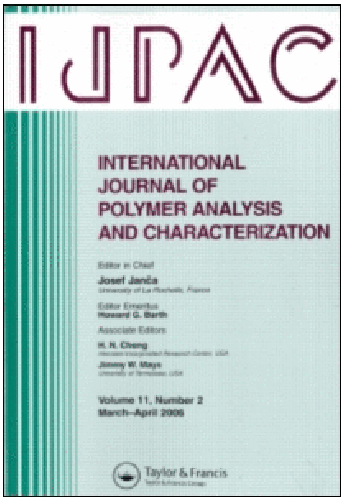

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Synthesis, Chain Flexibility, and Glass-Transition Temperature of Poly (2,2-Diphenylethyl Methacrylate)

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*Six poly(2,2-diphenylethyl methacrylate) samples, with relatively low polydispersity index (M_w/M_n:1.2–1.4) and M_w ranging from 14.4×10^4 to 184.4×10^4, were prepared by free-radical polymerization and fractionation. The dilute solution properties of the samples were studied by low-angle laser-light scattering in THF at 25°C and viscometry in a thermodynamically good solvent (toluene at 25°C) and in a Θ-solvent (*p*-xylene at 22°C). Differential scanning calorimetry was used for the T_g determination. The results are compared with those reported for poly(2-phenylethyl methacrylate) and poly(diphenylmethyl methacrylate).*

Keywords: Poly(2,2-diphenylethyl methacrylate); Synthesis; Solution properties; Chain flexibility; Characteristic ratio; Glass-transition temperature

INTRODUCTION

Chain flexibility lies at the heart of polymer physics[1] and therefore its determination is of vital importance for the prediction of polymer properties[2]. In this article we report the synthesis (free-radical polymerization), characterization (size exclusion chromatography, low-angle

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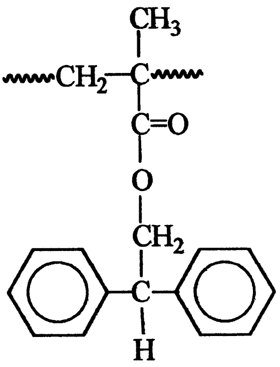

SCHEME 1. Poly(2,2-diphenylethyl methacrylate).

laser-light scattering (LALLS)), tacticity (*rr*, *mm*, *mr* triads by ^{13}C NMR), chain flexibility (C_∞ by viscosity under Θ-conditions), and glass-transition temperature, T_g (differential scanning calorimetry), of poly(2,2-diphenylethyl methacrylate) (Scheme 1).

The results are compared with those available for poly(2-phenylethyl methacrylate)[3] and poly(diphenylmethyl methacrylate)[4] in order to clarify the influence of the side group on C_∞, T_g, and tacticity of polymethacrylates.

EXPERIMENTAL

The monomer 2,2-diphenylethyl methacrylate was prepared by esterification of methacrylic acid (0.3 mol) with 2,2-diphenylethanol (0.25 mol), in 300 mL of refluxing benzene, in the presence of p-toluenesulfonic acid (5 g) as catalyst and methylene blue (1 g) as inhibitor. The progress of esterification was monitored by collecting the generated water into a calibrated Dean-Stark trap. The monomer was purified by repeated crystallization from methanol. ^1H NMR (200 MHz, $CDCl_3$ at 30°C) results 2,2- diphenylethyl methacrylate are δ 1.9 ppm (α-CH_3), 4.7 ppm (CH_2), 5.5 ppm (-CH=, trans to the esterified group), 6.0 ppm (-CH=, *cis* to the esterified group), 7.2–7.4 ppm (C_6H_5).

The monomer was polymerized at 50°C in benzene, distilled over CaH_2, using 2,2′-azobisisobutyronitrile (AIBN) as initiator recrystallized from methanol. Two polymerizations were conducted in sealed reactors under high-vacuum conditions. Details are given in Table I. The polymers were precipitated from the benzene solution by addition of

TABLE I Polymerization of 2,2-diphenylethyl methacrylate in benzene at 50°C with α, α′-bisisobutyronitrile as initiator

Polymerization	[Monomer] %(w/v)	[Initiator] (% w/v)	Yield (%)	Polydispersity $I = M_w/M_n$[a]
1	10.0	0.01	58	1.4
2	10.0	0.1	62	2.0

[a] Size exclusion chromatography in THF at 30°C.

methanol, repeatedly washed with methanol and dried, until they reached constant weight, in a vacuum oven at 50°C.

The poly(2,2-diphenylethyl methacrylate) (PDPEMA) samples were fractionated using toluene as a solvent and methanol as nonsolvent. Concentrations of less than 0.3% (w/v) and as low as 0.05% (w/v) were employed. Each polymer was separated into five to six fractions. Size exclusion chromatography (SEC) (Waters 501 pump, Waters 401 differential refractometer, four Phenomenex linear columns with porosity 500 to 10^6 Å) was used to determine polydispersity and to provide initial estimate of molecular weights relative to the polystyrene standards. Tetrahydrofuran (THF) at 30°C was the mobile phase at a flow rate of 1 mL/min and polystyrene standards were used for calibration. Six fractions of PDPEMA were selected based on polydispersity, SEC molecular weight, and sample quantity.

Tacticity was determined from the carbonyl intensity of the ^{13}C NMR spectrum of two fractions of PDPEMA (F1 and F4) in $CDCl_3$ at 25°C, taken with a 50.3 MHz NMR spectrometer. The downfield peak was assigned to the isotactic (*mm*) triads, the upfield to the syndiotactic (*rr*) triads, and the intermediate to the atactic (*mr* + *rm*) triads[5,6]. The percentages of isotactic, atactic, and syndiotactic triads, practically the same for the two fractions, were 8, 30, and 62% respectively.

The glass-transition temperature was determined for fractions F1 and F4 with a 2910 Modulated DSC (TA Instrument). The calibration was based on an indium standard, the sample weight was about 10 mg, and the heating rate was 10°C/min. An average value of $T_g = 87 \pm 0.5$°C, corresponding to the midpoint of the transition, was found.

The light-scattering experiments were carried out at 25°C in THF, distilled over sodium, with a Chromatix KMX-6 low-angle laser photometer, operating at a wavelength of 633 nm. The weight-average molecular weight, M_w, and second virial coefficient, A_2, values were obtained from $(Kc/\Delta R_\Theta)^{1/2}$ versus c plots, according to Berry's equation:

$$(Kc/\Delta R_\theta)^{1/2} = (1/M_w)^{1/2}(1 + 2A_2\,c)$$

where ΔR_θ is the excess Rayleigh ratio, K is a combination of known optical constants, and c is the concentration. The least-squares method was applied for analyzing the data. In all cases the correlation coefficient was better than 0.99.

The differential refractive index (DRI) increment dn/dc was determined under the same conditions ($\lambda = 633$ nm, THF, 25°C) with a Chromatix KMX-16 refractometer, calibrated with aqueous NaCl solutions. Measurements on several concentrations and different fractions yielded a value of 0.170 ± 0.002 mL/g for PDPEMA. For LALLS and DRI experiments, solvents and solutions were filtered through 0.2 μm pore-size nylon membrane filters directly into the scattering or the DRI cell.

Viscometry experiments were conducted in toluene at 25°C and *p*-xylene at 22°C, both distilled over CaH_2, by using Cannon-Ubbelohde viscometers with negligible kinetic energy corrections. Temperature was controlled to ±0.01°C, using a CT 1450/2 (Schott Geräte). Flow times for solvents and solutions were measured with the automatic viscosity measurements unit AVS 310. Flow times were reproducible within 0.015 s. Appropriate concentrations were chosen so that relative viscosities η_r ranged between 1.1 and 1.3. The flow time for the solvents was between 220 and 230 s. The intrinsic viscosity $[\eta]$, k_H, and k_k values were derived from the Huggins and Kraemer relationships

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c$$

$$(\ln \eta_r)/c = [\eta] + k_k[\eta]^2 c$$

Practically the same $[\eta]$ value was obtained from both plots. The least-squares method was applied for analyzing the data. In all cases the correlation coefficient was better than 0.99.

The cloud point T_c of five PDPEMA fractions in *p*-xylene, distilled over anhydrous calcium sulfate, was determined at a concentration of ~ 1 g/dL. These T_c values were utilized to determine an approximate value of Θ-temperature according to the Shultz-Flory equation[7]

$$1/T_c = 1/\Theta(1 + B/M_w^{1/2})$$

where Θ is the theta temperature and B a parameter depending on the specific volume of the polymer, the molar volume of the solvent, and the entropy of polymer dilution. The value determined as theta temperature, by applying the least-squares method, was 22°C.

RESULTS AND DISCUSSION

Weight-average molecular weight M_w, second virial coefficient A_2, and intrinsic viscosity $[\eta]$ values for the selected PDPEMA fractions are

TABLE II Low-angle laser-light scattering and viscometry results for poly (2,2-diphenylethyl methacrylate) fractions at 25°C

	F_1	F_2	F_3	F_4	F_5	F_6
$M_w\ 10^{-4}$[a]	14.4	29.6	39.7	66.8	128.8	184.4
$A_2\ 10^{4}$[a] (mL.mol.g^{-2})	1.9	1.7	1.5	1.3	1.1	0.9
$[\eta]_{\mathrm{Tol.}}$ at 25°C (dL/g)	0.198	0.295	0.363	0.543	0.859	1.31
$[\eta]_{p\text{-Xyl.}}$ at 22°C (dL/g)	0.115	0.167	0.196	0.250	0.350	0.411

[a] Low-angle laser-light scattering in THF at 25°C.

presented in Table II. Polydispersity index M_w/M_n and Huggins constant values vary in a rather narrow range (M_w/M_n: 1.2–1.4; k_H: 0.29–0.35 in toluene and 0.48–0.50 in *p*-xylene) for all six fractions; therefore in Table II, specific values are omitted. The Huggins coefficient values in both solvents are typical for random coils. In all cases $k_H + k_K$ is practically 0.5.

The dependence of the second virial coefficient A_2 on molecular weight, in THF at 25°C, in ln-ln plot is presented in Figure 1. The following equation was obtained by using the least-squares method:

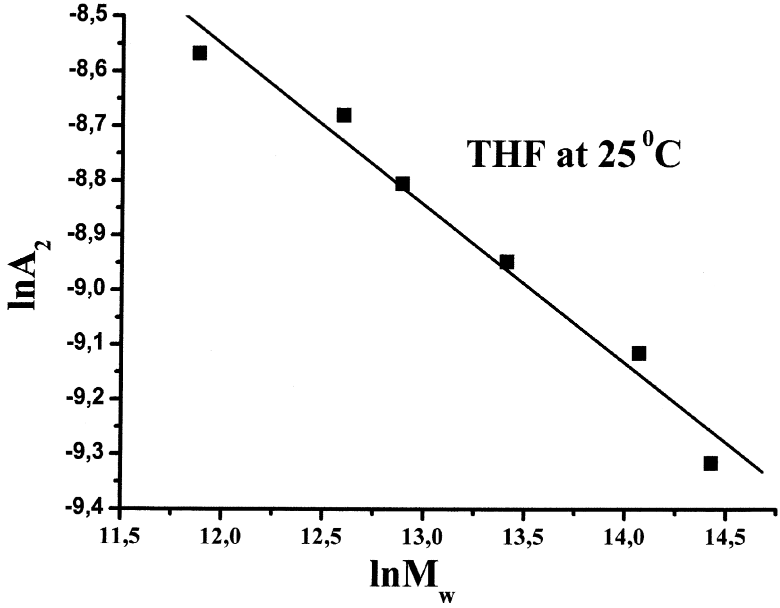

FIGURE 1 Second virial coefficient dependence of PDPEMA on the molecular weight.

$$A_2 = 6.3 \times 10^{-3} M_w^{-0.29} \text{ (THF at } 25^\circ \text{C, cc: 0.987)}$$

The value of the exponent is typical of the experimental results for flexible chains in thermodynamically good solvents[8,9] and very close to theoretical predictions[10,11].

From the ln-ln plots of [η] versus M_w for PDPEMA (Figure 2) the following Mark-Houwink-Sakurada (M-H-S) equations were obtained, using the least-squares method:

$$[\eta] = 2.96 \times 10^{-5} M_w^{0.73} \text{ (toluene at } 25^\circ \text{C, cc: 0.995)}$$
$$[\eta] = 3.06 \times 10^{-4} M_w^{0.50} \text{ (}p\text{-xylene at } 22^\circ \text{C, cc: 0.999)}$$

The values of the exponent lie in the usual range (0.5–0.8) observed for flexible polymers. It seems that 22°C in *p*-xylene is the accurate Θ-temperature of PDPEMA despite the fact that only one concentration (~ 1% w/v) was used for the determination of the cloud point. The value of the

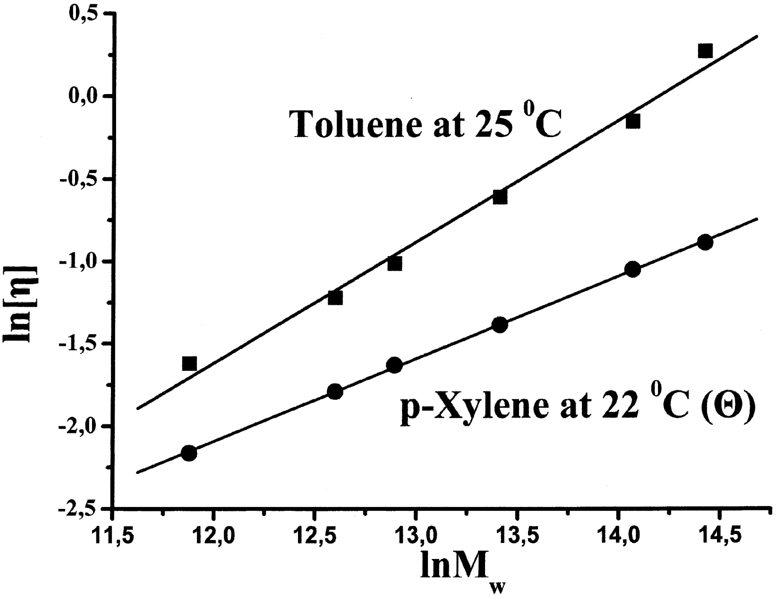

FIGURE 2 Mark-Houwink-Sakurada plots for PDPEMA fractions in toluene at 25°C (squares) and *p*-xylene at 22°C (circles).

pre-exponent parameter $K = 3.07 \times 10^{-4}$ dL.g^{-1} of the M-H-S equation $[\eta] = K\ M_w^{\alpha}$, under Θ-conditions, corresponds to K_θ, which is related to the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ of an isolated chain with molecular weight M, through Flory's well-known equation:

$$K_\theta = \Phi[\langle r^2 \rangle_0 / M]^{3/2}$$

Φ is Flory's universal viscosity constant. By adopting for Flory's constant Φ the experimental value of 2.5×10^{21} (cgs units)[12–14] and by using the polydispersity corrected value of $K_\theta = 3.13 \times 10^{-4}$dL.g^{-1}, assuming a Schulz-Flory distribution[15], the following relation between $\langle r^2 \rangle_0$ and M is obtained:

$$\langle r^2 \rangle_0 = 0.250\,M(\mathring{A}^2)$$

K_θ can also be extracted from intrinsic viscosity data in good solvents by using the Burchard-Stockmayer-Fixman[16–18] extrapolation method, according to the following equation:

$$[\eta]M_w^{-1/2} = K_\theta + 0.51\,B\,M_w^{-1/2}$$

By plotting $[\eta]M_w^{-1/2}$ versus $M_w^{-1/2}$ (Figure 3), the extrapolated value is practically the same as the one found for the Θ solvent *p*-xylene. The analysis of the plots shows that the B-S-F relation is valid over the entire molecular weight range for both solvents.

The most useful and widely used parameter for comparing chain flexibilities[19] of polymers is the Flory's characteristic ratio C_∞, which is defined as

$$C_\infty = \lim[\langle r^2 \rangle_0 / nl^2]$$

where n is the number of main chain bonds, $n = M/m_0$ (m_0 is the molecular weight of the monomeric unit), of length l. In our case $m_0 = 266$ and $l = 1.53$ Å. Therefore C_∞ for PDPEMA is calculated to be 14.2.

Table III summarizes the % *mm* triads, C_∞, and T_g values for poly(2,2-diphenylethyl methacrylate) (PDPEMA), poly(2-phenylethyl methacrylate) (PPEMA), and poly(diphenylmethyl methacrylate) (PDPMMA). The following remarks can be made by comparing the results:

(a) The *mm* triads of PDPEMA (8%) are practically the same as those of PPEMA (6%), but lower than those of PDPMMA (25%), meaning that the methylene flexible spacer prevents the phenyl rings interactions and thus the formation of helicoidal (*mm*) segments.

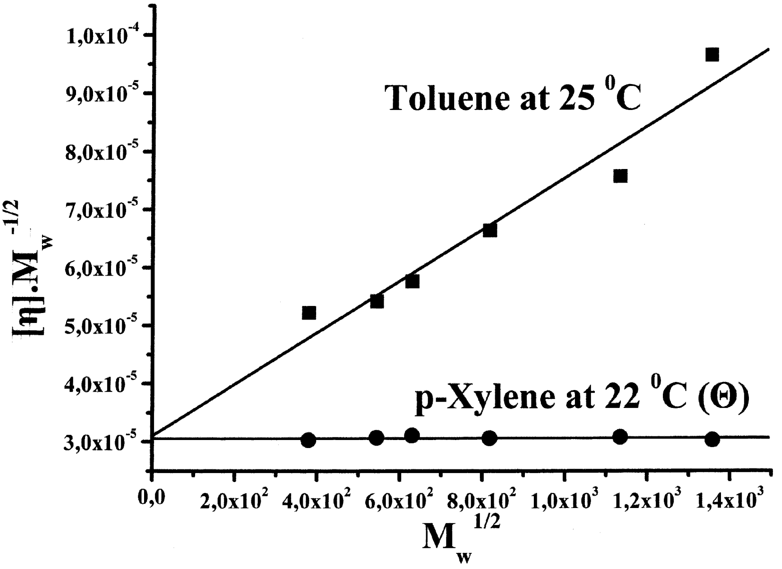

FIGURE 3 Burchard-Stockmayer-Fixman plots for PDPEMA fractions in toluene at 25°C (squares) and *p*-xylene at 22°C (circles).

TABLE III Isotactic triads (mm), characteristic ratio C_∞, and T_g values for poly(2-phenylethyl methacrylate) (PPEMA), poly(2,2-diphenylethyl methacrylate) (PDPEMA), and poly(diphenylmethyl methacrylate) (PDPMMA)

Polymer	Side group	*mm* (%)	C_∞	T_g (°C)
PPEMA	$-CH_2CH_2Ph$	8	11.3	42
PDPEMA	$-CH_2CHPh_2$	6	14.2	87
PDPMMA	$-CHPh_2$	25	14.0	not available

(b) The flexibility of PDPEMA ($C_\infty = 14.2$) is practically the same as that of PDPMMA ($C_\infty = 14.0$) despite of the higher distance of the diphenylmethyl group of PDPEMA from the main chain. It seems that the higher volume of the side group of PDPEMA balances the higher flexibility due to the presence of the methylene group.

(c) The replacement of a hydrogen of PPEMA by a phenyl group increases C_∞ from 11.3 to 14.2, which reflects the increased hindrance to rotation around main chain bonds as the side group size is increased. As a consequence the T_g of PDPEMA (87°C) is higher than that of PPEMA (42°C).

CONCLUSIONS

Poly(2,2-diphenylethyl methacrylate) (PDPEMA) of relatively narrow molecular weight distribution can be prepared by free-radical polymerization followed by fractionation. The comparison of the dilute solution and thermal properties of PDPEMA with those of poly(diphenylmethyl methacrylate) and poly(2-phenylethyl methacrylate) leads to the following conclusions: (a) the presence of the methylene spacer in the side groups has a strong influence on the microtacticity but not on the flexibility of the main chain and (b) an extra phenyl group in the side groups decreases the flexibility and increases the glass-transition temperature.

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