Solution properties and chain flexibility of polythiolmethacrylates: 1. Poly(phenyl thiolmethacrylate) and poly(*o*-methyl phenyl thiolmethacrylate)

Dionysis Kokkiaris, Costas Touloupis and Nikos Hadjichristidis
Department of Industrial Chemistry, The University of Athens, 13A Navarinou Street, Athens (144), *Greece*

(*Received* 5 *July* 1979; *revised August* 28 1980)

Dilute solution properties of poly(phenyl thiolmethacrylate) (PTPh) and poly(*o*-methylphenylthiolmethacrylate) (PTMPh) were studied by gel permeation chromatography, light scattering, osmotic pressure and viscosity measurements in different solvents. Relations between intrinsic viscosity $[\eta]$, *z*-average root-mean-square end-to-end distance $(\overline{r^2})^{1/2}$ and molecular weight $\overline{M}_w$ were established. The unperturbed dimensions were calculated by different methods using $\overline{M}_w$ and $[\eta]$. PTPh ($\sigma = 2.26$) and PTMPh ($\sigma = 2.27$) have practically the same flexibility, but both are more flexible than poly(phenyl methacrylate) ($\sigma = 2.50$). In our opinion, this is due to the change in the local intramolecular interaction and the higher flexibility of the sulphur-containing side group.

INTRODUCTION

The solution properties of polythiolmethacrylates have received no attention, despite the fact that acrylic polymers with sulphur in the side chain are elastomers with high stability towards heat and solvents and low degrees of swelling towards common fuels and lubricants[1,2].

In this paper poly(phenyl thiolmethacrylate) (PTPh) and poly(*o*-methylphenyl thiolmethacrylate) (PTMPh) were prepared and their solution properties were studied by gel permeation chromatography (g.p.c.), light scattering, osmometry and viscosity in different solvents. The results obtained were compared with those found for poly(phenyl methacrylate) (PPh)[3,4] and with each other. In this way the effect of the replacement of oxygen by sulphur and hydrogen by methyl groups in the *ortho* position of the phenyl group on the solution properties and flexibility of the main chain could be investigated.

EXPERIMENTAL

Monomers and preparation of polymers

Monomers, phenyl (TPh) and *o*-methylphenyl thiolmethacrylate (TMPh), were prepared by reaction of methacryloyl chloride[5] with thiophenol and *o*-thiocresol in aqueous sodium hydroxide solution[6].

Purification was achieved by repeated distillations under reduced pressure (TPh, 124°C/7.4 mmHz, TMPh, 100°C/1.2 mmHg) in the presence of iodine inhibitor. Yield: ~80%.
TPh: $C_{10}H_{10}OS$ (178.2). Calculated: C, 67.40; H, 5.66; S, 17.96. Found: C,67.30; H, 5.49; S, 18.00.
TMPh: $C_{11}H_{12}OS$ (192.2). Calculated: C, 68.73; H, 6.30; S, 16.65. Found: C, 68.60; H, 6.11; S, 16.57.

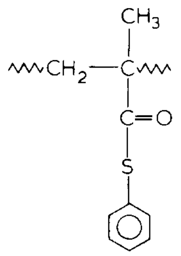
The purity of the monomers was found to be high (~100%) by gas chromatography.

The monomers were polymerized at 50°C in benzene solution (10% w/w) under vacuum ($\sim 10^{-6}$ mmHg) in the presence of 0.01, 0.03 and 0.06% (w/w) of 2,2'-azodiisobutyronitrile. The polymers formed were precipitated from the benzene solution by addition of methanol, washed repeatedly with the same solvent and dried at 50°C for several hours.

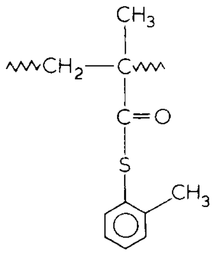
Microtacticity

The microtacticity was calculated from the ^{1}H n.m.r. spectrum of the polymer in *o*-dichlorobenzene (~20% (w/w)) at 120°C using a 300 MHz spectrometer.

The percentages of *mm, mr, rr* triads for poly(phenyl



a
Poly(phenyl thiolmethacrylate) (PTPh)



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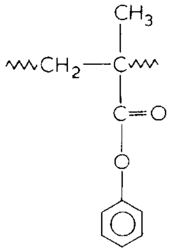
Poly(O-methylphenyl thiolmethacrylate) (PTMPh)



c
Poly (phenyl methacrylate) (PPh)

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Table 1 Poly(phenyl thiolmethacrylate) (PTPh), experimental values. $[\eta]$ = intrinsic viscosity; $(\bar{r}_z^2)^{1/2}$ = end-to-end distance; $(\bar{M}_w/\bar{M}_n)$ g.p.c. = polydispersity from g.p.c.; F1–F6 are PTPh fractions

	Solvent	Temperature (°C)	F1	F2	F3	F4	F5	F6
$[\eta]$ (dl g^{-1})	THF	25	0.368	0.260	0.195	0.175	0.145	0.107
	Benzene		0.312	0.245	0.180	0.167	0.142	0.105
	Toluene		0.275	0.205	0.155	0.150	0.125	0.095
	MEK		0.190	0.156	0.123	0.108	0.102	0.076
$\bar{M}_w \times 10^{-6}$			0.252	0.153	0.102	0.081	0.066	0.041
$A_2^* \times 10^4$ (ml mol g^{-2})	Benzene	35	1.8	1.9	2.2	2.3	2.5	2.7
$(\bar{r}_z^2)^{1/2}$ (Å)			285	230	180	a	a	a
$\bar{M}_n \times 10^{-6}$			0.181	0.116	0.085	0.068	0.055	0.034
$A_2 \times 10^5$ (ml mol g^{-2})	Toluene	37	7.8	8.5	8.5	8.9	9.3	9.7
$(\bar{M}_w/\bar{M}_n)_{\text{g.p.c.}}$	Toluene	35	1.4	1.35	1.2	1.3	1.2	1.2

a These values are lower than results accurately determined from light scattering

Table 2 Poly(*o*-methylphenyl thiolmethacrylate)(PTMPH), experimental values. $[\eta]$ = intrinsic viscosity; $(\bar{r}_z^2)^{1/2}$ = end-to-end distance; $(\bar{M}_w/\bar{M}_n)_{\text{g.p.c.}}$polydispersity from g.p.c.; K1–K6 are PTMPh fractions

	Solvent	Temperature (°C)	K1	K2	K3	K4	K5	K6
$[\eta]$ (dl g^{-1})	THF	25	0.400	0.285	0.225	0.175	0.120	0.108
	Benzene		0.385	0.270	0.205	0.161	0.115	0.100
	Toluene		0.351	0.261	0.194	0.150	0.110	0.097
$\bar{M}_w \times 10^{-6}$	Benzene	35	0.323	0.199	0.130	0.097	0.058	0.048
$A_2^* \times 10^{-4}$ (ml mol g^{-2})			1.3	1.5	1.9	2.0	2.2	2.7
$(\bar{r}_z^2)$			450	340	240	225	185	b
$\bar{M}_n \times 10^{-6}$	Toluene	37	0.243	0.161	0.110	0.084	0.048	0.038
$A_2 \times 10^5$ (ml mol g^{-2})			13.2	14.4	14.7	15.1	16.3	
$(\bar{M}_w/\bar{M}_n)_{\text{g.p.c.}}$	Toluene	35	1.4	1.3	1.3	1.2	1.3	1.4

b This value is lower than those that can be accurately determined from light scattering

thiolmethacrylate) (PTPh) and poly(*o*-methylphenyl thiolmethacrylate) (PMTPh) are given below, as are the values found previously for poly(phenyl methacrylate) (PPh)[3].

Polymer	*mm*	*mr*	*rr*
PTPh	16	38	46
PTMPh	16	39	45
PPh	14	41	45

It can be seen that replacement of oxygen by sulphur or the introduction of a methyl group in the *ortho*-position of the phenyl group does not change the microtacticity of the polymer.

Fractionation and polydispersity

The polymers were fractionated using a solvent/non-solvent system as described previously[4]. The polydispersity of the fractions was estimated by gel permeation chromatography (g.p.c.) in toluene, using a Waters GPC instrument, model 200, operating at 35°C, with four columns in series (Styragel: 3 x 10^6, 3 x 10^5, 3 x 10^4, 3 x 10^3 Å).

The method of Benoit *et al.*[7] was applied using the following Mark–Houwink relations) $[\eta]$ in dl g^{-1}):

$$[\eta] = 1.02 \times 10^{-4} \bar{M}_{w_{0.61}} \text{ (Polystyrene)}^8$$

$$[\eta] = 1.73 \times 10^{-4} \bar{M}_{w_{0.70}} \text{ (PTPh)}$$

$$[\eta] = 6.00 \times 10^{-4} \bar{M}_w \text{ (PMTPh)}$$

The polydispersity values, given in *Tables 1* and *2*, were corrected for diffusion spreading by the Smith method[9].

Light scattering, osmotic pressure and viscosity

Light scattering measurements were made with a FICA photometer at 35°C in benzene, using vertically polarized light at 436 nm ($R_{\text{benzene}}^{90^\circ\text{C}} = 51.1 \times 10^{-6}$ cm^{-1}, (ref 10)). The refractive index increment, d*n*/d*c*, measured under the same conditions using a differential refractometer, was (142 ± 2) x 10^{-3} cm^3 g^{-1} for PTPh and (133 ± 2) x 10^{-3} g^{-1} for PTMPh.

A Knauer electronic osmometer (Sartorius membrane) was used for osmotic pressure determinations in toluene at 37°C. The solvent was degassed before preparing the solutions. The viscosity of the polymers in tetrahydrofuran (THF), benzene, toluene and methyl ethyl ketone (MEK) was measured at 25°C with a Schott automatic viscometer.

The values of weight-average molecular weight $\bar{M}_w$, second virial coefficient A_2, *z*-average root-mean-square end-to-end distance $(\bar{r}_z^2)^{1/2}$, number-average molecular weight $\bar{M}_n$ and intrinsic viscosity $[\eta]$ are given in *Tables 1* and *2*.

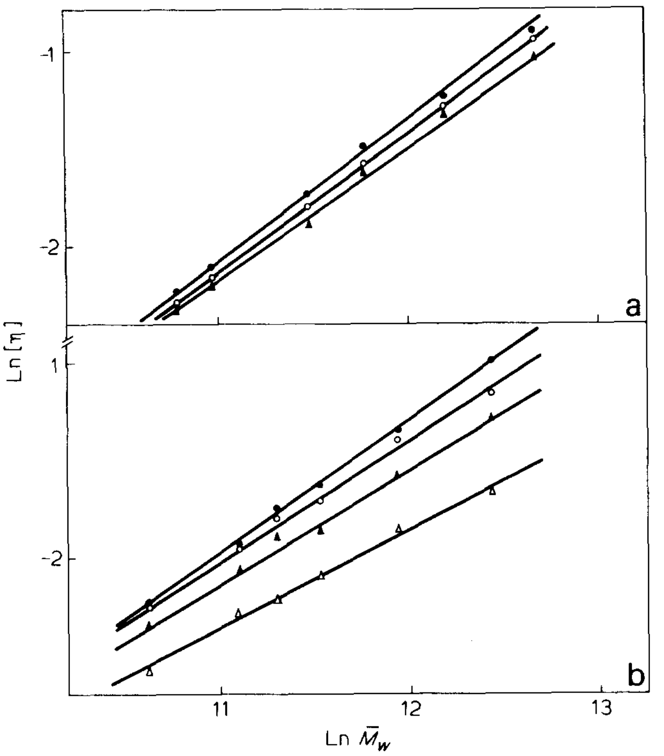

Figure 1 Molecular weight dependence of [η] (in dl g^{-1}) in different solvents at 25°C. (a) PTMPh; (b) PTPh. ●, THF; ○, benzene; ▲, toluene; △, MEK

RESULTS AND DISCUSSION

Mark–Houwink equations

Figure 1 shows conventional plots of $\ln[\eta]$ vs. $\ln\bar{M}_w$ for PTPh and PTMPh in different solvents at 25°C. Using the equation $[\eta] = K_a\bar{M}_w^a$ the following relations were obtained ([η] in dl g^{-1}):

Poly(phenyl thiolmethacrylate) (PTPh)

$[\eta] = 7.82 \times 10^{-5}\bar{M}_w^{0.68}$ (in THF at 25°C)

$[\eta] = 1.62 \times 10^{-4}\bar{M}_w^{0.61}$ (in benzene at 25°C)

$[\eta] = 1.77 \times 10^{-4}\bar{M}_w^{0.59}$ (in toluene at 25°C)

$[\eta] = 3.86 \times 10^{-4}\bar{M}_w^{0,50}$ (in MEK at 25°C)

Poly(o-methylphenyl thiolmethacrylate) (PTMPh)

$[\eta] = 4.07 \times 10^{-5}\bar{M}_w^{0.73}$ (in THF at 25°C)

$[\eta] = 4.75 \times 10^{-5}\bar{M}_w^{0.71}$ (in benzene at 25°C)

$[\eta] = 7.12 \times 10^{-5}\bar{M}_w^{0.67}$ (in toluene at 25°C)

The value of 0.5 of the exponent '*a*' proves that MEK is a θ solvent for PTPh at 25°C.

Relationship between chain dimensions and molecular weight

Figure 2 shows the plots of $\ln(\bar{r}_z^2)^{1/2}$ vs. $\ln\bar{M}_w$ for PTPh and PTMPh in benzene at 35°C. The best-fitlines are given as:

$(\bar{r}_z^2)^{1/2} = 0.35\bar{M}_w^{0.545}$ (PTPh in benzene at 35°C)

$(\bar{r}_z^2)^{1/2} = 0.32\bar{M}_w^{0.57}$ (PTMPh in benzene at 35°C)

According to Ptitsyn's theory[11] the exponent in the equation between $(\bar{r}_z^2)^{1/2}$ and $\bar{M}_w$ should be related to that of the Mark–Houwink equation, having the value $(a + 1)/3$. The values thus calculated are 0.535 (PTPh) and 0.565 (PTMPh), in good agreement with the experimental values 0.545 (PTPh) and 0.57 (PTMPh).

Estimation of unperturbed dimensions and flexibility factor

The value of K_θ yielding the unperturbed dimensions, $\bar{r}_o^2$, according to the equation:

$$K_\theta = \phi(\bar{r}_o^2/M)^{3/2}$$

(where ϕ is the Flory constant and $\bar{r}_o^2$ the mean-square unperturbed end-to-end distance) has been calculated by the methods of Stockmayer–Fixman, Kamide–Moore, Kurata–Stockmayer, Berry, Cowie, Fox–Flory and Inagaki–Suzuki–Kurata using the weight-average molecular weight and the intrinsic viscosities, as described previously[4]. K_θ values obtained by these methods, in spite of different theoretical treatments, are practically the same.

Figures 3 and *4* show the application of Stockmayer–Fixman and Kamide–Moore methods for the two polymers. The extrapolated K_θ values must be corrected by a polydispersity term which is about 1.03 by assuming a Schulz–Zimm distribution[11]. The corrected average values of K_θ are 3.95×10^{-4} dl g^{-1} for PTPh and 3.5×10^{-4} dl g^{-1} for PTMPh.

Taking the theoretical value of $\phi = 2.87 \times 10^{21}$ mol^{-1}, the relations between $(\bar{r}_o^2)^{1/2}$ in Å and the molecular weights are:

$$(\bar{r}_o^2)^{1/2} = 0.52M^{1/2}$$

$$(\bar{r}_o^2)^{1/2} = 0.50M^{1/2}$$

The flexibility factor σ is defined by:

$$\sigma = (\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$$

where $\bar{r}_{of}^2$ is the mean-square end-to-end distance assuming completely free rotation around the bond and is defined by:

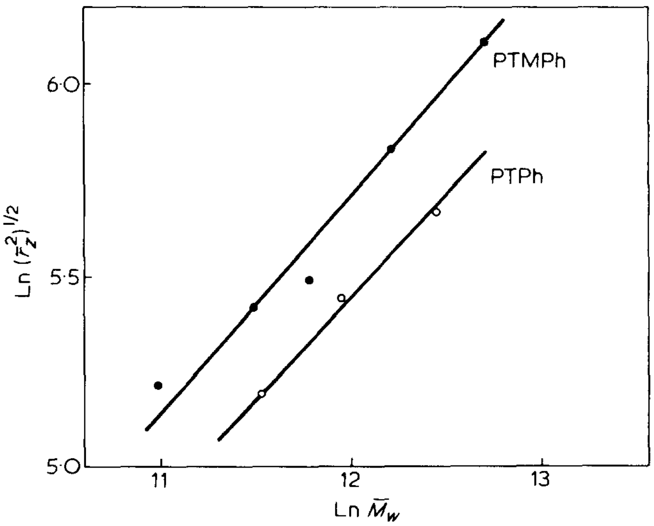

Figure 2 Molecular weight dependence of $(\bar{r}_z^2)^{1/2}$ (in Å$^{1/2}$) in benzene at 35°C

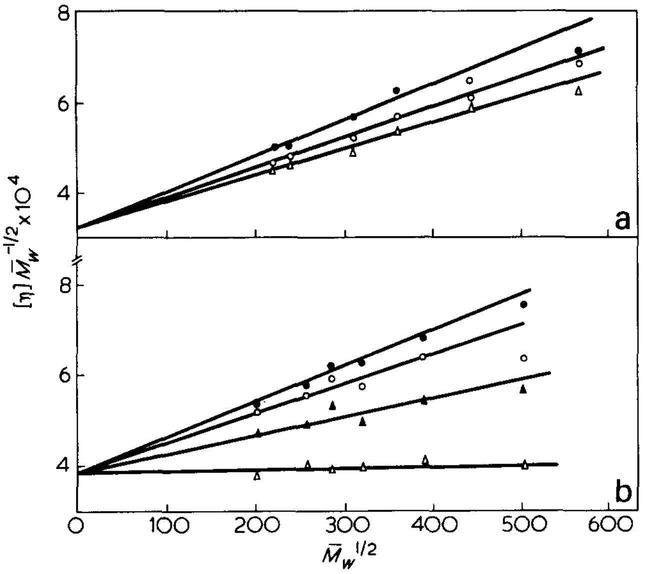

Figure 3 Stockmayer–Fixman plots at 25°C. (a) PTMPh; (b) PTPh. ●, THF; ○, benzene; ▲, toluene; △, MEK

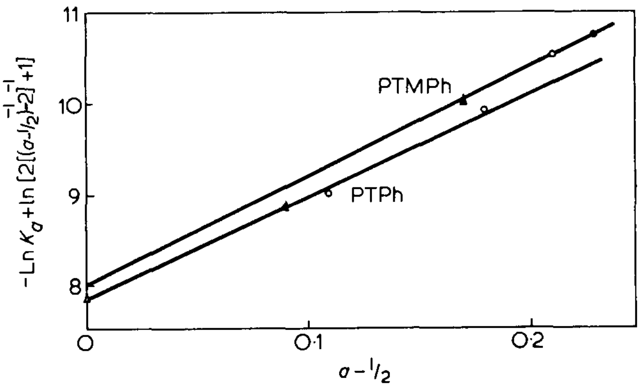

Figure 4 Kamide–Moore plot at 25°C. ●, THF; ○, benzene; ▲, toluene; △, MEK

$$\bar{r}^2_{\text{of}} = nl^2\,\frac{1+\cos\theta}{1+\cos\theta}$$

where n is the number of bonds in the main chain, l is the bond length (1.54 Å) and θ the supplement of the valence angle (109.5°C). Consequently the relations between $(\bar{r}^2_{\text{of}})^{1/2}$ in Å and the molecular weights are:

$$(\bar{r}^2_{\text{of}})^{1/2} = 0.23M^{1/2}$$

$$(\bar{r}^2_{\text{of}})^{1/2} = 0.22M^{1/2}$$

Table 3 Important characteristics for poly(phenyl thiolmethacrylate) (PT Ph) poly(*o*-methylphenyl thioimethacrylate) (PTMPh) and poly(phenyl methacrylate)(PPh)[3,4]

	Microtacticity (rr in %)	$K_\theta \times 10^4$ (dl g^{-1})	$(\bar{r}^2_0/M)^{1/2}$ (Å)	$(\bar{r}^2_{\text{of}}/M)^{1/2}$ (Å)	σ
PTPh	46	3.95	0.52	0.23	**2.26**
PTMPh	45	3.50	0.50	0.22	2.27
PPh	45	5.90	0.59	0.24	2.46

and the flexibility factor, σ, take the values 2.26 for PTPh and 2.27 for PTMPh.

CONCLUSIONS

Table 3 summarizes the important data characterizing poly(phenyl thiolmethacrylate) (PTPh), poly(*o*-methylphenyl thiolmethacrylate) (PTMPh) and poly(phenyl methacrylate) (PPh).

From *Table 3* it is clear that the flexibility of PTPh is higher than that of PPh. This difference mainly arises from the change in the local intramolecular interactions caused by the substitution of the oxygen atom by a sulphur atom. The higher flexibility of the sulphur-containing side group, due to the decrease in the energy barrier around the C—S bond[12], seems to also contribute to the increased flexibility of PTPh.

From *Table 3* it is also clear that the introduction of a methyl group in the *ortho* position of the phenyl group of PTPh does not change the chain flexibility of the polymer.

REFERENCES

1 McCurdy, K. and Prager, I. *J. Polym. Sci. (A-2)* 1964, 1185
2 Prager, I., McCurdy, K. and Rathman, C. *J. Polym. Sci. (A-2)* 1964, 1941
3 Hadjichristidis, N., Devaleriola, M. and Desreux, V. *Eur. Polym. J.* 1972, **8**, 1193
4 Hadjichristidis, N. *Makromol. Chem.* 1977, **178**, 1463
5 Stempel, G. H., Cross, R. P. and Mariella, R. P. *J. Am. Chem. Soc.* 1950, **72**, 2299
6 Sumrell, G., Ham, G. E. and Hornbaker, E. D. *J. Am. Chem. Soc.* 1958, **80**, 2509
7 Benoit, H., Grubisic, Z., Rempp, P., Decker, D. and Zilliox, Z.G. *J. Chim. Phys.* 1966, **63**, 1507
8 Roovers, J. E. L. and Bywater, S. *Macromolecules* 1972, **5**, 384
9 Smith, M. V. J. *Appl. Polym. Sci.* 1974, **18**, 925
10 Ehl, J, Loucheux, C., Reiss, C. and Benoit, H. *Makromol. Chem.* 1964, **75**, 35
11 Ptitsyn, O. B. *Esp. Fiz. Nauk.* 1959, **49**, 371
12 Rabie, A. M. *Eur. Polym. J.* 1972, **8**, 687