakurada plots for PPBMA in THF (■) and 1-chloroundecane (●).

Table V. Unperturbed Chain Parameters for PPEMA and PPBMA

Polymer	$K_\theta \times 10^4$ (dL/g ^{-3/2} mol ^{1/2})	C_∞
PPEMA	3.67	11.3
PPBMA	3.37	12.2

enced more by flexibility of the side group than by flexibility of the main chain).

Di Marzio and Gibbs¹² have successfully predicted T_g for poly(n -alkyl methacrylates) by viewing these systems as copolymers of poly(methyl methacrylate) with polyethylene. If the macromolecules of this work are viewed as copolymers of PPMA and polyethylene (having T_g values of 110 and -93°C , respectively¹¹), T_g values of 69, 42, and 8°C are computed for PBMA, PPEMA, and PPBMA, respectively. These values fit the experimental curve of Figure 3 almost perfectly.

C_∞ results for PPMA and derivatives with alkylene spacers are presented in Figure 4. The C_∞ value for PPMA is taken from Hadjichristidis et al.,¹³ while the value of 10.0 for PBMA is an average of results reported by Richards¹⁴ and Gargallo and co-workers.¹⁵ The introduction of a single methylene spacer on going from PPMA to PBMA leads to a large increase in conformational flexibility. It is well established^{1,2} that moving a rigid substituent, such as a phenyl group, away from the polymer backbone will lead to a decrease in C_∞ . Conversely, on increasing the length of the alkylene spacer (from

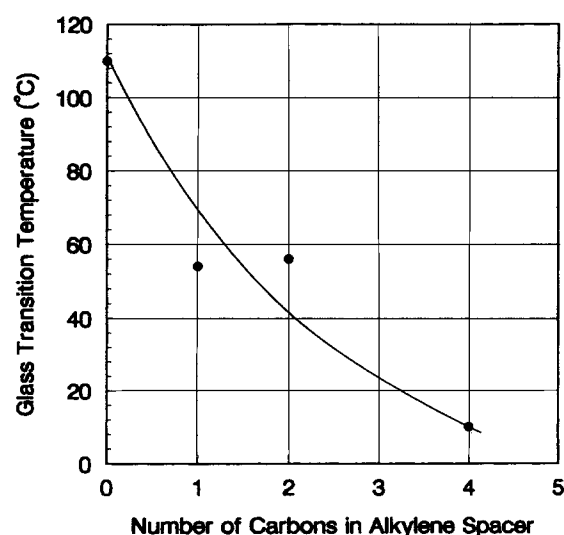


Figure 3. Variation of T_g with alkylene spacer length for PPMA and derivatives.

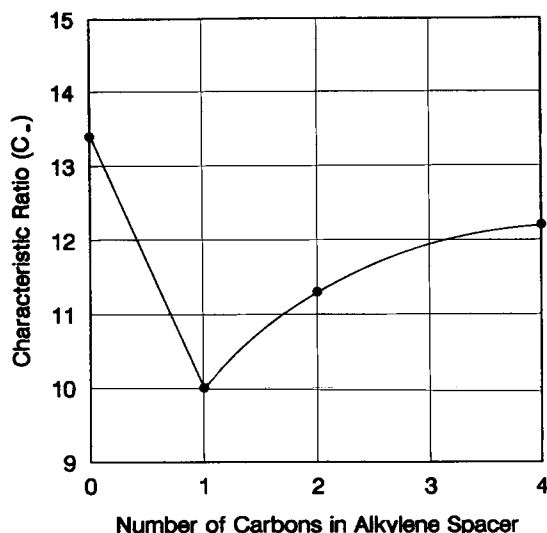


Figure 4. Dependence of C_∞ on alkylene spacer length for PPMA and derivatives.

methylene to ethylene to butylene) C_∞ is observed to increase. We believe that this decrease in chain flexibility for these latter materials mainly reflects their progressively larger sizes. Therefore, it appears that steric hindrances to rotation about main chain bonds in these materials reflect both overall substituent size and the proximity of bulky substituents to the main chain. The increase in size on going from phenyl to benzyl substituents is marginal, but the movement of the bulky aromatic ring away from the backbone greatly enhances the flexibility of the polymer. For PPMA and PPBMA the effect of increasing substituent size offsets the impact of moving the phenyl group further away from the main chain. Also, increasing the spacer length introduces flexibility which helps the phenyl groups to be placed in favorable positions for strongest interactions between aromatic rings. In this regard, recall that rather long flexible spacers (e.g., hexylene) normally are required for liquid crystal formation in certain methacrylate derivatives.³

Finally, we note that the results for k_H (Tables II and III) show typical behavior. The values obtained in the good solvent THF generally vary between ca. 0.3 and 0.4. Larger k_H values are measured in the theta solvents, as expected. It is interesting that $k_{H,\theta}$ values for PPMA are consistently larger than those for PPBMA. The $k_{H,\theta}$ values for the former are typical to those reported previously for

poly(methyl methacrylate) in several theta solvents.¹⁶ While k_H values in good solvents for a wide range of linear, flexible chains are quite constant, it is well established now that theta condition k_H values are quite system-dependent.^{17,18}

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