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Solution properties of poly(di-1′-methylalkyl itaconates)

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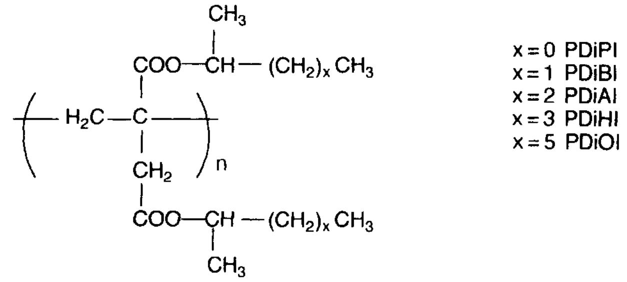
Di-1′-methylalkyl itaconates and the corresponding poly(di-1′-methylalkyl itaconates) (PD1′AI) containing 2-propyl (PDiPI), 2-butyl (PDiBI), 1′-methylbutyl (PDiAI), 1′-methylpentyl (PDiHI) and 1′-methylheptyl (PDiOI) groups as side chains were synthesized and characterized. The polymers were fractionated by fractional precipitation. The fractions were characterized by viscometry in THF and acetone, and by light scattering and size exclusion chromatography in THF. The K_a and a parameters of the Kuhn–Mark–Houwink–Sakurada equations were determined in THF and acetone. The stiffness of the polymer chain was estimated through the rigidity indices, σ, and the characteristic ratio, C_∞, using the conformational parameter K_Θ obtained from the Stockmayer–Fixman plots. The effect of the side-chain structure on the stiffness, conformational behaviour and glass transition temperatures, T_g, of these polymers is discussed and the results compared with those corresponding to other related polymer analogues. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(1′methylalkyl itaconates); chain stiffness; conformational parameters)

Introduction

Mono- and diesterification of itaconic acid can be carried out, giving monomers and polymers having either one or two of the carboxyl groups esterified per repeating unit[1,2]. The variation in the structure and length of the side chain leads to several polymer series with different properties[2–7]. In poly(monoitaconates), the effect of the length of the side chain and the presence of the free carboxyl group have been taken into account to explain the solution behaviour of these polymers[8,9]. Poly(diitaconates) with long side chains may be considered as brushlike polymers. They exhibit a particular conformational behaviour. On the other hand, unbranched poly(diitaconates) with short lateral chains show important changes in both the solution and solid-state properties[1,4–7]. In the case of poly(di-*n*-alkyl itaconates), there is a significant increase in steric hindrance because of the presence of two side groups per repeating unit, which has been reflected in the conformational behaviour. Motions corresponding to these groups will be inhibited as a whole due to the presence of adjacent substituents. The dielectric and mechanical behaviour of poly(di-*n*-alkyl itaconates) and poly(diisoalkyl itaconates) was recently reported[11]. Differences between these polymers and poly(*n*-alkyl methacrylate) analogues are found in the mechanical and dielectric spectra[11]; these have been attributed to the specific effect of the side-chain structure. In order to perturb the structure of the side chain, another adjacent substituent has been inserted in the poly(di-*n*-alkyl itaconates), *i.e.* leading to (di-1′-methylalkyl itaconates) which have a methyl group inserted in position 2 of the alkyl chain.

The aim of the present work is the introduction of branched side chains with different lengths into poly(diitaconates) in order to investigate the stiffness of the polymer chain. To reach this objective, the solution behaviour and the unperturbed chain dimensions are determined in a family of poly(di-1′-methylalkyl itaconates) (PD1′AI) containing 2-propyl (PDiPI), 1′-methylpropyl (PDiBI), 1′-methylbutyl (PDiAI), 1′-methylpentyl (PDiHI) or 1′-methylheptyl (PDiOI) groups as side chains (see *Scheme 1*).



Scheme 1

Experimental

The di-1′-methylalkyl itaconates were prepared by conventional acid-catalyzed esterification of itaconic acid (1 mol) with the corresponding alcohols (3–4 mol), using *p*-toluensulfonic acid in toluene[12,13]. The pure monomers were obtained by distillation of the crude products under reduced pressure (see *Table 1* for physical constants); the purity was confirmed by ^{1}H n.m.r., ^{13}C n.m.r. and i.r. spectroscopy.

Free radical polymerization of the monomers was carried out in the bulk between 323 and 343 K (depending on the monomer) using α,α'-azobis(isobutyronitrile) (AIBN) (about 0.3 mol%) as initiator under N_2 (polymerization time, between 40 and 70 h depending on the monomer; average conversion, about 70%). The reaction mixture was dissolved in chloroform, and the polymer was isolated by precipitation with petroleum ether. The polymers were

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Table 1 Boiling points (b.p.) of the monomers and refractive index increments d*n*/d*c* of the corresponding polymers in THF at 298 K

Monomer	b.p. (°C)	Pressure (torr)	Polymer	d*n*/d*c*
DiPI	180	62	PDiPI	0.089
DiBI	176	54	PDiBI	0.089
DiAI	188	60	PDiAI	0.091
DiHI	190	55	PDiHI	0.090
DiOI	188	40	PDiOI	0.092

purified by repeated dissolution and reprecipitation before drying *in vacuo* at 323 K.

The polymers were fractionated by solubility using benzene/methanol as the precipitant solvent pair. Several fractions, depending on the polymer, were obtained. Weight-average molecular weights ($\bar{M}_w$) of the samples were determined by static light scattering (SLS) and size exclusion chromatography (SEC) in THF using a Dawn-F light scattering instrument from Wyatt Technology, containing 15 permanently mounted detectors and an He–Ne laser at $\lambda = 632.8$ nm as the light source, and operated in the flow mode at 298 K. Refractive index increments for the polymers at 298 K are compiled in *Table 1*. Polydispersity indices ($\bar{M}_w/\bar{M}_n$) were obtained by SEC. A Perkin-Elmer high-performance liquid chromatograph equipped with a 6000 psi pump, a Perkin-Elmer differential refractometer model LC-25, a 175 μl injector and three Waters Associated UltraStyragel columns (10^3 Å, 10^4 Å and 10^5 Å) placed in series was used. Analysis of the elution data was performed according to the Rabek[14] using a computer program based on the normalization of the chromatograms. Refractive index increments (d*n*/d*c*) of the samples were determined using a Wyatt Optilab 903 interferometer (Wyatt Technology Corporation, Santa Barbara, CA) using a 2 mm P2 flow cell.

The glass transition temperatures, T_g, of the different polymers were measured using a Mettler TA-3000 system equipped with a TC-A 10 processor and a DSC-30 cell. The polymer samples were dried under reduced pressure in a vacuum oven prior to the measurements. The samples were weighed into the aluminium d.s.c. pans. Dry nitrogen was used as the purge gas and the thermograms were obtained in the range 308–453 K, at a scan rate of 10 K min^{-1}. Regular calibration of the instrument was carried using pure metal standards. The T_g values of the fractions were re-extrapolated to infinite $\bar{M}_w$ in order to obtain $T_{g\infty}$, *i.e.* the T_g value at infinitely large molecular weight at which T_g becomes constant.

All solvents were Merck analytical grade. Viscosity measurements at 298 K were performed with a Desreux–Bischoff dilution viscometer[15] with negligible kinetic energy correction. The intrinsic viscosity, [η], was determined by the usual extrapolations according to the classical Huggins and Kraemer relationships.

Results and discussion

The instrinsic viscosity, [η], for several fractions of PDiPI, PDiBI, PDiAI, PDiHI and PDiOI in two solvents, THF and acetone, together with $\bar{M}_w$ determined by SLS, evaluated from common Zimm plots, and the polysispersity indices, $\bar{M}_w/\bar{M}_n$, determined by SEC in THF, are compiled in *Table 2*. The Kuhn–Mark–Houwink–Sakurada (KMHS) K_a and *a* parameters were established through the classical log–log plots of [η] against $\bar{M}_w$, and the results are summarized in *Table 3*. These results show that THF is a good solvent, evaluated through the ***a*** values of the KMHS relationships ($a = 0.80$ to 0.67 from PDiPI to PDiOI). Acetone has an intermediate solvent power ($a = 0.62$ to 0.58 from PDiPI to PDiOI) (see *Table 3*). In general, the *a* values of the KMHS relationships are in good agreement with those usually found for linear flexible polymers[16]. The lowest *a* value is obtained for PDiAI, irrespective of the solvent considered (see *Table 3*). A similar behaviour is observed in the family of poly(*n*-alkyl methacrylates)[17] in the sense that anomalous behaviour is found for poly(*n*-hexyl methacrylate). In fact, Chinai and co-workers[18–22] studied the dilute solution properties of poly(*n*-alkyl methacrylates). They determined the effect of increasing side-chain length on the conformation of the polymer molecule in dilute solution. The quantities examined provide a measure of the chain extension with increasing side-chain length for the lower members of the series, and also of the reversal which occurs between the hexyl and octyl derivatives[17].

Table 2 Intrinsic viscosity [η]^a in THF and acetone at 298 K, weight-average molecular weight, $\bar{M}_w^b$, and polydispersity indices, $\bar{M}_w/\bar{M}_n$, for fractions of PDiPI, PDiBI, PDiAI, PDiHI and PDiOI

Parameter	Fraction					
	F_1	F_2	F_3	F_4	F_5	F_6
PDiPI						
[η]THF	1.705	1.49	1.16	0.842	0.50	0.225
[η]Acetone	0.68	0.596	0.487	0.463	0.285	0.135
$10^6\,\bar{M}_w$	0.978	0.870^c	0.646^c	0.417^c	0.219*	0.081
$\bar{M}_w/\bar{M}_n$	1.23	1.21	1.28	1.28	1.20	1.30
PDiBI						
[η]THF	0.775	0.605	0.51	0.45	0.42	0.37
[η]Acetone	0.457	0.3677	0.354	0.308	0.296	0.27
$10^6\,\bar{M}_w$	0.323^c	0.234	0.182^c	0.166^c	0.141	0.123
$\bar{M}_w/\bar{M}_n$	1.29	1.32	1.35	1.30	1.30	1.29
PDiAI						
[η]THF	0.922	0.713	0.617	0.537	0.50	0.24
[η]Acetone	0.462	0.357	0.308	0.295	0.275	0.138
$10^6\,\bar{M}_w$	0.436^c	0.295^c	0.234	0.195^c	0.173^c	0.044
$\bar{M}_w/\bar{M}_n$	1.32	1.25	1.28	1.29	1.31	1.37
PDiHI						
[η]THF	0.89	0.36	0.285	0.235	0.205	0.17
[η]Acetone	0.40	0.169	0.139	0.12	0.109	0.095
$10^6\,\bar{M}_w$	0.346^c	0.083^c	0.063^c	0.045	0.035	0.0257
$\bar{M}_w/\bar{M}_n$	1.30	1.32	1.33	1.30	1.30	1.30
PDiOI						
[η]THF	0.944	0.685	0.422	0.288	0.237	–
[η]Acetone	0.425	0.32	0.206	0.15	0.13	–
$10^6\,\bar{M}_w$	0.400^c	0.251^c	0.117	0.0708	0.050	–
$\bar{M}_w/\bar{M}_n$	1.20	1.21	1.22	1.23	1.22	–

[a] In decilitres per gram at 298 K
[b] In grams per mole
[c] Determined by static light scattering in THF at 298 K

Table 3 The K_a and *a* parameters of the MHKS relationship in THF and acetone for PDiPI, PDiBI, PDiAI, PDiHI and PDiOI at 298 K

Polymer	THF		Acetone	
	$10^5\,K_a$	*a*	$10^5\,K_a$	*a*
PDiPI	2.6	0.80	12.4	0.62
PDiBI	5.03	0.76	52.4	0.53
PDiAI	47.9	0.58	58.0	0.51
PDiHI	25.6	0.64	29.7	0.56
PDiOI	16.5	0.67	23.7	0.58

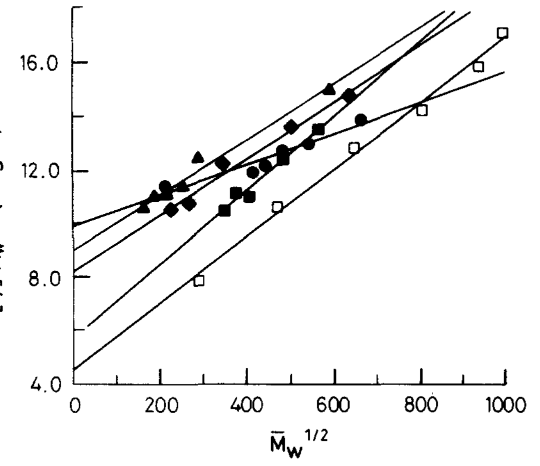

Figure 1 Stockmayer–Fixman plots for (□) PDiPI, (◆) PDiBI, (●) PDiAI, (▲) PDiHI, and (■) PDiOI

The effect of the side-chain structure on the solution behaviour of this family of poly(diitaconates) should be of interest in order to become confident about their thermodynamic and conformational behaviour. To obtain information about the conformational state of the polymers under study, ideal chain dimensions were determined from viscosity measurements in two solvent. The Stockmayer–Fixman (SF)[23] equation was employed for this purpose

$$\frac{[\eta]}{\bar{M}_w^{1/2}} = K_\Theta + 0.51\Phi_\Theta B\bar{M}_w^{1/2} \tag{1}$$

where B is the long-range interaction parameter related to the excluded volume effect and Φ_Θ is the universal Flory constant ($\Phi_0 = 2.51 \times 10^{21}$ mol^{-1}). The linear representation of $[\eta]/\bar{M}_w^{1/2}$ *versus* $\bar{M}_w^{1/2}$ allows us to obtain the conformational parameter K_Θ related to the unperturbed chain dimensions $(\langle r^2\rangle_0/M)^{1/2}$ by the equation

$$K_\Theta = \Phi_0\left(\frac{\langle r^2\rangle_0}{\bar{M}_w}\right)^{3/2} \tag{2}$$

Figure 1 shows the Stockmayer–Fixman representation for all the polymers studied in THF at 298 K, as an example of this kind of representation. *Table 4* compiles the K_Θ and B values for all the polymers under study in THF and acetone. *Table 5* summarizes the unperturbed chain dimensions $(\langle r^2\rangle_0/M)^{1/2}$ together with the root mean square end-to-end distance for a completely free rotation around the bonds, $(\langle r^2\rangle_{0f}/M)^{1/2}$, which is obtained by considering the basic polymeric structure for all the polymers under study. The stiffness of the polymer chain can be evaluated using the rigidity factor σ and the characteristic ratio C_∞[24] defined classically as

$$\sigma = \left(\frac{\langle r^2\rangle_0}{\langle r^2\rangle_{0f}}\right)^{1/2} \tag{3}$$

and

$$C_\infty = \lim_{n\to\infty}\left(\frac{\langle r^2\rangle_0}{nl^2}\right) \tag{4}$$

Table 4 The K_Θ (cm^3 g$^{3/2}$) and B (cm^3 mol^{-2} g^{-2}) parameters obtained from the Stockmayer–Fixman plots for PDiPI, PDiBI, PDiAI, PDiHI and PDiOI

Polymer	10^4 K_Θ		10^{28} B	
	THF	Acetone	THF	Acetone
PDiPi	4.5	4.7	9.80	1.64
PDiBI	5.7	7.5	8.8	0.72
PDiAI	9.9	6.3	4.60	0.52
PDiHI	9.0	5.2	8.21	1.38
PDiOI	8.2	5.1	8.41	1.42

Table 5 Molecular parameters for PDiPI, PDiBI, PDiAI, PDiHI and PDiOI.

Polymer	$(\langle r^2\rangle_{0f}/M)^{1/2}$ (Å)	$(\langle r^2\rangle_0/M)^{1/2}$ (Å)	σ	C_∞	$T_{g\infty}$ (K)
PDiPI	0.211	0.564[a]	2.67	14.3	320
		0.572[b]	2.71	14.7	
PDiBI	0.198	0.610[a]	3.08	18.9	320
		0.669[b]	3.38	22.8	
PDiAI	0.187	0.733[a]	3.92	30.7	319
		0.631[b]	3.37	22.7	
PDiHI	0.178	0.710[a]	3.99	31.8	326
		0.592[b]	3.33	22.1	
PDiOI	0.163	0.689[a]	> 4.0	> 32.0	332
		0.588[b]	3.61	22.6	

[a]THF [b]Acetone

where n is the number of main-chain bonds of mean square length l^2. *Table 5* also compiles the σ and C_∞ values for poly(di-1'-methylalkyl itaconates) (PD1'AI) studied here in THF and acetone. *Figure 2a* is a representation of the C_∞ values (determined from THF) against the number of carbon atoms in the polymer side chain for PD1'AI, poly(di-*n*-alkyl itaconate) (PDnAI) analogues, and for poly(*n*-alkyl methacrylates) (PnAMAs) taken from the literature[18,25]. The high values of C_∞ found for the higher members of the series of PD1'AI would indicate that these polymers should be analyzed in terms of a wormlike

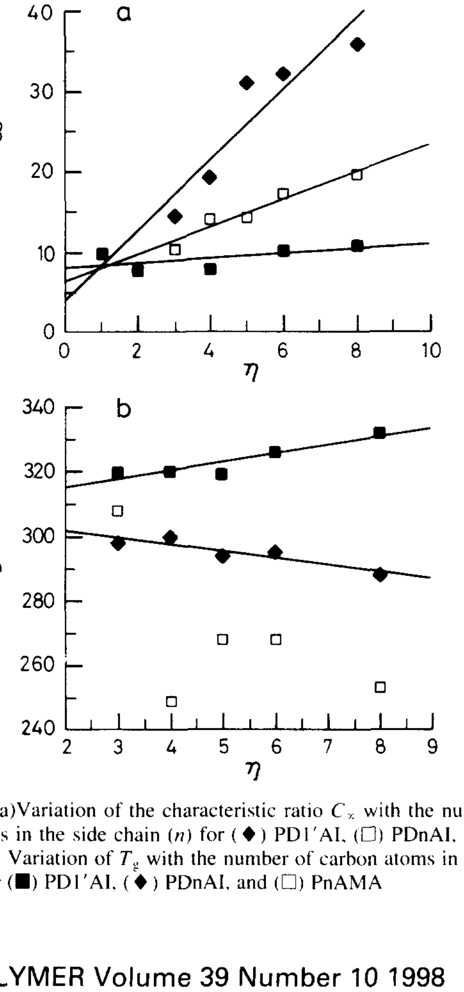

Figure 2 (a)Variation of the characteristic ratio C_∞ with the number of carbon atoms in the side chain (n) for (◆) PD1'AI, (□) PDnAI, and (■) PnAMA. (b) Variation of T_g with the number of carbon atoms in the side chain (n) for (■) PD1'AI, (◆) PDnAI, and (□) PnAMA

polymer model instead of a linear flexible one. As can be seen, in general the stiffness order is PD1'AI > PDnAI > PnAMA. As the side chain becomes shorter, all the polymers reach similar σ and C_∞ values, because from $n=2$ the structures are similar in the case of PDiAI and PDnAI. A similar trend is also observed for the variation of the glass transition temperature at infinite molecular weight, $T_{g\infty}$, as shown in *Figure 2b*, *i.e.* the $T_{g\infty}$ values for PD1'AI are higher than those for PDnAI. In the same figure, T_g data corresponding to PnAMA, taken from the literature[25], are also included. The differences in the rigidity of these families of polymers, having the same number of carbon atoms in the side chain, could be explained in terms of hydrophobicity and/or steric hindrance due to the different degrees of local branching in the side chain. D1'AI groups should hinder the rotation of the side chain to a greater extent, and the hydrophobic interaction could perhaps be affected by the difference in geometry of the groups. On the other hand, as the side chain decreases, in both families of polymers the σ and C_∞ values tend to the same value, which is in good agreement with the polymer structures considered. Another factor to take into account in the stiffness of a polymer chain is the molar volume (V_m) of the side chain. However, in the case of PD1'AI and PDnAI, V_m is very similar for both groups; therefore, the differences in rigidity should be attributed to the factors described above.

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