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

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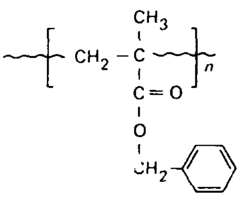
The dilute solution behaviour of poly(2-thiophenmethyl methacrylate) (PTMM) has been studied in THF and thiophen (good solvents) and chlorobenzene (θ-solvent) at 298 K, by intrinsic viscosity, size-exclusion chromatography (SEC) and osmotic pressure measurements. The Kuhn–Mark–Houwink–Sakurada relationships were established. The flexibility factor σ and the thermodynamic parameter B were calculated using the Stockmayer–Fixman equation. The results obtained are compared with those previously found for poly(benzyl methacrylate) (PBzM) and discussed in terms of the specific influence of the aromatic nature of the side group.

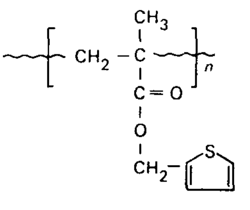
(Keywords: poly(2-thiophenmethyl methacrylate); solution properties; chain flexibility; theta solvent; aromatic poly(methacrylate)s; poly(benzyl methacrylate); poly(2-furfurylmethyl methacrylate))

INTRODUCTION

We have previously described the conformational behaviour of poly(penthachlorophenyl methacrylate)[1], as part of a systematic investigation of poly(methacrylate)s with aromatic rings. It was proposed that the presence of chlorine atoms partly hinders interactions between the aromatic rings. The different chain flexibility between the chlorinated poly(phenyl methacrylate)s was explained by two effects: (i) the specific interactions and/or (ii) the bulkiness of the side group[1,2]. Recent work in this laboratory has been focused on the preparation, solid state and solution properties, of poly(methacrylate)s with aromatic rings of different aromaticity in the pendant ester group. Furan, thiophen, selenophen and tellurophen form a very interesting series of four stable aromatic ring compounds, which differ in the nature of the hetero-atom. All available information indicates that thiophen is more aromatic than furan and that both are less aromatic than benzene[3,4].

In this paper, the solution properties of poly(2-thiophenmethyl methacrylate) (poly[1-(2-thiophenmethoxycarbonyl)-1-methylethylene]) (PTMM) are reported. The results are compared with those found for poly(benzyl methacrylate) (PBzM)[5,6] and are discussed in terms of the specific influence of the aromatic nature of the side group. The role of the hetero-atom on the glass transition temperature T_g, and chain flexibility σ in these first two members of the series, are also studied.


Poly (benzyl methacrylate)
(PBzM)


Poly (2–thiophenmethyl methacrylate)
(PTMM)

EXPERIMENTAL

Monomer and polymer preparation

Thiophenmethyl methacrylate (TMM) was prepared by reaction of methacryloyl chloride[7] with thiophenmethanol according to Burtle *et al.*[8] and purified by distillation under reduced pressure (80°C/1 mm Hg) in the presence of hydroquinone, yield: 78%. The purity was confirmed by n.m.r. and i.r. spectroscopy. ^{1}H n.m.r. ($CDCl_3$): (p.p.m.) = 7.9–7.4 (m, 3H); 6.57 (m, 1H); 5.96 (m, 1H); 5.70 (s, 2H); 2.08 (s, 3H). I.r. (KBr): 3100, 1715, 1630, 1440, 1290, 1150, 1005, 705 cm^{-1}.

Elemental analysis: calc.: C, 59.34%; H, 5.49%; S, 17.58%. Found: C, 59.30%; H, 5.53%; S, 17.54%.

The monomer was polymerized at 50°C in benzene solution under vacuum with 2,2′-azoisobutyronitrile as initiator. The concentration of the monomer was 20 wt% and that of the initiator ranged from 5×10^{-3} to 20×10^{-3} wt%. The polymer dissolved in benzene was precipitated by methanol, washed repeatedly and dried under vacuum at 40°C to constant weight.

Polymer fractionation was effected in the usual way using benzene–methanol as solvent–precipitant mixtures. Six fractions of poly(2-thiophenmethyl methacrylate) (PTMM) were chosen among those obtained from three preparations.

Polymer characterization

The weight-average molecular weights $\bar{M}_w$ of PTMM, were measured by size-exclusion chromatography (SEC) using a Perkin–Elmer high performance liquid chromatograph (HPLC) equipped with a 6000 psi (0.84 Pa) pump, a differential refractometer LC-25, and a 175 μl injector. Three Waters Associates Ultra Styragel™ columns (10^3 Å, 10^4 Å, 10^5 Å) were used in series[5]. Samples were eluted with tetrahydrofuran (THF). The apparatus was calibrated with polystyrene samples of narrow molecular weight distribution characterized by

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light scattering measurements. The flow-rate was 1 ml/min and the volume of the injected polymer solution was always 5 μl. A universal calibration curve was used for the treatment of the data. The number-average molecular weights, $\bar{M}_n$ of the fractions were determined in chlorobenzene at 298 K (θ-condition) using a Hewlett-Packard Model 502 High Speed Membrane Osmometer and a gel cellophane membrane. Before use, membranes were treated successively with distilled water, 2-propanol/water, 2-propanol/chlorobenzene and chlorobenzene. The results were analysed using the classic equation: $\pi/c = RT(1/\bar{M}_n + A_2c)$ where π is the osmotic pressure (in cm of solvent), c the concentration of polymer solution in g dl^{-1}, A_2 the second virial coefficient and $\bar{M}_n$ the number-average molecular weight.

Intrinsic viscosity

Viscosity measurements in THF, thiophene and chlorobenzene at 25°C were determined using a Desreux-Bischoff dilution viscometer[9] having negligible kinetic energy corrections.

Differential scanning calorimetry

The glass transition temperatures were measured by differential scanning calorimetry (d.s.c.) using a Perkin-Elmer DSC-1B apparatus. Heating rates of up to 16 K min^{-1} were used.

RESULTS AND DISCUSSION

Table 1 lists the solvents and non-solvents for poly(2-thiophenmethyl methacrylate) (PTMM). Intrinsic viscosity $[\eta]$ was measured at 298 K for fractions F$_1$ to F$_6$ in tetrahydrofuran (THF), thiophen and chlorobenzene. The lowest value (0.094 dl g^{-1}) was found for F$_6$ in the worst solvent (chlorobenzene) and the highest value (0.837 dl g^{-1}) was found for F$_1$ in the best solvent (THF).

Table 1 Solvents and non-solvents for PTMM

Solvent	δ (cal cm^{-3})$^{1/2}$	Solubility^a
Hydrocarbon solvents		
n-Heptane	7.4	0
Cyclohexane	8.2	0
Toluene	8.9	0
Benzene	9.2	+
Chlorinated hydrocarbons		
Carbon tetrachloride	8.6	0
Chloroform	9.3	+
Chlorobenzene	9.5	+
Dichloromethane	9.7	+
Dichlorobenzene	10.0	+
Oxygenated solvents		
Ethyl acetate	9.1	+
Tetrahydrofuran	9.1	+
Methyl isobutylketone		0
Acetone	9.9	+
1-4 Dioxane	10.0	+
1-Hexanol	10.7	0
2-Propanol	11.5	0
Ethanol	12.7	0
Methanol	14.5	0
Sulphurated solvents		
Thiophen	9.8	+
Carbon disulphide	10.0	0

^{a}Soluble, +; insoluble, 0

Table 2 Number-average molecular weights $\bar{M}_n$, weight-average molecular weights, $\bar{M}_w$, and polydispersity factor ($\bar{M}_w/\bar{M}_n$) for poly(thiophenmethyl methacrylate) fractions

Fractions	$\bar{M}_n \times 10^{-5\,a}$	$\bar{M}_{w(g.p.c.)} \times 10^{-5}$	$\bar{M}_w/\bar{M}_n{}^b$
F$_1$	4.57	5.90	1.29
F$_2$	2.81	3.37	1.20
F$_3$	2.35	2.85	1.21
F$_4$	1.96		
F$_5$	1.34	1.42	1.08
F$_6$	0.48		—

^{a}From osmotic pressure measurements in chlorobenzene at 298 K
^{b}$\bar{M}_w$ from g.p.c.

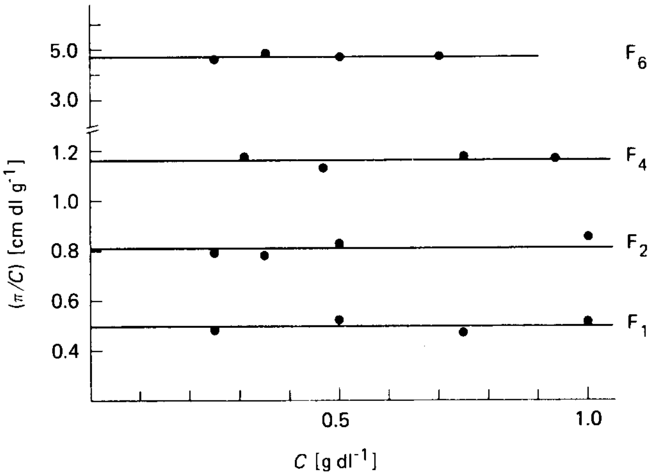

Figure 1 Variation of the reduced osmotic pressure $\pi \times c^{-1}$ (π, in cm of solvent, c in g dl^{-1}) with the concentration c for fractions F$_1$, F$_2$, F$_4$ and F$_6$ of poly(2-thiophenmethyl methacrylate) in chlorobenzene at 298 K (θ-condition)

The number-average molecular weight, $\bar{M}_n$, the polydispersity, and the weight-average molecular weights $\bar{M}_w$ (g.p.c.) for the fractions of the polymer studied are summarized in *Table 2*. From the usual log–log plots of $[\eta]$ vs. $\bar{M}_n$ for PTMM in THF, thiophen (good solvent) and chlorobenzene (θ-solvent). The following relationships were obtained for the Kuhn–Mark–Houwink–Sakurada equations: $[\eta] = 6.95 \times 10^{-5} \times \bar{M}_n^{0.72}$ (THF, 298 K), $[\eta] = 9.00 \times 10^{-5} \times \bar{M}_n^{0.66}$ (thiophen, 298 K), $[\eta] = 43.5 \times 10^{-5} \times \bar{M}_n^{0.50}$ (chlorobenzene, 298 K, θ-condition). All relations refer to $[\eta]$ in units of dl g^{-1}.

The exponent values lie in the range observed for flexible polymers[10]. The results obtained for poly(2-thiophenmethyl methacrylate) show that $[\eta]$ is accurately proportional to $\bar{M}_n^{0.50}$ for chlorobenzene (ideal solvent). This behaviour was tested by osmometric measurement. The osmotic pressure π in chlorobenzene at 298 K is independent of polymer concentration $c(A_2 = 0)$. Results are given for four fractions in *Figure 1*.

To find the value of the conformational parameter K_θ, leading to the unperturbed dimension $\langle r^2 \rangle_0^{1/2}$ given by $K_\theta = (\langle r^2 \rangle_0/M)^{3/2} = [\eta]/M^{1/2}$, the Burchard–Stockmayer–Fixman (BSF) equation[11,12] was employed (see *Figure 2*). This Figure shows that there is a common point of intersection for the three lines. The values of the thermodynamic parameter B show normal behaviour, i.e. B increases with the thermodynamic solvent power and becomes zero at the θ-condition. The B values are assembled in *Table 3*. *Table 3* also summarizes the viscometric constants K_a and a for this polymer.

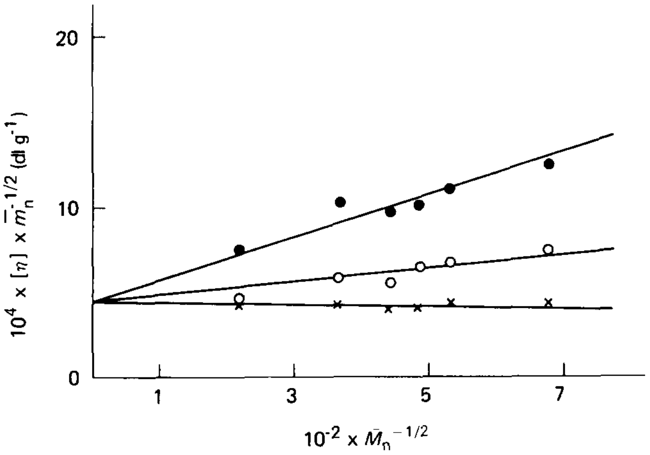

Figure 2 Stockmayer–Fixman plots for poly(2-thiophenmethyl methacrylate) in THF (●); thiophen (○) and chlorobenzene (×) at 298 K

Table 3 Thermodynamic parameters for PTMM in different solvents at 298 K

Solvents	$K_a \times 10^5$	a	$B \times 10^{28}$ (cm^3 mol^2 g^{-2})
THF	6.95	0.72	9.15
Thiophen	9.00	0.66	2.98
Chlorobenzene (θ)	4.35	0.50	0.00

The experimental value of K_θ extrapolated from the BSF plot is 4.40×10^{-2} cm^3 g$^{-3/2}$ mol$^{1/2}$. The polymolecularity correction factor was calculated using the Sutter–Kuppel[13] and Bareiss methods[14], assuming a Schulz–Zimm[15,16] distribution for each fraction. The correction factor is ~ 1.03 for $\bar{M}_w/\bar{M}_n < 1.30$.

According to these factors the corrected value for K_θ should be 4.50×10^{-2} cm^3 g$^{-3/2}$ mol$^{1/2}$. The relation between the root mean square end-to-end distance for the unperturbed chain $\langle r^2 \rangle_0^{1/2}$ and M is found to be:

$$\langle r^2 \rangle_0^{1/2} (\text{Å}) = 0.94 M^{1/2} \quad \text{or} \quad \langle r^2 \rangle_0 (\text{Å}) = 0.560 M^{1/2}$$

taking for ϕ_0 the value of 2.1×10^{21} (cgs), for polymers having a narrow molecular weight distribution[17], or 2.5×10^{21} which has been considered to be the best experimental value established from viscosity and light scattering measurements[17].

The value of $\langle r^2 \rangle_0^{1/2} / \langle r^2 \rangle_{0f}^{1/2}$ (σ), that represents the influence of steric hindrance on the flexibility of the main chain was found to be $\sigma = 2.60$ (2.45), with a root mean square end-to-end distance of the freely rotating chain, $\langle r^2 \rangle_{0f}^{1/2}$ (Å) $= 0.232\ M^{1/2}$.

The most useful parameter for comparison of average unperturbed chain dimensions of random-coil chains is Flory's[18] characteristic ratio C_∞, which is defined by

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

where n is the number of main chain bonds of a mean-square length l^2.

We have compared the conformational parameters obtained for PTMM with those of PBzM taking into account that both polymers have aromatic rings in the side chain and have the same flexible spacer group ($-CH_2$). We have also compared the T_g values for these polymers and that of poly(furfurylmethyl methacrylate) (PFMM) in which the sulphur atom has been replaced by an oxygen atom and therefore shows different aromaticity.

Table 4 summarizes the relevant data characterizing PTMM and PBzM, from which is clear that PTMM behaves as a flexible chain. The information in *Table 4* also shows that the introduction of the thiophenmethyl group instead of a benzyl group is accompanied by a change in the flexibility of the main chain. This table summarizes the T_g and σ values for the polymers containing benzyl and thiophenmethyl groups.

Table 5 shows some characteristics of the aromatic compounds which have been introduced in the lateral chain of these polymethacrylic esters. In this table, we also show the T_g and σ values for the corresponding polymers for comparison. We have inserted in *Table 5* the T_g value for poly(furfurylmethyl methacrylate) (PFMM), i.e. the oxygenated analogues.

The aromaticity and molar volume of thiophen are different from that of benzene (see *Table 5*). Therefore, thiophenmethyl groups seemingly increase the degree of steric hindrance relative to benzyl groups. The higher glass transition temperature of PTMM agrees with this observation in the sense that PTMM has a more rigid main chain than PBzM. PFMM shows a higher T_g than PTMM and PBzM. According to the molecular model, the presence of the hetero-atom sulphur and oxygen on the lateral chain could hold responsibility for this conformational behaviour, although it is difficult to explain this behaviour. The results would suggest a special type of packing of thiophenmethyl rings that restricts chain mobility. Nevertheless, according to the T_g values, there is a correlation between aromaticity and T_g in the sense that T_g increases when the aromaticity decreases. Probably the steric hindrance to rotation is affected by the molar volume and aromaticity of the side groups. As the

Table 4 Molecular parameters for PTMM and PBzM

	PTMM	PBzM
$K_\theta \times 10^2$ (cm^3 g$^{-3/2}$ mol$^{1/2}$)	4.4	3.9
$(\langle r^2 \rangle_0 / M)^{1/2}$ (Å)	0.594[a]	0.571[a]
$(\langle r^2 \rangle_{0f} / M)^{1/2}$ (Å)	0.228	0.232
σ	2.60[a]	2.46[a]
	2.45[b]	2.32[b]
C_∞	11.4[a]	10.0[b]
	10.8[b]	10.0[b]
T_g (K)	345	328

[a] Calculated with $\phi_0 = 2.1 \times 10^{21}$ (cgs)
[b] Calculated with $\phi_0 = 2.5 \times 10^{21}$ (cgs)

Table 5 Some characteristics of the three aromatic compounds[3] which have been introduced in the lateral chain of these polymethacrylic esters and the T_g and σ values for the corresponding polymethacrylates

Compound	V_m[a] (ref. 3)	A[b] (ref. 3)	T_g (K)	σ[c]
Benzene	88.8	13.9	328	2.32
Thiophen	78.9	11.6	345	2.45
Furan	72.6	7.67	378[d]	–

[a] Molar volume in cm^3 mol^{-1}
[b] $A = \Delta\delta_1 V_m^{2/3}$. Aromaticity estimated from the $\Delta\delta_1$, difference between the chemical shifts of aromatic protons in pure liquid and in an infinitely dilute in a non-polar solvent
[c] With polymolecularity corrections
[d] Unpublished results

molar volume and aromaticity decrease, there is a special kind of puckering of the side groups increasing the steric hindrance to rotation.

Finally we can conclude that it is very difficult to explain the values of the conformational parameters (σ and C_∞) of these polymers, because apparently they are not much influenced by the characteristics of the aromatic rings (molar volume and aromaticity) of the side chain and could be interpreted as evidence of a certain type of packing between thiophen groups. We are at present working with other polymethacrylates containing hetero-atoms in the side chain in order to clarify the conformational behaviour of a series of poly(methacrylate)s with hetero-atoms in the side chain.

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