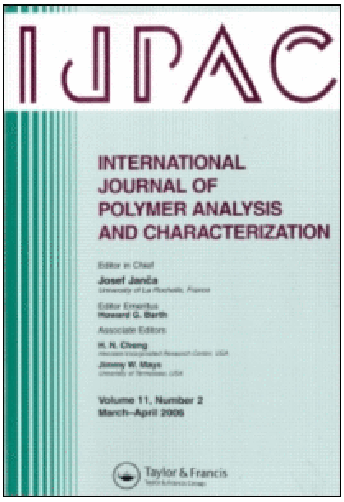

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Polymethacrylates Containing Indanyl Groups 2. Synthesis, Solution Properties and Unperturbed Dimensions of Poly(1-indanyl methacrylate)†

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The synthesis and the dilute solutions properties of poly(1-indanyl methacrylate) (P1-IM) in THF and 1–4 dioxane at 298 K (Θ-solvent) were studied by viscosity, classical light scattering and size exclusion chromatography (SEC) measurements. The Kuhn-Mark-Houwink-Sakurada relationships were established in the solvents studied. The unperturbed dimensions were determined by using the Stockmayer-Fixman extrapolation. From these results, the rigidity parameter σ was determined. The results show that the rigidity of P1-IM is higher than that of poly(5-indanyl methacrylate). The influence of the nature of the spacer group methylene or cyclic group is discussed and also compared with previous results found for another aromatic poly(methacrylates) series.

Keywords: Poly(1-indanyl methacrylate), solution properties, SEC, light scattering, viscosity, unperturbed dimensions

INTRODUCTION

The rigidity of the polymeric chain is a property that determines many characteristics of the polymers in both solid state as well as in solution [1–4]. In the case of aromatic poly(methacrylates), ortho substituents show a great steric hindrance to rotation and therefore a significant rigidity factor,

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which is reflected in different solution properties.[5,6] Recently, we have studied the flexibility in poly(methacrylic acid) esterified with a phenol-containing saturated cyclic, specifically, poly(5-indanyl methacrylate) (P5-IM).[7] We have compared the rigidity factor of this polymer with those of poly(phenyl methacrylate) (PPhM) and poly(4-*tert*-butyl methacrylate) (PBPhM), previously reported.[8,9]

From the comparison of the rigidity factor σ obtained for PPhM and PBPhM, it was clear that the introduction in the para position of *tert*-butyl substituent in the phenyl groups of poly(phenyl methacrylates) slightly changes the flexibility of the chain. A similar result was observed for poly(5-indanyl methacrylate).

The aim of the present work is to obtain information about the conformational, and viscometric behaviur of poly(1-indanyl methacrylate) [(poly[1-(indanyloxy carbonyl)-1-methylethylene]) (P1-IM) and to compare its properties with that of P5-IM.

EXPERIMENTAL

Preparation of Monomer and Polymer

The monomer 1-indanyl methacrylate was prepared by reaction of methacryloyl chloride[10] with 1-indanol in benzene solution using N,N-dimethylaniline as the acid acceptor. Purification was achieved by distillation under reduced pressure. The monomer was characterized by ^{1}H-NMR and FTIR which showed good agreement with the expected structure.

The monomer was polymerized at 323 K in a benzene solution under vacuum using 2,2′-azoisobutyronitrile (AIBN). The polymer was solubilized in THF and reprecipitated in petroleum ether. This process was repeated several times in order to purify it, and then dried at 323 K for several hours.

Solubility and Fractionation

The solubility of P1-IM in several solvents was tested at room temperature. The polymer was fractionated by standard precipitation procedures using THF as the solvent and petroleum ether as the nonsolvent. Five fractions were obtained.

Measurements

Viscosities of P1-IM fractions in THF and 1,4-dioxane, were determined at 298 K using a Desreux-Bischoff dilution viscometer,[11] having negligible kinetic energy corrections. THF and 1,4-dioxane used as solvents were analytical grade or freshly purified just before use.

The light scattering measurements for the different fractions of P1-IM in THF were carried out using a commercial multiangle light scattering laser photometer (Dawn-F) from Wyatt Technology Corp. containing 15 permanently mounted detectors. He-Ne Laser at $\lambda = 632.8$ nm was used as the light source. The dn/dc values were determined in THF on a Wyatt/Optilab 903 interferometric refractometer.

Precautions were taken to eliminate dust from the solutions. Dust was removed from samples by filtering them through a 0.22 –μm Millipore filter in a laboratory-built-holder.

The polydispersity indices (M_w/M_n) of the samples chosen for this study were determined by size exclusion chromatography (SEC) using a Perkin Elmer high performance liquid chromatograph (HLPC) equipped with a 6000 psi (0.84 Pa) pump, a differential refractometer LC-25, injector of 175 μL, and Shodex 803/S, 804/S and 805/S columns in series (molecular weight range $10^4 - 5 \times 10^6$). The samples were eluted with THF, the flow rate was 1 mL/min and the volume of the injected polymer solution was always 5 μL. Detailed procedure about the analysis of the elution data have been reported earlier.[5]

The partial specific volume was determined in THF at 298 K by using an Anton Paar DMA 55 digital densitometer.

The glass-transition temperatures (T_g) of the polymer were measured with a Mettler TA-3000 system equipped with a TC-A 10 Processor with DSC-30 cell. Dry nitrogen was used as purge gas and thermograms measured at a scan rate of 10 K/min.

RESULTS AND DISCUSSION

The weight-average molecular weight M_w and the polydispersity of the fractions of the polymer studied are summarized in Table I.

The relationships between M_w and intrinsic viscosity $[\eta]$ for P1-IM can be represented by the Mark-Houwink empirical equation:

TABLE 1 Weight average molecular weights M_w, intrinsic viscosities [η], and Huggins constants k_H of poly(1-indanyl methacrylate) fractions in THF and 1,4-dioxane at 298 K

Fraction	$M_w \times 10^{-5}$ *	$M_w/M_n^{\dagger}$	*THF*		*1,4-dioxane*	
			[η]	k_H	[η]	k_H
1	6.50	1.21	0.530	0.24	0.404	0.54
2	4.96	1.20	0.454	0.20	0.375	0.56
3	2.82	1.22	0.333	0.26	0.270	0.58
4	1.10	1.23	0.192	–	0.170	0.48
5	0.40	1.37	0.110	0.27	0.100	0.62

* From light scattering in THF at 298 K
† From SEC

$$[\eta] = K_a M_w^a \qquad (1)$$

The constants K_a and a in Equation (1) were determined from the plot of log [η] against log M_w (Fig. 1). The mathematical expressions showing this relation were calculated by the method of least squares:

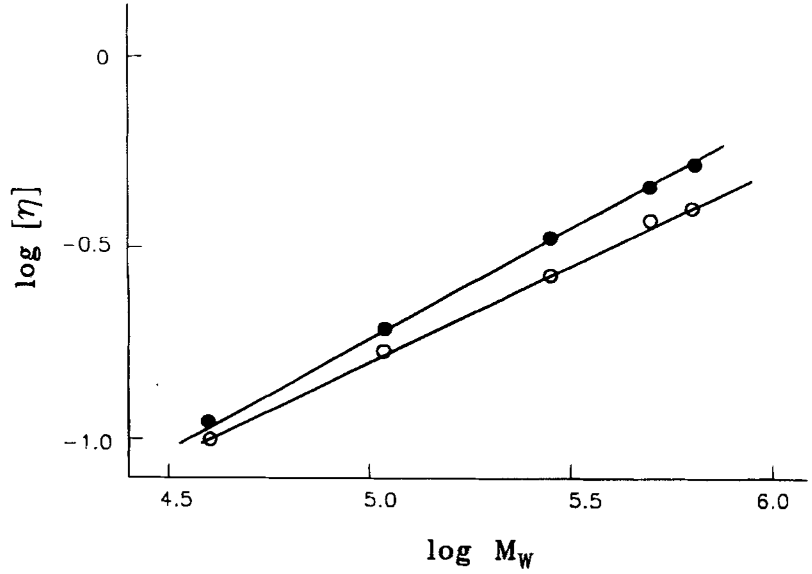

FIGURE 1 Double logarithmic plot of intrinsic viscosity [η] (in dL g^{-1}) vs weight average molecular weight M_w for P1-IM in THF (●), 1,4-dioxane (○) at 298 K.

$$[\eta] = 2.55 \times 10^{-4} \times M_w 0.57 \quad THF \quad 298K$$
$$[\eta] = 5.10 \times 10^{-4} M_w 0.50 \quad 1,4\,dioxane \quad 298K$$

The results obtained in 1,4-dioxane show that $[\eta]$ is proportional to $M_w^{0.50}$ for an ideal solvent (Θ solvent).

The variation of A_2 with the molecular weight shows the expected behavior[12] (Fig. 2): A_2 changes with molecular weight as predicted by theory:

$$A_2 = 2,38 \times 10^{-3} M_w^{-0.16} \tag{2}$$

The Stockmayer-Fixman equation[13] was employed to find the value of the conformational parameter K_Θ, to obtain the unperturbed dimension $\langle r_o^2 \rangle^{1/2}$.

$$\phi\left(\frac{r_0^{-2}}{M}\right)^{3/2} = \frac{[\eta]_\theta}{M^{1/2}} \tag{3}$$

The plots are given in Figure 3. The value of K_Θ obtained by this relation is practically the same for the Θ-solvent and the good solvent. As shown in

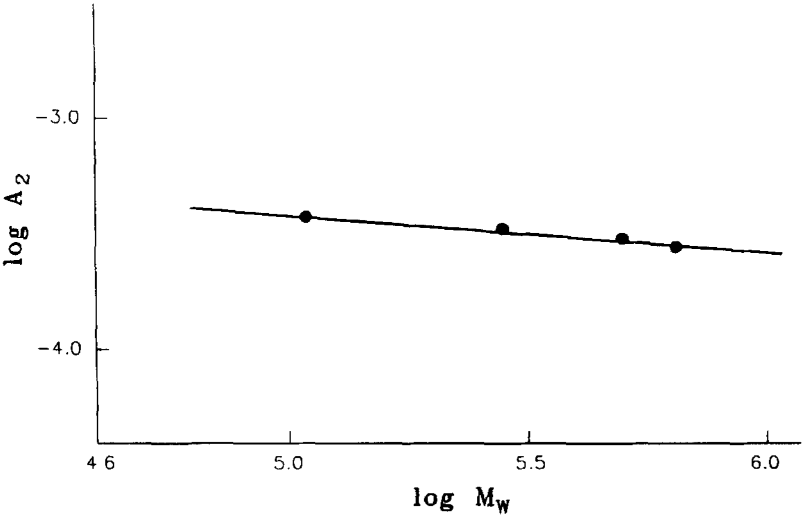

FIGURE 2 Double logarithmic plot of the second virial coefficient A_2 vs weight average molecular weight M_w of P1-IM in THF solutions at 298 K.

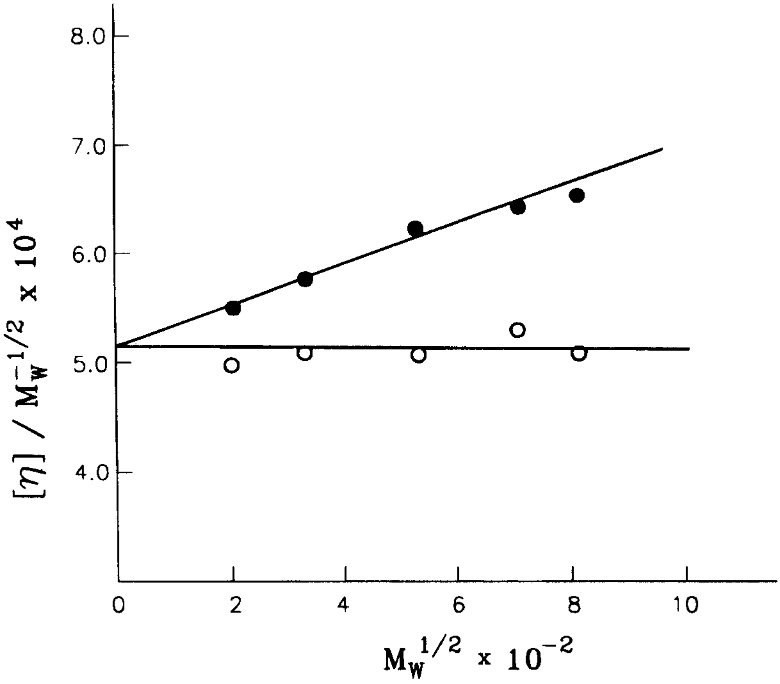

FIGURE 3 Stockmayer-Fixman plot for P1-IM in THF (●), 1,4-dioxane (○) at 298 K.

Figure 3, there is a common point of intersection for the two lines. The values of the thermodynamic parameter B show normal behavior.

Using the value of 5.15×10^{-4} for K_Θ, we find the relation between the root-mean-square end-to-end distance for the unperturbed chain and *M* to be

$$< r_0^2 >^{1/2} = 0.591\ M^{1/2} \quad \mathring{A} \tag{4}$$

with a ϕ_o value of 2.50×10^{21}, without a polydispersity correction.

The root-mean-square end-to-end distance assuming completely free rotation around the bond is

$$< r_{01}^2 >^{1/2} = 0.217\ M^{1/2} \quad \mathring{A} \tag{5}$$

The value of $\langle r_o^2 \rangle^{1/2} / \langle r_{o1}^2 \rangle^{1/2}$ (σ) that represents the effect of steric hindrance on the flexibility of the chain was found to be $\sigma = 2.72$. The term K_Θ

$M_0^{3/2}$ is also used to compare the chain rigidity[9] with M_0 = weight of the repeating unit.

In Table II, the results of the conformational parameters for P1-IM and three polymers previously reported[7,8,14] are given. It is clear that poly(1-indanyl methacrylate) is more rigid than poly(5-indanyl methacrylate) and poly(phenyl methacrylate). It seems reasonable to accept that the presence of a cyclic spacer group in place of a methylene group leads to a different lateral packing of the side groups.

In order to investigate the influence of the chemical structure of the lateral group on partial specific volume $\bar{v}_2^0$, we have determined the partial specific volumen at 298 K from density measurements through the equation

$$\bar{v}_2^0 = \rho_1^{-1}\left[1-\rho_1^{-1}\left(\frac{\partial\rho}{\partial w_2}\right)^0\right] \tag{6}$$

where ρ_1 is the solvent density and $(\partial\rho/\partial w_2)^0$ is the slope of the plot of the solution density ρ vs. polymer weight fraction w_2; superscript zero is the extrapolated magnitude at infinite dilution. We found that the experimental values of partial specific volume in solution $\bar{v}_2^0$ show variation when the substituent of the repeat unit is 1-indanyl or 5-indanyl. The values are 0.8183 (cm^3g^{-1}) and 0.7976 (cm^3g^{-1}) for poly(5-indanyl methacrylate) and poly(1-indanyl methacrylate), respectively. The polymer is more contracted when the pendant groups attached to the main chain of the polymer have the phenyl group with a cyclic spacer. In this respect, not only the size, as has been reported, but also the nature of the side group of the polymer affects the partial specific volume $\bar{v}_2^0$. Furthermore, the value of T_g for P1-IM (345 K) reflects a higher rigidity of polymer segments than for P5-IM (338 K).

TABLE II Flexibility factors $K_\theta M_0^{3/2}$ and σ of Some Aromatic Polymethacrylates

Polymer	$K_\theta \times 10^4$	$K_\theta M_0^{3/2}$	$\sigma = \frac{<r_0^2>^{1/2}}{<r_0^2>^{1/2}}$	*Ref.*
Poly(phenyl methacrylate)	5.60	1.16	2.46	14
Poly(benzyl methacrylate)		0.91	2.32	15
Poly(5-indanyl methacrylate)	4.40	1.26	2.58	16
Poly(1-indanyl methacrylate)	5.15	1.48	2.72	(*)

(*)This work.

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