Synthesis, solution properties and chain flexibility of poly(2,6-dimethylphenyl methacrylate)

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The dilute solution properties of poly(2,6-dimethylphenyl methacrylate) (PDMP) in various solvents were studied by viscosity, size exclusion chromatography (s.e.c.) and osmotic pressure measurements. The Kuhn–Mark–Houwink–Sakurada (KMHS) relationships were established. The unperturbed dimensions $\langle r^2\rangle_0^{1/2}$, the rigidity factor σ, the characteristic ratio C_∞, and the thermodynamic parameters were determined by using the Stockmayer–Fixman equation, from viscometric data in good and theta conditions in pure and mixed solvents. The results show that preferential adsorption of water in the mixture THF/water, should not play an important role in the determination of the conformational parameters in this system. In addition, the measured rigidity of PDMP can be explained assuming that this polymer behaves as a kinked-chain molecule. The conformational behaviour of this polymer is analysed in terms of the effect of the side chain structure in relation to poly(phenyl methacrylate) (PPh).

(Keywords: poly(2,6-dimethylphenyl methacrylate); chain flexibility; characteristic ratio; theta condition; aromatic poly(methacrylates); solution properties)

INTRODUCTION

The rigidity of the chain in poly(methacrylic) esters and their dilute solution properties depend, in a significant way, on the spatial volume of the side groups of the macromolecules and on their specific interactions[1–4]. The size and nature of bulky side groups seem to play an important role in the conformational behaviour of this type of polymer. Abundant experimental evidence of this dependence can be found in the literature[1–8]. On the other hand, the preferential adsorption behaviour in mixed solvents of polymers with bulky side groups also depends on the bulkiness of the side chain[9,10].

Because of the bulky side groups, these kind of polymers also present high $T_g(\infty)$ values[5–8]. Most of the bulky side group polymer systems reported are composed of an aromatic ring with *para* substitution[1,4,11,12]. However, few reports deal with the di-*ortho*-substitution in the aromatic ring of the side group. Otsu *et al.*[13] have studied the effect of the *ortho*-alkyl substituents on radical polymerization of phenyl methacrylates. Velickovic' *et al.*[14] have recently studied phenyl methacrylates with *ortho* and *para* substituents in the aromatic ring and they found that these monomers do not obey classical kinetics of polymerization. On the other hand, these authors showed that with *ortho*-substitution, increasing size of the substituents decreases the overall rate of polymerization.

The aim of this work is to investigate the effect of the di-*ortho*-substitution of the aromatic ring in the side chain on the conformational and thermodynamic behaviour of polymer solutions. For this reason we have studied the solution properties of poly(2,6-dimethylphenyl methacrylate [(poly[1-(2,6-dimethylphenoxy carbonyl)-1-methylethylene])] (PDMP). Fractions of this polymer have been examined in different solvents with variable thermodynamic solvent power by viscosimetric, osmometric and size exclusion chromatography (s.e.c.) measurements.

EXPERIMENTAL

Monomer and polymer preparation

2,6-dimethylphenyl methacrylate (DMP) was prepared by the reaction of methacryloyl chloride (50% solution in benzene) in the presence of triethylamine. DMP was purified by passing the concentrated reaction product through alumina to remove the unchanged phenol[13] and distilled under reduced pressure (1 mmHg, 92–93°C). Moreover, it was identified by infra-red (i.r.) and ^{1}H nuclear magnetic resonance (n.m.r.) and elemental analysis.

DMP i.r. (KBr cm^{-1}): 3080, 2980, 1655, 1725, 1370, 1630, 640. ^{1}H n.m.r. ($CDCl_3$, ppm): 7.12 (m, 3H); 6.40–6.44 (m, 1H); 5.74–5.80 (m, 1H); 2.18 (s, 6H); 2.12 (s, 3H).

Elemental analysis: calculated C, 75.78%; H, 3.37%; found: C, 75.69%; H, 3.40%.

The monomer was polymerized at 323 K in benzene solution under vacuum in the presence of 2,2′-azobisisobutyronitrile (AIBN) (3×10^{-3}–7×10^{-2} mol l^{-1}). The polymer was fractionated by standard precipitation procedures using benzene as solvent and methanol as non-solvent. Appropriate fractions were chosen for this study.

Measurements

Osmometric measurements were carried out with a Hewlett–Packard high speed membrane osmometer (model 502) in toluene solution at 299.5 K. The measurements were usually made at four or six different

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Table 1 Number average molecular weight M_n, weight average molecular weight M_w, and polydispersity factor (M_w/M_n) for PDMP fractions

Fraction	M_n ($\times 10^{-5}$)^a	M_w ($\times 10^{-5}$)^b	M_w/M_n^{b}
1	7.30	8.23	1.13
2	4.08	4.97	1.22
3	3.95	4.13	1.05
4	3.24	3.87	1.19
5	—	3.32	1.26
6	1.40	1.64	1.17
7	1.00	1.13	1.14
8	0.91	1.06	1.16
9	0.72	0.91	1.27
10	—	0.75	1.16
11	—	0.57	—
12	—	0.34	—

[a] From osmotic pressure measurements in toluene, at 299.5 K
[b] From size exclusion chromatography

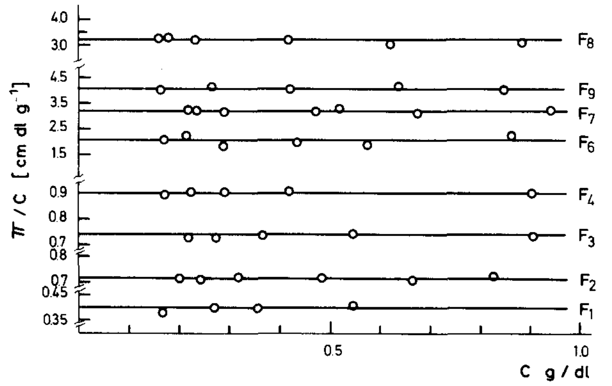

Figure 1 Variation of the reduced osmotic pressure πc^{-1} (π in cm of solvent, c in g dl^{-1}) with the concentration c for eight fractions of PDMPh in toluene at 299.5 K (theta condition)

concentrations and extrapolated to infinite dilution in order to determine the number average molecular weight, M_n. The weight average molecular weight (M_w) and the heterogeneity index (M_w/M_n) were determined by s.e.c. with a Perkin-Elmer high performance liquid chromatograph (h.p.l.c.), equipped with a 6000 psi pump, a differential refractometer LC-25, and an injector of 175 μl. Three Water Associates Ultra Styragel™ columns (10^3, 10^4 and 10^5 Å) in series were used. Samples were eluted with THF and the flow rate was 1.0 ml min^{-1}. The columns were first calibrated with standard polystyrene samples of narrow molecular weight distribution in order to obtain the universal calibration curve. The volume of the injected polymer solution was always 5 μl. The analysis of the elution data was performed according to the Rabek[15] treatment of the data, with the aid of a computer program based on normalization of the chromatograms.

The viscosities of the polymer solutions in the different solvents at 298 K were measured with a Desreux-Bischoff dilution viscometer[16] and intrinsic viscosity [η] was determined by the usual extrapolation of the reduced specific viscosity η_{sp}/c and $\ln \eta_r/c$ vs. c (where η_r is relative viscosity).

Solvents used were analytical grade chemicals from Merck (FRG) and Burdick and Jackson Lab. Inc. (USA).

RESULTS AND DISCUSSION

The M_n determined by membrane osmometry, the M_w determined by s.e.c., and M_w/M_n for the different fractions studied are summarized in *Table 1*. *Figure 1* presents the variation of the reduced osmotic pressure (πc^{-1}) with the concentration for the eight fractions studied. This figure shows that the osmotic pressure function π in toluene at 299.5 K is independent of polymer concentration c, which indicates that toluene is a theta solvent ($A_2 = 0$). From intrinsic viscosity data, we have determined the solubility parameters according to the method described by Gee[17]. According to this method the solubility parameter obtained for PDMP is 9.6 cal$^{1/2}$ cm$^{-1/2}$.

From the usual log–log plot of [η] vs. M_w for PDMP in chlorobenzene, THF, toluene and THF/water mixtures (theta solvents) the Kuhn–Mark–Houwink–Sakurada (KMHS) equations ([η] = $K_a M^a$) were established. *Figure 2* shows these plots. *Table 2* summarizes the K_a and a values obtained from *Figure 2*. The results obtained for PDMP show that [η] is accurately proportional to M_n for toluene (ideal solvent). This behaviour was tested by osmometric measurements (see *Figure 1*).

Chlorobenzene is the best solvent for the polymer studied. The general viscometric behaviour of this polymer seems to be normal in the sense that a increases as the thermodynamic strength of the solvent increases and $a = 0.50$ in the theta solvent including the binary mixture, THF/water (90.6/9.4) (v/v).

As shown in *Table 2*, theta conditions were obtained in a pure and in a binary solvent, toluene and THF/water (90.6/9.4) (v/v) at 298 K for PDMP. The K_a values obtained in theta conditions (K_θ) are very similar in the single solvent and in the binary mixture for PDMP. The preferential adsorption behaviour in poly(alkylphenyl methacrylates) in a THF/water mixture has been recently studied[7,18]. In these systems, water is preferentially adsorbed and the magnitude of the adsorption is

Table 2 Thermodynamic parameters for PDMP in different solvents at 298 K

Solvents	K_a ($\times 10^4$)	a	B ($\times 10^{28}$) (cm^3 mol^2 g^{-2})
Chlorobenzene	1.84	0.65	5.91
THF	3.31	0.59	3.38
THF/H$_2$O (θ)	7.50	0.50	<0
Toluene (θ)	7.80	0.50	0.00

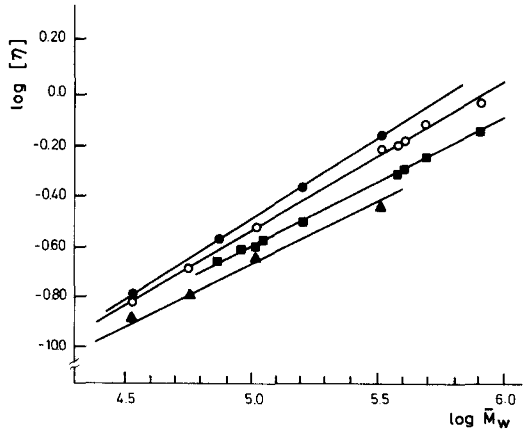

Figure 2 Double logarithmic plot of intrinsic viscosity [η] vs. weight average molecular weight M_w, for PDMPh in chlorobenzene (●), THF (○), toluene (■), THF/water (θ) (▲)

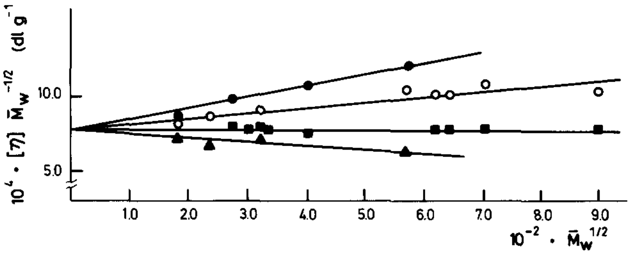

Figure 3 Stockmayer–Fixman plots for PDMPh in chlorobenzene (●), THF (○), toluene (■), THF/water (θ) (▲), at 298 K

Table 3 Molecular parameters for PDMP and PPh

	PPh[a]	PDMP
$K_\theta \times 10^{-2}$ (cm^3 g$^{-3/2}$ mol$^{1/2}$)	5.6	7.7
$(\langle r^2\rangle_0/M)^{1/2}$ (Å)	0.607	0.675
$(\langle r^2\rangle_{0f}/M)^{1/2}$ (Å)	0.242	0.223
σ	2.51	3.02
C_∞	12.6	18.3
$T_{g(\infty)}$ (K)	403	462
δ (cal$^{1/2}$ cm$^{-1/2}$)	—	9.6

[a] Values taken from reference 3

drastically dependent on the polymer structure. However, in this polymer it is rather low.

In order to investigate the effect of the side chain structure on the rigidity of the chain in PDMP we have also determined the conformational parameter (K_θ) related to the unperturbed dimension of the polymer chain, from data in good solvents. For this reason the Stockmayer–Fixman[19] treatment of the data was used in order to obtain K_θ. According to this method, the conformational parameter can be obtained through the equation:

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

where B is the long range interaction parameter dealing with the excluded volume theory, and Φ_0 is the Universal Flory Constant with a best experimental value of 2.51×10^{21} dl mol^{-1} g^{-1}. Therefore, K_θ and B can be obtained from the intercept and the slope of the plots of $[\eta]/M_w^{1/2}$ vs. $M_w^{1/2}$. *Figure 3* shows these plots in different solvents for PDMP. The system shows only one intercept for K_θ ($K_\theta = 7.7 \times 10^{-4}$), in single and binary solvents.

Table 2 also summarizes the thermodynamic parameter B. These values are in good agreement with the viscometric parameters K_a and a in the sense that high values of a and B are obtained in the best solvent and $a = 0.5$ and $B = 0$ in theta conditions.

The heterogeneity index correction factor for K_θ was calculated using the Sutter–Kuppel[20] and Bareiss[21] method assuming a Schulz–Zimm[22,23] distribution for each fraction. The correction factor is ~1.03 for $M_w/M_n < 1.3$ (ref. 21).

From the K_θ values we have calculated the unperturbed chain dimension $\langle r^2\rangle_0^{1/2}$ by using the classical equation:

$$K_\theta = \Phi_0[\langle r^2\rangle_0/M]^{3/2} \tag{2}$$

Table 3 summarizes the values of the unperturbed dimensions calculated from equation (2). In the same table we list the rigidity factor σ ($\sigma = \langle r^2\rangle_0^{1/2}/\langle r^2\rangle_{0f}^{1/2}$) obtained from the experimental $\langle r^2\rangle_0^{1/2}$ and the theoretical value for a free rotating polymer chain, by taking as a model a hypothetical polymethylene chain whose unperturbed end-to-end chain dimension is represented by $(\langle r^2\rangle_{0f}^{1/2})$ (ref. 24). The following $\langle r^2\rangle_{0f}^{1/2}$ value was obtained: $\langle r^2\rangle_{0f}^{1/2} = 0.223M^{1/2}$. The hindrance to rotation of the polymer chain is represented by σ. Therefore σ is a parameter which is a measure of the effect of the structure on the rigidity of the polymer chain.

The characteristic ratio, C_∞, as defined by Flory[24], relates the unperturbed root-mean-square end-to-end distance to chain length, and is expressed as:

$$C_\infty = \lim_{n\to\infty} [\langle r^2\rangle_0/nl^2] \tag{3}$$

where n is the number of main chain bonds of a mean square length l. This parameter has been calculated from experimental values of $(\langle r^2\rangle_0/M)^{1/2}$. We have compared the conformational parameters obtained for this polymer with that of poly(phenyl methacrylate) (PPh). It is clear that conformational parameters increase as the volume of the side chain and steric hindrance in the aromatic ring increases.

Table 3 also summarizes the glass transition temperatures of these polymers determined at infinite molecular weight, i.e. $T_g(\infty)$ (ref. 25). The high value of T_g reflects the higher rigidity of the polymer segments in PDMP than PPh. The results in *Table 3* show that an increase in the volume of the substituent in the aromatic ring leads to an enhancement of C_∞. This behaviour seems to indicate that the steric hindrance introduced in the side chain of these aromatic polymers exerts a marked influence on the conformational parameters.

Finally we can conclude that the introduction of methyl groups in the *ortho* position in the aromatic ring of these kinds of polymers play an interesting role in the conformation of the macromolecules, specially in the rigidity and in the solution properties. By comparing PDMP with PPh, it is confirmed that the effect of the *ortho*-substituted methyl groups on the unperturbed dimensions is very noticeable. These observations are in agreement with rotational isomerization theory, applied to the study of other polymers with large substituents[26]. Large substituents present important hindrances to internal rotation.

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