

Solution properties of poly(2-selenolymethyl methacrylate)

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The dilute solution behaviour of poly(2-selenolymethyl methacrylate) has been studied in THF and chlorobenzene at 298 K, by intrinsic viscosity, size-exclusion chromatography and osmotic pressure measurements. The Kuhn–Mark–Houwink–Sakurada relationships were established. The conformational parameters σ and C_∞ , and the thermodynamic parameters B and A_2 were calculated. The results obtained are compared and discussed with those previously found for poly(benzyl methacrylate) and poly(2-thienylmethyl methacrylate).

(Keywords: poly(2-selenolymethyl methacrylate); solution properties; chain flexibility; poly(2-thienylmethyl methacrylate); aromaticity index; hetero atom)

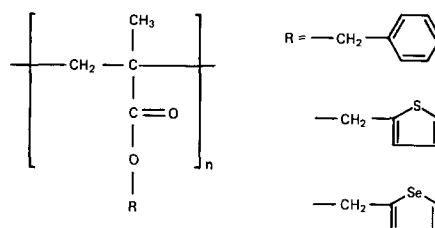
INTRODUCTION

The effect of the side chain structure on several properties of synthetic macromolecules has been extensively described for a number of systems^{1–5}. The effect of hetero atoms in the side chain has not been thoroughly investigated yet for aromatic polymethacrylates. In a previous paper, we have reported the solution properties and chain flexibility of poly(2-thienylmethyl methacrylate), and we have analysed the effect of the hetero atom on the solution properties and flexibility of the polymer by comparison with poly(benzyl methacrylate)⁶. The influence of the different aromaticity of the side chain on the conformational behaviour of these polymers is not clear. Furan, thiophene, selenophene and tellurophene form a very interesting series of stable aromatic rings, which differ in the nature of the hetero atom and therefore in aromaticity. Although this term is ambiguous⁶, the concept summarizes the whole of those chemical and physical properties typical of benzene, the 'aromatic' molecule par excellence.

It has been reported⁷ that the introduction of one oxygen atom in the cyclohexyl ring of poly(cyclohexyl methacrylate) reduces the rigidity of the polymer chain and this behaviour has been attributed to a minor stiffness of the side chain covering the whole stiffness of the macromolecule. Thus the tetrahydropyranyl group seemingly would exert a lesser degree of steric interference than the corresponding cyclohexyl group⁷. It is interesting to consider the planarity and rigidity of the side group. In the case of aromatic rings this characteristic is mainly conditioned by the aromaticity of the side ring. According to the literature^{8,9} the order of aromaticity found for the different hetero atom containing aromatic rings is benzene > thiophene > selenophene.

In this paper, the solution properties of poly(2-selenolymethyl methacrylate), PSeM (systematic name poly[1-(2-selenolymethoxycarbonyl)-1-methyl-

ethylene]) are reported. The conformational parameters of this polymer are compared with those of other poly(aryl methacrylates) containing aromatic rings of different aromaticity. The role of the hetero atom and the spacer group $-\text{CH}_2-$ on the glass transition temperature in this polymer is also studied and compared with that of the first two members of the series.



EXPERIMENTAL

Monomer and polymer preparation

2-Selenolymethanol was synthesized according to the procedure described in the literature^{10–12}. Selenolymethyl methacrylate was synthesized by the reaction of methacryloyl chloride and 2-selenolymethanol according to the procedure described by Burtle and Turek¹³, and was characterized by i.r. and ¹H n.m.r. as previously reported¹⁴.

The monomer was polymerized at 333 K in benzene under vacuum with 2,2'-azobisisobutyronitrile (AIBN) as initiator according to the procedure previously described¹⁴. The concentration of the monomer was 20 wt % and that of the initiator ranged from 5×10^{-3} to 20×10^{-3} wt % of AIBN. The polymer dissolved in benzene was precipitated in methanol, washed repeatedly and reprecipitated several times. The white solid was dried under vacuum at 308 K, to constant weight.

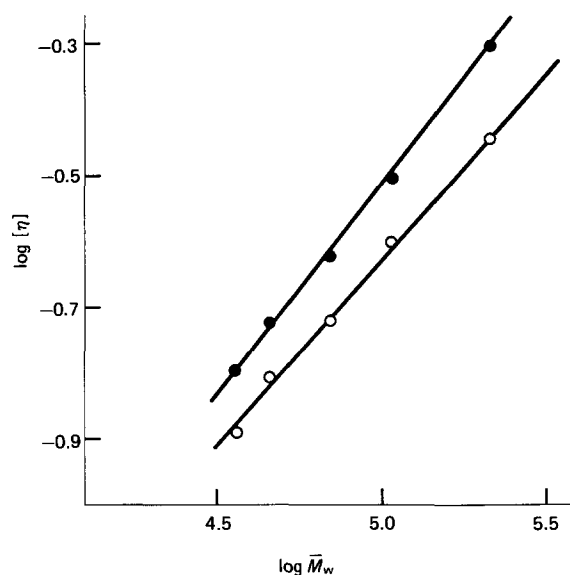
Polymer fractionation was performed at 298 K in the usual way by fractional precipitation, using benzene–

Table 1 Intrinsic viscosity, $[\eta]$, weight-average molecular weights, \bar{M}_w , number-average molecular weights, \bar{M}_n and polydispersity factor (\bar{M}_w/\bar{M}_n) for poly(selenolymethyl methacrylate) fractions (1–5)

	Solvent	1	2	3	4	5
$[\eta]$ (dl g ⁻¹)	THF	0.493	0.308	0.238	0.190	0.160
	Chlorobenzene	0.357	0.250	0.190	0.156	0.129
\bar{M}_w ($\times 10^{-5}$)	THF	2.10	1.07	0.70	0.46	0.36
$(\bar{M}_w/\bar{M}_n)_{g.p.c.}$		1.33	1.33	1.33	1.26	1.33
Osm. \bar{M}_n ($\times 10^{-5}$)	Chlorobenzene	1.70	0.88	—	—	0.35 ^a

^a From vapour pressure osmometry**Table 2** Viscometric and thermodynamic parameters for poly(2-selenolymethyl methacrylate) in different solvents at 298 K

Solvents	$K_a \times 10^4$ (dl g ⁻¹)	a	$B \times 10^{28}$ (cm ³ mol ² g ⁻²)	$A_2 \times 10^4$ ^a (cm ³ g ⁻² mol)
THF	1.81	0.65	7.28	1.63 (F ₁)
Chlorobenzene	3.63	0.56	4.67	0.59 (F ₂)

^a From osmometric measurements**Figure 1** Intrinsic viscosity ($[\eta]$) versus weight-average molecular weight (\bar{M}_w) for PSeM in THF (●) and chlorobenzene (○) at 298 K

methanol as the solvent precipitant pair. Seven fractions of PSeM were obtained. From these fractions only five were selected for study in solution.

Polymer characterization

The weight-average molecular weights, \bar{M}_w , of PSeM were measured by size exclusion chromatography using a Perkin–Elmer high performance liquid chromatograph equipped with a 6000 psi (0.84 Pa) pump, a differential refractometer LC-25, and a 175 μ l injector. Three Waters Associates Ultra StyragelTM columns (10³, 10⁴ and 10⁵ Å) were used in series¹⁴. Samples were eluted with tetrahydrofuran (THF). The apparatus was calibrated with polystyrene samples of narrow molecular weight distribution characterized by light scattering measurements. The flow rate was 1 ml min⁻¹ and the volume of the injected polymer solution was always 5 μ l. A universal calibration curve was used for the treatment of the data. The number-average molecular weight, \bar{M}_n of one

fraction (F₅) was determined in chlorobenzene at 333 \pm 0.001 K by vapour pressure osmometry using a Knauer VPO Osmometer (model 11,0) equipped with a universal thermistor probe. For two fractions of higher molecular weight (F₁ and F₂), \bar{M}_n was determined by membrane osmometry using chlorobenzene at 298 K and a Hewlett Packard high speed membrane osmometer (model 502).

Intrinsic viscosity

Intrinsic viscosity measurements in THF and chlorobenzene at 298 K were performed by using a Desreux–Bischoff dilution viscometer¹⁵, having negligible kinetic energy corrections.

Differential scanning calorimetry

The glass transition temperatures were measured by differential scanning calorimetry using a Perkin–Elmer DSC-1 B apparatus. Heating rates of up to 16 K min⁻¹ were used.

RESULTS AND DISCUSSION

Table 1 summarizes intrinsic viscosity $[\eta]$, in THF and chlorobenzene at 298 K, \bar{M}_w determined by exclusion chromatography and \bar{M}_n . The polydispersity indices are also summarized in Table 1. From these results Kuhn–Mark–Houwink–Sakurada (KMHS) relationships were established by using the classical log–log plots of $[\eta]$ vs. \bar{M}_w in THF and chlorobenzene at 298 K (Figure 1). Figure 1 shows that straight lines were obtained. The following relationships were obtained for the KMHS equations: $[\eta] = 1.81 \times 10^{-4} \bar{M}_w^{0.65}$ (THF, 298 K), $[\eta] = 3.63 \times 10^{-4} \bar{M}_w^{0.56}$ (chlorobenzene, 298 K). (All relations refer to $[\eta]$ in units of dl g⁻¹.)

The values of the a exponent lie in the range observed for linear and flexible polymers¹⁶. It is interesting to note that in the case of poly(2-thienylmethyl methacrylate), chlorobenzene is the θ -solvent at 298 K and $[\eta]$ is proportional to $\bar{M}_w^{0.50}$. However, for PSeM, chlorobenzene is a bad solvent but not a θ -solvent, and the exponent $a=0.56$ at 298 K and A_2 (the second virial coefficient) is slightly positive (see Table 2). We could not find a single θ -solvent for this polymer.

In order to obtain information about the unperturbed state of this polymer, we have used one of the excluded volume theories by using intrinsic viscosity measurements in good solvents.

To obtain the value of the conformational parameter K_θ , leading to the unperturbed dimension $\langle r^2 \rangle_0^{1/2}$, the Burchard–Stockmayer–Fixman (BSF) equation^{17,18} was employed (see Figure 2). Figure 2 shows that there is not a common point of intersection for the two lines. This result indicates that this polymer shows a solvent-dependent

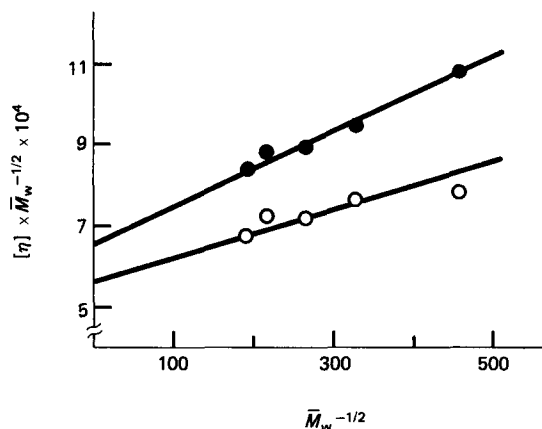


Figure 2 Burchard-Stockmayer-Fixman plots for PSeM fractions in THF (●) and chlorobenzene (○)

value for K_θ . From the slopes of Figure 2 we obtain the thermodynamic parameter B , dealing with the excluded volume parameter. This parameter shows a normal behaviour in the sense that B is higher in the better solvent (THF), and is lower in the worse solvent (chlorobenzene). The experimental B values are in good agreement with the a values obtained from the KMHS equation and the A_2 values. From these results, the general behaviour of PSeM seems to be normal for a linear flexible polymer.

Table 2 summarizes the values of the thermodynamic parameter B obtained from the BSF equation and the second virial coefficient A_2 and the K_a and a values for this polymer. The experimental K_θ values (in $\text{dl g}^{-3/2} \text{mol}^{1/2}$) obtained by extrapolation of the BSF plots are 6.5×10^{-4} and 5.6×10^{-4} in THF and chlorobenzene, respectively. These K_θ values are very high, reflecting a high degree of rigidity of the polymer chain.

Taking for K_θ the values of 5.6×10^{-4} and 6.5×10^{-4} for PSeM in chlorobenzene and in THF at 25°C , respectively, the relationship between the root-mean-square end-to-end distance for the unperturbed chain $\langle r^2 \rangle_0^{1/2}$ and M was found to be: $\langle r^2 \rangle_0^{1/2} = 0.580 M^{1/2} \text{ \AA}$ in chlorobenzene; and $\langle r^2 \rangle_0^{1/2} = 0.607 M^{1/2} \text{ \AA}$ in THF.

A value of $2.5 \times 10^{21} \text{ mol}^{-1}$ in the BSF equation, was used for Φ_0 , as it is considered the best experimental value established from intrinsic viscosity and light scattering measurements¹⁹ without a polydispersity correction. The root-mean-square end-to-end distance assuming completely free rotation around the bond is:

$$\langle r^2 \rangle_0^{1/2} = 0.204 M^{1/2} \text{ \AA}$$

The value of $0.204 M^{1/2}$ was calculated according to $(\langle r^2 \rangle_0^{1/2}/M)^{1/2} = 3.08/M_0^{1/2} = 0.204$ where $M_0 = 228.96$.

The values of $\sigma = \langle r^2 \rangle_0^{1/2} / \langle r^2 \rangle_0^{1/2}$, the steric factor of the chain was found to be 2.84 in chlorobenzene and 2.98 in THF (Table 3).

The most useful and widely used parameter for comparisons of average unperturbed chain dimensions of random-coil chains is Flory's²⁰ characteristic ratio C_∞ defined as:

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

Table 3 summarizes the data characterizing PSeM and PTM and PB₂M. From these results it is clear that the hetero atom Se in the pendant ester group exerts a stronger degree of steric interference than the S atom in the corresponding polymethacrylate.

In Table 4 we have compared some general characteristics of the pendant groups: the volume of the lateral group, the atomic weight of the hetero atom, the aromaticity index A and B_A (ref. 21) with the flexibility of the polymeric chain when these groups are incorporated into the main chain. It is clear that PSeM is the most extended chain. Thus the Se atom seemingly exerts a greater degree of interference than the corresponding S atom on the rotation of the lateral chain. However, the glass transition temperature value of PSeM does not support this behaviour. We have no explanation for this result.

Substitution of S by Se is expected to result in better conductivity due to the increased metallic character of Se (preliminary experiments are in progress to study this), a decrease in electronegativity, and perhaps also to greater participation of d orbitals⁸. The rate of electrophilic substitution in selenophene is greater than for thiophene⁹. However, it is difficult to correlate the characteristics of the group incorporated on the lateral chain with the main chain flexibility of the polymers considered here.

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Table 3 Molecular parameters for PB₂M, PTM and PSeM

	PB ₂ M	PTM	PSeM
$K_\theta \times 10^4$ ($\text{dl g}^{-3/2} \text{mol}^{1/2}$)	3.9 ⁽⁶⁾	4.4 ⁽⁶⁾	5.6 6.5
$\langle \langle r^2 \rangle_0^{1/2} / M \rangle$ (\AA)	0.538	0.560	0.607 ^a 0.638 ^b
$\langle \langle r^2 \rangle_0^{1/2} / M \rangle$ (\AA)	0.232	0.228	0.204
σ	2.32	2.41	2.98 ^a 3.13 ^b
C_∞	10.8	12.2	18.02 ^a 19.9 ^b
T_g (K)	328	345	333

^a From chlorobenzene data

^b From THF data

Table 4 Some general characteristics of the three aromatic compounds which have been incorporated in the lateral chain of these polymethacrylates and the flexibility parameter values found for these polymers

Compound	V_m^a	A^b	B_A^c	C_∞	σ
Benzene	88.8	13.93	5.00	10.0	2.46
Thiophene	78.9	11.56	3.85	11.4	2.60
Selenophene	85.2	10.44	2.94	18.02 11.91	2.98 3.13

^a Molar volume in $\text{cm}^3 \text{mol}^{-1}$ (ref. 21)

^b $A = \Delta\delta_1 V_m^{2/3}$. Aromaticity estimated from $\Delta\delta_1$, difference between the chemical shifts of aromatic protons in pure liquid and at infinite dilution in a non-polar solvent²¹

^c Aromaticity index, $B_A = 1/\Sigma\Delta\delta_2$ determined through²¹ the effect of methyl substitution on ring proton shifts of thiophene and selenophene

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