Synthesis and solution properties of comb-like poly(mono-n-alkyl-itaconates): 2. Poly(monododecyl itaconate)

A. León
Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile, Casilla 5659-Correo 2, Santiago, Chile

and L. Gargallo* and D. Radić
Facultad de Química (502), Pontificia Universidad Católica de Chile, Casilla 6177-Santiago, Chile

and A. Horta
Departamento de Química Fisica, Universidad a Distancia (UNED), 28040 Madrid, Spain
(Received 20 November 1989; revised 14 March 1990; accepted 22 March 1990)

The monoester of itaconic acid with n-dodecyl alcohol was synthesized and polymerized. Polymer fractions were characterized by viscometry, size exclusion chromatography (s.e.c.) and light scattering. Thermodynamic and dimensional parameters were determined and calculated. The results found are 67 Å for the statistical segment length l and 8 Å for the chain diameter d. These results are compared with those reported previously for a similar compound.

(Keywords: comb-like polymer; poly(monoalkyl itaconate); statistical segment length; solution properties)

INTRODUCTION

The observation of phenomena occurring in dilute solutions of linear long-chain poly(monoester) derived from itaconic acid, as poly(monodecyl itaconate) (PMDI)[1] has stimulated the interest to study these phenomena in other poly(monoitaconates). The solution properties of these polymers, which may be considered as typical comb-like polymers, generally depict a deviation from expected properties for flexible linear polymers, mainly due to high rigidity, aggregation, and chain thickness effects. In this work, several poly(monododecyl itaconate) (PMDoI) fractions have been used in order to analyse the validity of some excluded volume theories, and to calculate some thermodynamic and conformational parameters.

EXPERIMENTAL

Monomer and polymer preparation

The esterification was performed under reflux using 10% excess (moles) of alcohol, and about 2 ml of acetyl chloride to ensure slightly acidic conditions, according to the method previously described[1–3] (yield 60%). The reaction product was crystallized from petroleum ether and the procedure was repeated at least twice to ensure total elimination of unreacted alcohol. The monomer is a white crystalline solid (m.p. = 346–348 K). The purity was confirmed by ^{1}H n.m.r. and i.r. spectroscopy. The polymer was prepared in bulk using azo-bis-isobutyronitrile (AIBN) (0.4% mol) as initiator, in previously degassed, vacuum sealed ampoules. Polymerization time was 4 h, and conversion of monomer to polymer was 72%.

The polymer samples were dissolved in about the same weight of a chloroform/ethanol mixture (1:1 by volume) and then precipitated in methanol, repeating the same procedure for total elimination of unreacted monomer. The polymer was vacuum dried and weighed.

The polymer was fractionated by standard precipitation procedures using n-butanol as solvent and methanol/water mixture (2:1 by volume) as non-solvent, in a similar way to PMDI[1]. The same fractions were chosen and numbered 1 to 9.

Polymer characterization

The viscosity measurements were performed in a Desreux–Bischoff[4] dilution viscometer in THF at 298 K. The capillary size chosen was such that kinetic energy corrections were negligible and the temperature was controlled to ±0.02°C. Intrinsic viscosities $[\eta]$ were obtained by means of the usual extrapolation of the reduced specific viscosity η_{sp}/c and $(\ln \eta_r)/c$ *versus* c (η_r denotes the relative viscosity and c the concentration in g dl^{-1}).

The weight-average molecular weights ($\bar{M}_w$) were measured by light scattering, using THF as solvent. The measurements were performed by means of a Sofica, model 42000 photogoniodifusometer, using green light with a wavelength of 546 nm. The cell was calibrated at a temperature of 298 K. The equipment was calibrated with benzene, and the Rayleigh ratio was 16.3×10^{-6} cm^{-1}. The corresponding refractive index incre-

---

* To whom correspondence should be addressed

0032-3861/91/040761-03

ments of the solutions were measured with a Brice–Phoenix differential refractometer, model BP-2000V, using light of 546 nm, in thermostatically controlled cells held at 298 K. The apparatus was previously calibrated with KCl standard solutions. For the molecular weight determination, the classical Zimm double extrapolation plot was used.

The weight-average molecular weights were also determined by size exclusion chromatography (s.e.c.) by means of a Perkin Elmer (h.p.l.c.) liquid chromatograph, equipped with a 6000 psi pump, a differential refractometer, Perkin Elmer, model LC-25, and an 175 μl injector. Three Waters Associates Ultra Styragel columns connected in series were used (10^3 Å, 10^4 Å, 10^5 Å). The samples were eluted with THF, at a speed of 1 ml min^{-1}. The apparatus was calibrated with poly(styrene) samples of narrow molecular weight distribution.

The analysis of the elution data was performed according to the Rabek[5] treatment of the data, with the aid of a computer program based on the normalization of the chromatograms[5]. All solvents were Merck analytical grade.

RESULTS AND DISCUSSION

The light-scattering data were evaluated from common Zimm plots. From these type of plots the weight-average molecular weight $\bar{M}_w$, and the second virial coefficient A_2 were obtained (see *Table 1*). The intrinsic viscosity values $[\eta]$ of nine fractions of PMDoI determined at 298 K in THF solutions, together with values of some Huggins viscometric constants k_H, are summarized in *Table 1*. *Table 1* also includes the polydispersity indices of the fractions $\bar{M}_w/\bar{M}_n$ determined by s.e.c.

Kuhn–Mark–Houwink–Sakurada (KMHS) relation for PMDoI in THF was established as $[\eta] = 1.12 \times 10^{-4}\bar{M}_w^{0.65}$ in THF at 298 K. *Figure 1* shows the linearity found for PMDoI. It can be seen that THF is a good solvent for PMDoI. The molecular weight dependence of A_2 in THF can provide some information concerning the heat of mixing[6]. The variation of A_2 with $\bar{M}_w$ at 298 K is represented on a log–log graph by a straight line (*Figure 2*).

$$\log A_2 = \log K_1 - b \log \bar{M}_w$$

$$(\log K_1 = -2.41,\ b = -0.20)$$

where K_1 and b are constants: 3.9×10^{-3} and -0.20 respectively.

Table 1 Intrinsic viscosity $[\eta]$ and Huggins constant, k_H, in THF, weight average molecular weight $\bar{M}_w$, second virial coefficient A_2 in THF, determined by light scattering and polydispersity indices for PMDoI

Fraction	$[\eta]$	k_H	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$^{a}	$A_2 \times 10^4$
F_1	0.350	0.59	2.33	1.28	3.30
F_2	0.250	0.85	1.24	1.27	3.40
F_3	0.180	0.89	0.83	1.27	4.30
F_4	0.145	0.85	0.63	1.26	4.08
F_5	0.130	–	0.55	1.25	4.40
F_6	0.110	0.76	0.36^a	1.27	–
F_7	0.090	–	0.28^a	1.28	–
F_8	0.070	–	0.20^a	1.28	–
F_9	0.065	–	0.17^a	–	–

^{a}Determined by s.e.c.

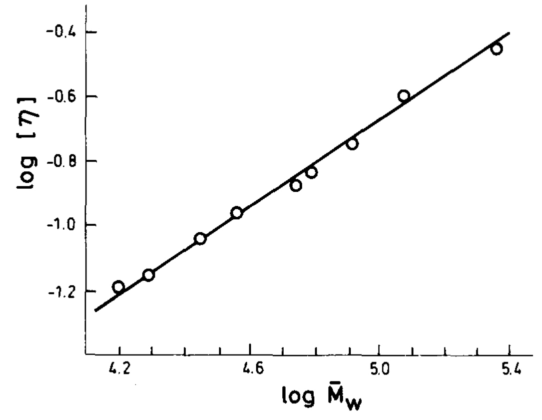

Figure 1 Double logarithmic plots of intrinsic viscosity $[\eta]$ *versus* weight-average molecular weight $\bar{M}_w$ for PMDoI in THF, at 298 K

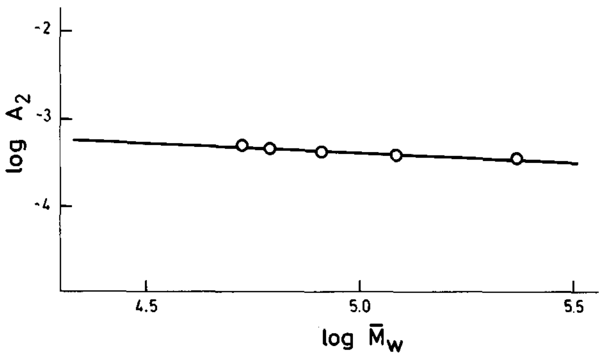

Figure 2 Double logarithmic plots of A_2 *versus* weight-average molecular weight $\bar{M}_w$ of poly(monododecyl itaconate) in THF at 298 K

The second virial coefficient A_2 decreases with increasing molecular weight. This behaviour indicates an endothermal system.

In order to estimate chain rigidity of PMDoI, we have represented our viscosity data according to the Burchard–Stockmayer–Fixman plot (BSF)[7]. This treatment is not satisfactory for this polymer. The data deviate from the linearity usually found for linear flexible polymers. A rough extrapolation of the BSF plot would yield $K_\theta \simeq 0.4 \times 10^{-3}$ and $\langle r^2 \rangle_0/nl^2 \simeq 7$. This value is too low for a chain with long side chains[8]. At the same time it was found[9] that the excluded-volume effect sets in if $L/l > 50$. The L/l values for the polymer studied $\ll 50$ and therefore BSF treatment cannot be used. This behaviour was also observed for poly(monodecyl itaconate) in THF[1].

It seems reasonable then to try an explanation, which according to the current theories accounts for macromolecules with high rigidity, such as wormlike chain model by a similar way for PMDI[1]. The Yamakawa–Fujii–Yoshizaki theory[10,11] of intrinsic viscosity for the helical wormlike chain or wormlike cylinder capped with hemispheres can be cast in a Flory–Fox fashion, as:

$$[\eta] = \Phi_0 \left(\frac{lL}{M}\right)^{3/2} M^{1/2} F \qquad L/l \geqslant 2.278 \qquad (1)$$

where L is a contour length of the chain, l is twice the persistence length or the Kuhn statistical segment length, Φ_0 is the viscosity constant ($\Phi = 2.87 \times 10^{21}$), and F is a function of L/l and of d/l where d is the cross-section diameter or thickness of the molecule. F is given by the

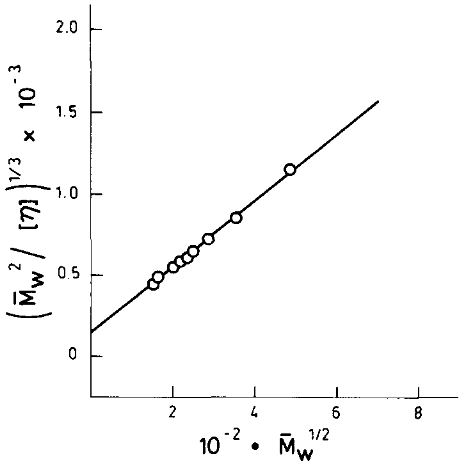

Figure 3 Yamakawa–Fujii plot for PMDoI in THF at 298 K

theory as:

$$1/F = 1 - \sum_{j=1}^{4} C_j \left(\frac{l}{L}\right)^{j/2} \tag{2}$$

with C_j coefficients dependent on d/l whose numerical values are given by Yamakawa *et al.*[11]. Bohdanecký has shown[12] that a simplified version of the theory is:

$$1/F^{1/3} = B_0 + A_0(l/L)^{1/2} \tag{3}$$

with B_0 and A_0 a function of d/l. According to this approximation of Bohdanecký, the plot of $(\bar{M}^2/[\eta])^{1/3}$ *versus* $M^{1/2}$ should be linear, with slope B_η equal to $B_0\Phi_0^{-1/3}(M/Ll)^{1/2}$ and intercept A_η equal to $A_0\phi_0^{-1/3}M/L$.

In *Figure 3* we show our results of $[\eta]$ in THF plotted in this way. We can see that they describe a good linear behaviour. Some of the points represented are outside the strict range of validity of the simplified equation[10]. However, even those points fit well in the linear together with the others.

From the plot in *Figure 3* we obtain for PMDoI: $A_\eta = 1.5 \times 10^2$ ($\mathrm{g\,cm^{-1}\,mol^{-2/3}}$) and $B_\eta = 2.02$ ($\mathrm{g^{1/2}\,cm^{-1}\,mol^{-1/6}}$).

From $B_\eta = B_0\Phi_0^{-1/3}(M/Ll)^{1/2}$ we can calculate the statistical segment length, l, and from $A_\eta = A_0\Phi_0^{-1/3}M/L$ the chain diameter d. First we need M/L.

The contour length of a chain having fixed bond length, b, and fixed valence angle θ, can be calculated as:

$$L = (M/M_0)2b\sin(\theta/2) \tag{4}$$

(M_0 is the molecular weight of the repeating unit). The valence angle of the poly(itaconate) chain has been estimated before by conformational analysis[8]. Values of $\theta' = 112°$ and $\theta'' = 110°$ alternate along the backbone[11]. Here we use the mean $\theta = 111°$ in equation (4), together with $b = 1.53$ Å, and we get $2b\sin(\theta/2) = 2.52$ Å. A similar value of 2.5 Å has been used before for the poly(methacrylate)s[13].

Here $B_0 = 1.0$ for the range of d/l values of interest. Then, from B_η above we get l and from A_η we get A_0. This yields d, using the tabulation of A_0 as a function of d/l (ref. 9). The results found are: $l = 67$ Å and $d = 8$ Å for poly(monododecyl itaconate).

The value of l found is largely indicative of a rather stiff chain. It is larger than for poly(n-alkyl methacrylates). For example, $l = 29$ Å has been determined for poly(n-dodecyl methacrylate)[13] at $T = \theta$. Our results of $[\eta]$ in THF at 298 K are not at $T = \theta$. Therefore, some influence of excluded volume should be contained in our l value.

The value of d found is reasonable if we compare it with the chain extension of the n-alkane molecules. Thus, for the alkane with 10 C–C bonds, the root mean square end–end distance is $\langle r_0^2 \rangle^{1/2} = 9.5$ Å (ref. 14) and its maximum extension or contour length 12.6 Å.

To calculate l and d for PMDoI, we have used a theory which does not take into account the perturbing effect of excluded volume. It only describes the effect of chain rigidity or stiffness. However, a similar analysis for the second virial coefficient A_2 values of poly(monodecyl itaconate)[1] applied to poly(monododecyl itaconate) also indicates that the high A_2 values found experimentally are compatible with rodlike behaviour of short chains.

CONCLUSIONS

In conclusion, the properties of the PMDoI chains as revealed by the analysis of the viscometric and light scattering results are close to those of poly(monodecyl itaconate) previously reported[1], but in this case the non-linearity of the viscosity–molecular weight relationship does not appear because the molecular weight of the fractions is lower.

ACKNOWLEDGEMENTS

We express our thanks to DICYT Universidad de Santiago de Chile, DIUC Pontificia Universidad Católica de Chile and Fondo Nacional de Ciencias (FONDECYT) for financial support. A fellowship from Proyecto PNUD-UNESCO CHI-84/006, awarded to A.L. is gratefully acknowledged. We are grateful to the colleagues of Polymer Group, Departamento de Química Física, Universidad Complutense for kind cooperation and technical assistance.

REFERENCES

1. León, A., Gargallo, L., Horta, A. and Radić, D. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 2337
2. Gargallo, L., Radić, D. and León, A. *Makromol. Chem.* 1985, **186**, 1289
3. Balcer, B. R., Shaub, R. E. and Williams, G. *J. Org. Chem.* 1952, **17**, 122
4. Desreux, V. and Bischoff, J. *Bull. Soc. Chim. Belg.* 1950, **59**, 93
5. Rabek, J. F. 'Experimental Methods in Polymer Chemistry', Wiley, New York, 1983, Ch. 32, p. 527
6. Wolf, B. A. and Adam, H. J. *J. Chem. Phys.* 1981, **75**, 4121
7. Stockmayer, W. and Fixman, M. *J. Polym. Sci. Part C* 1963, **1**, 137
8. Saiz, E., Horta, A., Gargallo, L., Hernández-Fuentes, I. and Radić, D. *Macromolecules* 1988, **21**, 1736
9. Norisuye, T. and Fujita, H. *Polymer J.* 1982, **14**, 143
10. Yamakawa, H. and Fujii, M. *Macromolecules* 1974, **17**, 128
11. Yamakawa, H. and Yoshizaki, T. *Macromolecules* 1980, **13**, 633
12. Bohdanecký, M. *Macromolecules* 1983, **16**, 1483
13. Tricot, M. *Macromolecules* 1986, **19**, 1286
14. Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969