Polymer conformation and viscometric behaviour: 7. Synthesis and solution properties of poly(monoethylphenyl itaconate)

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(Received 16 April 1992; revised 15 March 1993)

Monoethylphenyl itaconate was synthesized and polymerized. Polymer fractions were characterized by viscometry and light scattering. Thermodynamic and dimensional parameters were determined and calculated. The results are compared with those of poly(benzyl itaconate)s previously reported.

(Keywords: poly(monoethylphenyl itaconate); conformational parameter; theta binary solvent; specific volume; second virial coefficient)

INTRODUCTION

Poly(itaconic acid) derivatives have been studied widely from both a fundamental and a practical point of view. The first systematically described, aromatically substituted poly(itaconate) was poly(diphenyl itaconate) (PDPhI)[1]. Velicković and Filipović[2] have investigated the unperturbed dimensions of the homologous series of poly[bis(phenyl-n-alkyl) itaconate]s by introducing methylene groups between the phenyl and ester functions in the substituents. But no information has been reported about poly(monoalkylphenyl ester)s. The phenomena occurring in dilute solutions of poly(monoester)s derived from itaconic acid have stimulated our interest to study these phenomena in other poly(monoitaconate)s[3–6]. In this particular case, several poly(monoethylphenyl itaconate) (PMEPhI) fractions have been used in order to analyse and calculate some thermodynamic and conformational parameters. The solution properties of PMEPhI have been studied in two media: THF (a good solvent) and cyclohexane/methanol (1/2) (a theta binary solvent).

EXPERIMENTAL

Monomer and polymer preparation

Monoethylphenyl itaconate (MEPhI) was prepared by esterification of itaconic acid (1 mol) with the phenethyl alcohol (3–4 mol) using acetyl chloride as catalyst. The pure monomer was obtained by recrystallization from benzene (melting point 347–348 K, yield 40%); the purity was confirmed by ^{1}H n.m.r. and i.r. spectroscopy.

Radical polymerization of MEPhI was carried out in bulk under N_2 using azobisisobutyronitrile (AIBN) (0.1 mol%) as initiator. The solubility of PMEPhI in several organic solvents was tested at room temperature; as a result, THF was chosen as solvent and petroleum ether as non-solvent for fractionations of PMEPhI. Six fractions were obtained.

Polymer characterization

Viscosity and molecular weight determinations. Viscosities of PMEPhI fractions were measured using a Desreux–Bischoff[7] dilution viscometer with THF and a binary mixture of cyclohexane/methanol (1/2, v/v) at 298 K. Kinetic energy corrections were not necessary. The light-scattering measurements for the fractions were carried out at 298 K using a Malvern PCS System 4700 particle analyser equipped with an He–Ar laser (638 nm) as the light source. The corresponding refractive indices of the solutions were measured in a Brice–Phoenix BP-2000 V differential refractometer previously calibrated with KCl standard solutions. Weight average molecular weights $\bar{M}_w$ and second virial coefficients A_2 were determined by means of the classical Zimm extrapolation plot. The polydispersity indices of the samples chosen for this study were determined by size exclusion chromatography (SEC). Detailed procedures have been reported earlier[3].

Differential scanning calorimetry (d.s.c.)

The thermal behaviour of PMEPhI in the temperature range 300–500 K was examined using a Mettler TA 3000 differential scanning calorimeter equipped with a TCA-10 processor. Heating rates of up to 10 K min^{-1} were used.

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0032-3861/93/224774-03

RESULTS AND DISCUSSION

Intrinsic viscosities $[\eta]$ were calculated for six fractions of PMEPhI in two media: THF and a binary solvent cyclohexane/methanol (CH/MeOH, 1/2, v/v). The results are summarized in *Table 1*. Light-scattering data were evaluated from common Zimm plots. From this type of plot the weight average molecular weight $\bar{M}_w$ and the second virial coefficient A_2 for each fraction were obtained. The corresponding polydispersity indices $\bar{M}_w/\bar{M}_n$ are summarized in *Table 1*, together with light-scattering data in THF.

Mark–Houwink–Kuhn–Sakurada (MHKS) relationships for PEMPhI in THF and CH/MeOH (1/2) were established: $[\eta]=4.75\times10^{-5}\bar{M}_w^{0.70}$ in THF and $[\eta]=37.0\times10^{-5}\bar{M}_w^{1/2}$ in CH/MeOH (1/2) at 298 K. *Figure 1* shows the linearity found for PEMPhI. It can be seen that THF is a good solvent and CH/MeOH (1/2) is a theta binary solvent for PMEPhI.

The variation of A_2 with $\bar{M}_w$ at 298 K was established by the empirical relationship $A_2=6.51\times10^{-2}\bar{M}_w^{-0.18}$. This dependence can provide information concerning the heat of mixing, according to Wolf and Adam[8]. The second virial coefficient A_2 decreases with increasing molecular weight, and this behaviour indicates an endothermic system.

In order to investigate the effect of the side-chain structure on the rigidity of the side chain in PMEPhI we determined the conformational parameter K_θ, related to the unperturbed dimensions of the polymer chain, from data in a good solvent. The Stockmayer–Fixman treatment[9] was used in order to obtain K_θ. According to this method, the conformational parameters can be obtained through the equation

$$[\eta]/\bar{M}_w^{1/2}=K_\theta+0.51\phi_0 B\bar{M}_w^{1/2} \qquad (1)$$

where B is the long-range interaction parameter dealing with the excluded volume theory, and ϕ_0 is the universal Flory constant where the best experimental value is 2.51×10^{21} dl mol^{-1} g^{-1}. Therefore, K_θ and B can be obtained respectively from the intercept and the slope of the plot of $[\eta]/\bar{M}_w^{1/2}$ *versus* $\bar{M}_w^{1/2}$. *Figure 2* shows such plots for PMEPhI in THF (a good solvent) and CH/MeOH (1/2) (a theta binary solvent). The B value is in good agreement with the viscometric exponent a in the sense that a high value of a (0.70) and a positive value of B (3.8×10^{-28}) are obtained in the best solvent and $a=0.50$ and $B=0$ in the theta binary solvent. The K_θ value is 3.7×10^{-4}.

From the K_θ value we have calculated the unperturbed dimension $\langle r^2\rangle_0^{1/2}$ using the classical equation[10]

$$K_\theta=\phi_0(\langle r^2\rangle_0/M)^{3/2} \qquad (2)$$

Table 2 gives the unperturbed dimensions for PMEPhI. In the same table the rigidity factor σ ($=\langle r^2\rangle_0^{1/2}/\langle r^2\rangle_{0f}^{1/2}$) is listed. This is obtained from the experimental $\langle r^2\rangle_0^{1/2}$ and the theoretical value for a freely rotating polymer

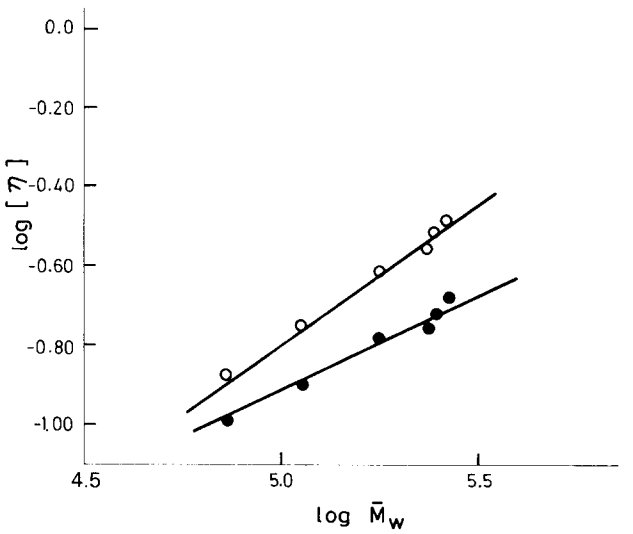

Figure 1 Double logarithmic plots of intrinsic viscosity $[\eta]$ *versus* weight average molecular weight $\bar{M}_w$ for PMEPhI in (○) THF and (●) CH/MeOH (1/2, v/v) at 298 K

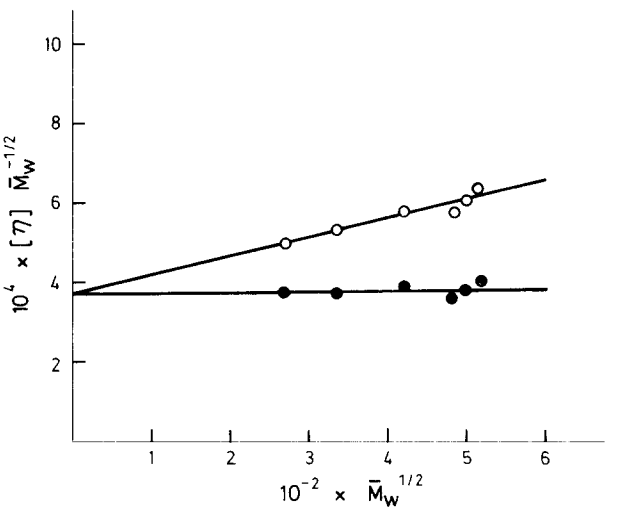

Figure 2 Stockmayer–Fixman plots for PMEPhI in (○) THF and (●) CH/MeOH (1/2, v/v) at 298 K

Table 1 Some parameters for the PMEPhI fractions

Fraction	$[\eta]$ (THF) (dl g^{-1})	Huggins constant k_H	$[\eta]$ (CH/MeOH) (dl g^{-1})	$10^{-5}\bar{M}_w$[a]	10^4A_2 (THF) (cm^3 mol g^{-2})	$\bar{M}_w/\bar{M}_n$[b]
1	0.330	0.40	0.210	2.65	–	1.26
2	0.305	0.36	0.191	2.49	0.96	1.24
3	0.280	0.30	0.175	2.37	1.05	1.25
4	0.240	0.40	0.168	1.77	1.93	1.24
5	0.180	0.36	0.125	1.13	3.29	1.25
6	0.135	0.46	0.101	0.73	3.30	1.24

[a] From light-scattering measurements in THF at 298 K
[b] From size exclusion chromatography

Table 2 Molecular parameters for PMEPhI, PMBzI and PDBzI

	PMBzI[a]	PMEPhI	PDBzI
$10^2 K_\theta$ (cm^3 g$^{-3/2}$ mol$^{1/2}$)	72.0	37.0	23.0
$(\langle r^2\rangle_0/M)^{1/2}$ (Å)	0.660	0.529	0.434
$(\langle r^2\rangle_{0f}/M)^{1/2}$ (Å)	0.207	0.201	0.175
σ	3.18	2.63	2.51
C_∞	20.4	14.0	12.7
T_g (K)	356	342	301
V_{sp} (cm^3 g^{-1})	0.7497[b]	0.7751[b]	0.7940[c]

[a] Values taken from ref. 4
[b] Calculated by addition of group contributions from Van Krevelen[12]
[c] From density measurements[13]

chain by taking as a model a hypothetical polymethylene chain whose unperturbed end-to-end chain dimension is represented by $\langle r^2\rangle_{0f}^{1/2}$.

The characteristic ratio C_∞ as defined by Flory is expressed by

$$C_\infty = \lim_{n\to\infty} (\langle r^2\rangle_0/nl^2) \quad (3)$$

where n is the number of main-chain bonds of 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 those of poly(benzyl itaconate)s (PMBzI) and poly(dibenzyl itaconate) (PDBzI)[4], see *Table 2*.

Table 2 also summarizes the glass transition temperatures T_g of these polymers. The results summarized in *Table 2* show that the introduction of another methylene group in the side chain leads to an enhancement of the flexibility of the polymer chain. C_∞, σ and T_g decrease from PMBzI to PMEPhI. The information shown in *Table 2* indicates that the esterification of poly(itaconic acid) with one or two benzyl groups is accompanied by a change in the flexibility of the main chain, the rigidity of PMBzI being higher than that of PDBzI[11]. Therefore, PDBzI shows a rigidity factor very similar to that of PMEPhI. We have tried to compare the σ values for the three polymers studied under the same conditions. It is observed that poly(monoethylphenyl itaconate), in which the aromatic ring of the side group is separated from the chain by a dimethylene spacer group, and poly(dibenzyl itaconate), which contains two aromatic rings in the side group, exhibit nearly the same rigidity in THF solutions.

The values of the specific volumes V_{sp} of the poly(itaconate)s indicate a difference in chain-packing efficiency. The densities decrease with increasing monomer molecular mass, as can be seen in *Table 2*. There is also an effect on the magnitude of T_g owing to the introduction of an additional methylene group into the middle of the substituent, in between the ester function and the ring (*Table 2*).

It is difficult to draw a general conclusion, but the thermodynamic and conformational parameters are consistent with the structures of these polymers.

ACKNOWLEDGEMENTS

We express our thanks to Dirección de Investigación, Pontificia Universidad Católica de Chile (DIUC) and Fondo Nacional de Ciencias (FONDECYT) for financial support. We are also grateful to Dr E. Saiz from Departamento de Química Física, Universidad de Alcalá de Henares, Spain, for providing the light-scattering laboratory and for giving kind cooperation and technical assistance.

REFERENCES

1 Velicković, J. and Plasvić, M. *Eur. Polym. J.* 1975, **11**, 377
2 Velicković, J. and Filipović, J. *Macromolecules* 1984, **17**, 611
3 Gargallo, L., Radić, D. and León, A. *Makromol. Chem.* 1984, **186**, 1289
4 Yazdani-Pedram, M., Gargallo, L. and Radić, D. *Eur. Polym. J.* 1985, **21**, 707
5 León, A., Gargallo, L., Horta, A. and Radić, D. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 2337
6 León, A., Gargallo, L., Radić, D. and Horta, A. *Polymer* 1991, **32**, 761
7 Desreux, B. and Bischoff, J. *Bull. Soc. Chim. Belg.* 1950, **59**, 93
8 Wolf, B. A. and Adam, H. J. *J. Chem. Phys.* 1981, **75** (8), 4121
9 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. C* 1963, 137
10 Flory, P. J. and Fox, T. G. *J. Am. Chem. Soc.* 1951, **73**, 1904
11 Yazdani-Pedram, M., Gargallo, L. and Radić, D. *Eur. Polym. J.* 1985, **21**, 461
12 Van Krevelen, D. W. 'Properties of Polymers', 2nd Edn, Elsevier, Amsterdam, 1976, p. 232
13 Hernández-Fuentes, I., Horta, A., Gargallo, L., Abradelo, C., Yazdani-Pedram, M. and Radić, D. *J. Phys. Chem.* 1988, **92**, 2974