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The synthesis and characterization of poly(itaconic) acid

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SUMMARY

Poly(itaconic acid)(PIA)was obtained indirectly, by the hydrolysis of PIA esters and directly by the polymerization of itaconic acid in water or methanol at 30°C. The first method was not satisfactory but the second gave better results. The elemental composition of the synthetized samples deviated very little from the calculated values. Several crude polymers were fractionated in methanol/isopropanol and the fractions characterized by viscosity and light scattering. The statistically calculated LVN/M_w relation,valid for the undissociated polymer, was treated according to the method of Stockmayer and Kurata, to calculate the unperturbed dimensions and to compare them with those of other polymers.

INTRODUCTION

Poly(itaconic acid) (PIA) derived from itaconic acid (IA), i.e. methylenesuccinic acid, was for the first time describned by Sheperd[1] and Tate[2], who reported the possibility to polymerize IA with free radical initiators, in spite of its 1,1' disubstituted ethylenic structure. The product, however, differed slightly in elemental composition from the calculated values,indicating a deficiency of C and O, due to side reactions during the polymerization. The unusual course of the reaction was also observed by Nagai[3], Braun and El Sayed[4], Gaffurov[5] and Nakamoto[6], when performing the reaction either in aqueous K-persulphate solutions or in organic solvent with peroxide initiators at 50–70°C. Brown and El Sayed[4] proposed a mechanism involving the elimination of CO_2, due to partial macroradical decomposition in the propagation step. The mechanism was supported by CO_2 evolution and the detection of lactone and acetal structures in the IR spectra of PIA. The carboxyl content amounted to 45–50% of the expected value and the structural formula was close to $(C_4H_6O_4)_x$ instead of $(C_5H_6O_4)_x$.
The inconsistent composition, observed also by other investigators, is the reason why characterizations of PIA in dilute solution have so far been inadequately described in the literature. The aim of this work was to summarize our attempts to prepare PIA, to synthetize the polymer at low temperature[7] and to characterize it in dilute solution.

EXPERIMENTAL

The first group of experiments were attempts to hydrolyze poly(monomethyl itaconate)(PmMI),poly(diethylitaconate)(PDEI),poly(di-isopropylitaconate) (PDiPI) and poly(di-sec.butyl itaconate) into PIA by hydrolyzing the polymers by boiling with dilute KOH for several hours. Promising results were obtained with PmMI and PDiPI, i.e. the conversions were above 50 %.However completeconversions could not be attained, even with PDEI in acompletely homogeneous system , using water/methanol as solvent. The second group of experiments was to prepare poly(di-tert butyl

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itaconate), but these experiments failed due to the low thermal stability of the monomer. The third group of experimets involved the preparation of disilylitaconate by reacting trichlorosilane and IA in benzene in the presence of triethylamine at 45°C, excluding any moisture from the system. The diester was separated by vac. distillation at 110°C and 0.05 mm Hg and polymerized in bulk in vac.sealed ampules with 0.05 mol % of AIBN at 45°C for several days.The polymer was purified by repeated precipitation with ethanol from an acetone solution. After exposing the polymer to the influence of the atmosphere for 24 hours its solubility changed : the original solubility in acetone, chloroform and acetone was lost and it became soluble only in methanol and water, due to the spontaneous hydrolysis with air moisture. IR spectra recorded after 1, 2 and 24 hours exposure revealed the disappearance of the $-CH_3$(2980 cm^{-1}),$(CH_3)_3Si$ (1220 cm^{-1}) and Si-O-Si groups and indicated the gradual transformation of the silyl ester polymer into PIA(Sample PIA-1). The results were confirmed by converting the PIA into poly (dimethyl itaconate) (PDMI), by reaction with diazomethane.

PIA was finally preparted by a method proposed by Grespos et al.[7], by polymerizing IA in an acidified aqueous $K_2S_2O_8/K_2S_2O_5$ initiator/activator solution at 30°C for a period of several days. The system contained 100 g of IA and 5 g of each of the salts per 1000 ml of 0.1 molar HCl. (Sample PIA-2). A second sample was obtained by attempting to polymerize 30 g of IA in 150 ml of methanol with 0.05 mol/1 AIBN for 30 days at ambient temperature(PIA-3). In both cases the polymers were precipitated from the system with petroleum ether and thoroughly dried in vac. at room temperature before characterization.The yield of PIA was close to 70 %.

Limiting viscosity numbers (LVN)(ccm/g) were determined in a dilution type viscometer at 25,0 ± 0.1°C in water or methanol. PIA-3 was fractionated by precipitation in methanol/isopropanol at 25°C. Refractive index increments were determined on a Brice-Phoenix differential refractometer at 20°C and light scattering measurements on a Brice Phoenix 2000 instrument in a C-101 cylindrical cell. M_w was determined according to the method of Zimm[8].The Kuhn-Mark-Houwink-Sakurada relation was determined by the least squares method from M_w and LVN values ofthe fractions, while the unperturbed dimesions were calculated according to the experimental procedure of Stockmayer and Kurata[9], represented by the following equation :

$$[\eta]^{2/3}M^{1/3} = K_\theta^{2/3} + 0.363\,B\,\Phi\,g(\alpha)M_w^{2/3}/[\eta]^{1/3}$$

where Φ is the universal viscosity constant, and B a thermodynamic interaction parameter, incorporating a correction factor, applied iteratively to obtain a more precise K_θ intercept. From K_θ the steric factor and the characteristic ratio C_∞ ,describing the unperturbed dimensions were obtained (cf.lit[13,14]).

RESULTS AND DISCUSSION

All the samples obtained were white hygroscopic powders, easily soluble in waterand methanol but insoluble in other solvents The IR spectra were practically identical for all three samples, except for a small shoulder in PIA-1 at 1760 and 1820 cm^{-1}, indicating a small content of lactone structures. The results of elemental analyses , including several previously quoted results from the literature, are presented in Table 1.The last row refers to PDMI, obtained after the esterification

Polymer	% C	% H	% O	ref.
PIA, calculated for $(C_5H_6O_4)_x$	46.15	4.61	49.24	
PIA - 1	46.42	5.46	48.12	
PIA - 2	46.00	5.09	48.91	
PIA - 3	45.51	5.17	49.32	
PIA	41.89	5.32	52.79	ref.1
PIA	43.50	5.70	50.80	ref.2
PDMI, calc.for $(C_7H_{10}O_4)_x$,	53.16	6.33	40.51	
PDMI,.from PIA-1,by methylation	52.85	6.31	40.84	

of PIA-3 with diazomethane, to confirm indirectly the composition of PIA. The results in the table indicate good agreement for the PIA samples 1, 2 and 3, while those of other authors are deficient in oxygen. The composition of PDMI, obtained after the methylation of PIA-1, indirectly confirms the correct composition of the starting PIA.

PIA is a typical weak polyelectrolyte acid, due to the possibility of the dissociation of the carboxyl groups. in aqueous media. Leaving the problem of polyelectrolyte behaviour for a future investigation, the viscosity measurements were rerstricted to methanol or slightly acidified aqueous solutions. LVN were calculated according to the Fouss equation[10] ,

$$[\eta]_{sp.} /c = A /(1 + B.c^{1/2})$$

where A is the limiting viscosity number LVN and B a constant, reflecting the polymer/solvent interaction.The following LVN (ccm/g) results at 25°C were obtained : water, PIA-1 123.4 , PIA-3 21.8 ; methanol, PIA-1 119.0, PIA-2 44.5, PIA-3 19.1).

The results of fractionation are shown in Table 2. For the calculation of M_w the following dn/dc values were determined : 0.160 (water) and 0.115 (methanol). The light scattering was performed only in methanol.

Fraction	mass(g)	LVN,(ccm/g)	M_w
1.	0.313	22.0	108.600
2.	0.238	20.7	97.200
3.	0.251	20.1	80.500
4.	0.339	15.4	59.400
5.	0.310	11.6	49.500
6.	0.264	9.3	47.000
7.	0.295	8.7	31.700
8.	0.315	8.2	30.000

The KMHS equation was obtained from the above values by the least squars method :

$$[\eta] = 1,51 \cdot 10^{-3} M_w^{0.82}$$

The very high exponent indicates that methanol is a very good solvent for PIA, probably as the result of strong solvation between the solvent and polymer by H-bonding, supporting coil expansion. This is in contrast to the relation published for poly(methacrylic acid)[11] in methanol at 25°C, with an exponent of only 0.50 but a much higher coefficient K.

The PIA unperturbed dimensions were calculated according to the Stockmayer Kurata procedure, outlined previously[9,13,14]. The first extrapolation for K_θ gave a result of 15,4.10(exp-3) (ccm/g) and the second a corrected K_θ = 18,4.10(exp-3) (ccm/g). the great difference between two extrapolations is a consequence of the high exponent a = 0.82. A third extrapolation proved to be insignificant. From the final K_θ the steric factor σ, reflecting the short range interaction, and the characteristic ratio[12] C_∞ were obtained :

$$\sigma = 1.51 \quad \text{and} \quad C_\infty = 4.63$$

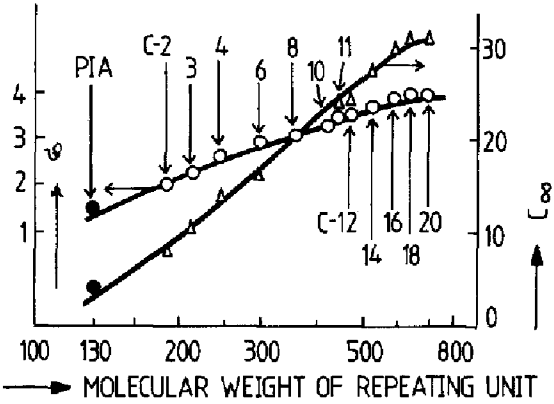

Figure 1 : The plots of the steric factor σ (o) and the characteristic ratio C_∞(▲) of poly(di-n-alkyl itaconates) vs. the molar mass M_o of the repeating unit ; (●) represent the new results obtained for PIA (M_o = 130).

The results of σ and C_∞ for undissociated PIA are in very good agreement with those published previously for the polymer homologous series of poly(di-n-alkyl itaconates)[13,14]. Fig.1 is an extension of Fig.4 from ref[14], showing σ and C_∞ for poly(itaconates), substituted with n-alcanols [C-2 is e. g. PDEI and C-10 poly(di n-decyl itaconate)].The two curves represent the increase of the two parameters with increasing substituent size,i.e.with the increase of the molar mass of the repeat units, plotted on the abscissa.The values obtained for PIA(M_o=130)are presented with full circles.The PIA values fit both curves very well.PIA can therefore be considered to represent the first member of this series with the substituent R = H,of relatively small volume,which does not affect significantly the free rotation of the two substituents present in each monomer residue of the chain.

REFERENCES

1. G.S.Marvel and T.H.Shepherd, J.Am.Chem.Soc., **24**, 599 (1959)
2. B.E.Tate, Makromol.Chem., 111, 176 (1967)
3. S.Nagai, T.Uno and K.Yoshida, Kobunshi Kagaku, **127**, 748 (1960)
4. D.Braun and I.A.Aziz El Sayed, Makromol.Chem., **96**, 100 (1966)
5. L.Gafurov, L.N.Semenova and M.A.Askarov, Uzb.Khim.Zh.,15, 71 (1968)
6. H.Nakamoto, Y.Ogo and T.Imoto, Makromol.Chem. **111**, 104 (1968)
7. E.Grespos, D.J.Hill, J.H. O'Donnel, P.D.O'Sullivan and C.L.Young, Makromol.Chem., Rapid Commun. **5**, 489 (1984)
8. B.H.Zimm, J.Chem.Phys., **16**, 1063 (1948)
9. M.Kurata and W.H.Stockmayer, Fortschr.Hochpolym.Forsch.,3, 403 (1963)
10. R.Fouss, J.Polym.Sci., **3**, 603 (1948)
11. "Polymer Handbook", J.Brandrup and E.Immergut, Editors, Interscience New York, 1975, IV-9
12. P.J.Flory, in "Statistical Mechanics of Chan Molecules", Interscience New York, 1974, p. 1-18
13. J.Velickovic and S.Vasovic, Makromol.Chem., **153**, 207 (1972)
14. J.Veličković and J.Filipović, Makromol.Chem., **185**, 569 (1984).

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