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SYNTHESIS AND SOLUTION PROPERTIES OF POLY(DIPHENYL ITACONATE)

J. Veličković* and M. Plavšić

Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Yugoslavia;
Institute of Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

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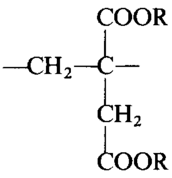
Abstract—Solid diphenyl itaconate monomer was obtained by esterification in the presence of diphosphorus pentoxide and polymerized in bulk with AIBN as initiator. The non-film forming polymer powder was characterized by fractionation, viscosity measurements, light scattering and other techniques. The relation $[\eta] = 3{\cdot}6 \times 10^{-3}\bar{M}_w^{0{\cdot}70}$, obtained for toluene at 25° was extrapolated to θ-conditions by various procedures: the σ-value of 2·60 for unperturbed dimensions indicates a less pronounced influence of phenyl compared with other C_6 hydrocarbon substitutes.

INTRODUCTION

Many aromatically substituted vinyl polymers are known and described in the literature [1]. Polymers with unsubstituted phenyl groups are, however, not numerous. Among acrylics, polymers of phenyl acrylate and phenyl methacrylate have been mentioned [2] but the properties of the latter were investigated only quite recently [3,4]. Except for poly(*p*-vinylphenyl ether), described by Barb in 1959 [5], polymers of the vinylidene —$CH_2CR_1R_2$— type with aromatic rings in both substituents seem not to have been mentioned, probably because of the general difficulty of polymerizing vinylidene monomers with two bulky substituents.

In our systematic investigation on diesters of itaconic acid which, in spite of the presence of two similar substituents, easily polymerize to well-defined high molecular weight products, we described the series of polymers of di-*n*-alkyl itaconates considering synthesis and solution properties [6–8]. Esters of itaconic acid with hydroaromatic and aromatic alcohols, including phenol, have been briefly considered [9]. Following a recent paper on poly(dicyclohexyl itaconate) [10], this communication is devoted to poly(phenyl itaconate) (PDFI), having the repeat unit:



$$-CH_2-\overset{\displaystyle COOR}{\underset{\underset{\displaystyle COOR}{\displaystyle CH_2}}{C}}-$$

where R represents the phenyl residue.

Excluding the patent literature, there is no reference to this polymer in the literature on itaconic acid derivatives, surveyed previously [6–10].

EXPERIMENTAL

Monomer synthesis

Diphenyl itaconate (DFI) was obtained by reacting itaconic acid and phenol in benzene in the presence of diphosphorus pentoxide. The acid (0·25 moles) was dissolved in solvent (150 cm³) by stirring and refluxing. Phenol (1 mole) dissolved in benzene (1:1) was then added; the system was heated to reflux and P_2O_5 (1 mole) added in small portions: the reflux temperature was then maintained for 4 hr.

After cooling to ambient temperature, the reaction mixture was washed several times to remove the phosphoric acid and unreacted phenol; the organic layer was then separated and dried; the solvent was removed in a rotary vacuum evaporator. The crude residue was dissolved in diethyl ether, washed with water, dried and again evaporated to dryness. The residue was dissolved in hot petroleum spirit (b. range 65–80°); upon standing overnight in a refrigerator, white crystals of DFI separated. After two recrystallizations from petroleum spirits, a m.pt. of 67° was obtained. The yield was only about 30%.

Polymerization

The polymer was obtained by mixing powdered monomer and α,α' azo-bis-isobutyronitrile (AIBN) in a glass tube which was then sealed under vacuum. The tube was placed in a bath at 70° and the melt homogenized by vigorous shaking; the polymerization continued for several hours until a highly viscous or solid product was formed. In some cases, a small amount of benzene was added into the tubes before sealing. In a few cases after melting at 70°, polymerization was performed at 60°, thus obtaining the polymer from solid monomer. The product was isolated by dissolving the reaction mixture in benzene and precipitating with methanol. After three reprecipitations, the polymer was dried to constant weight in vacuum at 40°.

Characterization

The solubility of polymer in various solvents was determined at room temperature, as described previously [8]. The u.v. absorption spectra of both monomer and polymer in chloroform were determined on a Unicam 500 spectrophotometer. Specific refractive index increments were measured with a Brice–Phoenix Differential Refractometer (Model 2000) at 20·00 ± 0·02° with light of 436 nm. Weight average molecular weights were determined on a Brice–Phoenix Light Scattering apparatus (Model 2000) at room temperature in butanone with unpolarized light of 436 nm; the data were evaluated by the method of Zimm [11]. Limiting viscosity numbers were determined in an Ubbelohde viscometer at 25·00 ± 0·02°, without corrections for kinetic effects.

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* Address for correspondence: Faculty of Technology and Metallurgy, 11000 Belgrade, Karnegijeva 4, Yugoslavia.

Table 1

Sample	Temp.	AIBN (% wt)	LVN (cm^3/g)	Mol. wt* 10^{-3}
1	70	0·50	24·3	296
2	70	0·25	34·0	477
3	60	0·60	26·5	334
4	70	0·50	18·1	194
5	70	0·36	26·4	333

* Calculated from the LVN–M relation in this text.

The polymer samples were fractionated on a Baker–Williams type column, supported on acid-washed glass beads, within a temperature range from 40·0 to 20·0° in benzene–methanol, and a concentration range from 72 to 62·5% of benzene by volume.

RESULTS AND DISCUSSION

The details of polymer syntheses are presented in Table 1.

After precipitation with non-solvent or by evaporation of solvent from solution, irrespective of molecular weight, polymer was obtained as small irregular particles or flakes which could be easily crushed into fine powder. Thus PDFI is a non-film forming polymer at ambient temperature.

The elemental analyses of monomer and polymer agreed well with calculated values:

	C (%)	H (%)
Calculated (for monomer and polymer)	72·33	4·96
Found (DFI monomer)	72·49	4·93
Found (PDFI polymer)	72·18	5·20

By i.r. analysis and titration, no carboxyl groups could be detected indicating the absence of half-esters in the products. The u.v. absorption spectra of both monomer and polymer indicate a strong absorption in the 250–280 nm region. In relation to poly(styrene) [7] the maximum of absorption is shifted from 262 to 259 nm, and the specific absorption coefficient k (referring to the absorption of a 0·1% solution in a 10 mm cell) is 1·57 [k for poly(styrene) is 2·17], indicating the existence of a linear correlation between the absorption and weight fraction of phenyl in these polymers.

Table 3. Specific refractive index increments of PDFI

Solvent	ν (ml/g)	Solvent	ν (ml/g)
Ethyl acetate	0·191	Benzene	0·083
Butanone	0·189	Chlorobenzene	0·060
Toluene	0·087	Styrene	0·040

The density of the polymer is very high for a vinyl polymer (compare [1]). From two independent determinations by picnometry utilizing methanol as the suspending liquid, a value of 1·25 g/cm³ was found for the powder, indicating close packing of the chains.

Observations of polymer solubility are summarized in Table 2. The solvents are arranged into three groups according to chemical composition and value of solubility parameter δ_s.

In spite of the large surface of the powdered polymer, solution at ambient temperature is very slow. The results indicate that PDFI is only soluble in solvents with δ_s values between 8·5 and 12 and of aromatic, nonpolar and medium hydrogen bonding character. The solubility region is thus in rough agreement with the polymer solubility parameter $\delta_p = 9{\cdot}8$, calculated by the method of Small [12].

The specific refractive index increments, determined in order to select a solvent for light scattering studies, are presented in Table 3.

By plotting the ν-values against the refractive index of the solvent, a straight line is obtained. The reciprocal of the slope yields a value of only 1·13 cm³/g for the polymer density (cf. e.g. [7]), which is low compared with the result obtained directly; from the intersection with the x-axis, the refractive index of the polymer in its pure state should be $n_{20} = 1{\cdot}592$.

For fractionation, the two first samples indicated in Table 1 were selected. Every sample was originally divided into about 50 individual fractions, which were then recombined to produce sufficient material for characterization. The cumulative distribution curves are presented in Fig. 1.

In connection with Fig. 1, it should be commented that the larger value of LVN of the second sample

Table 2. Solvents and non-solvents for PDFI

Solvent	δ_s $(cal/cm^3)^{1/2}$	Solubility*	Solvent	δ_s $(cal/cm^3)^{1/2}$	Solubility
Hydrocarbons			Oxygenated hydrocarbons		
Iso-octane (2,2,4-trimethyl pentane)	6·9	0	Hexyl acetate	8·35	0
n-Hexane	7·3	0	Amyl acetate	8·45	0
n-Heptane	7·4	0	Butyl acetate	8·55	+
n-Octane	7·4	0	n-Propyl acetate	8·8	+
Cyclohexane	8·2	0	Ethyl acetate	9·1	+
Xylene	8·8	+	Methyl acetate	9·5	+
Ethylbenzene	8·8	+	n-Butanone	9·3	+
Toluene	8·9	+	Acetone	9·9	0
Benzene	9·2	+	Cyclopentanone	10·4	+
Styrene	9·3	+	Tetrahydrofurane	9·1	+
			1,4-Dioxane	10·0	+
Chlorinated hydrocarbons			Dimethyl formamide	10·6	+
Butyl chloride	8·4	0	2-Ethylphenyl alcohol	11·6	+
Carbon tetrachloride	8·6	+	Benzyl alcohol	12·1	+
Chloroform	9·3	+	n-Butanol	11·4	0
1,2-Dichloroethane	10·2	+	Methanol	14·5	0

* 0—insoluble, + soluble.

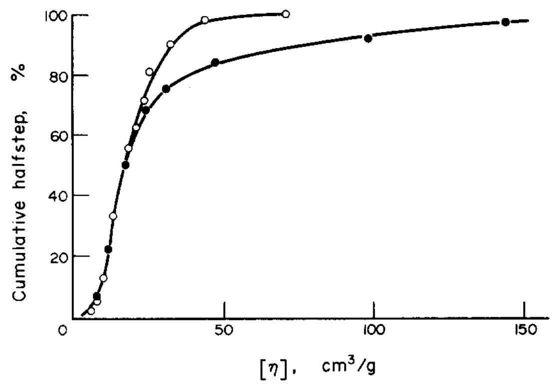

Fig. 1. Cumulative distribution curves of PDFI; ● sample obtained at 70° with 0·25% AIBN; ○ at 70° with 0·50% AIBN.

is a consequence of the broadening of the distribution in the region of higher mol. wt, while the main portions of the curves in the lower and medium mol. wt region practically coincide.

The average value of the Huggins constant from LVN-measurements of whole polymers and fractions is 0·36, indicating that toluene is a good solvent in the thermodynamic sense for this polymer.

Kuhn–Mark–Houwink–Sakurada (KMHS) relation

The KMHS relation for toluene at 25·00° was calculated statistically, applying the least squares method, from 20 pairs of LVN and $\overline{M}_w$-values; the following relation was obtained:

$$[\eta] = 3{\cdot}6 \times 10^{-3}\,\overline{M}_w^{0\cdot70}\,(\mathrm{cm^3/g}). \qquad (1)$$

In Fig. 2 the above relation is compared with the corresponding relations for poly(styrene) [6] ($K = 11{\cdot}45 \times 10^{-3}$; $a = 0{\cdot}71$) and poly(dicyclohexyl itaconate) [10] ($K = 13{\cdot}1 \times 10^{-3}$; $a = 0{\cdot}62$) in the same solvent. The strong shift to the right of the PDFI-relation compared with poly(styrene) indicates smaller hydrodynamic radii of the PDFI molecules in solution, coiled to a greater extent than poly(styrene). On the other hand, practically identical exponents a for the first two polymers must in part result from the common phenyl substituent in both polymers and solvent, while in the third case (i.e. phenyl from the solvent and cyclohexyl from the polymer) lower compatibility causes the exponent to decrease to 0·62.

Second virial coefficients, A_2, calculated from the Zimm plots obtained from light scattering measurements, decrease monotonically from about 6·3 to $4{\cdot}5 \times 10^{-5}$ in the range of mol. wt from 10^5 to 6×10^5. The linear dependence between A_2 and $\overline{M}_w$ was established with the least squares method and is

$$A_2 = 30{\cdot}4 \times 10^{-5}\,\overline{M}_w^{-0\cdot14}\,(\mathrm{mol\ cm^3/g^2}). \qquad (2)$$

This relation agrees well with a theoretical relation due to Bohdanecky [13]:

$$A_2 = 0{\cdot}7\,K_\theta^{0\cdot3}(B\Phi_0)^{0\cdot7}\,\overline{M}^{-0\cdot15}, \qquad (3)$$

where K_θ represents the KHMS constant K for θ-conditions and Φ_0 is the universal Flory constant.

The determination of K$_\theta$ *by various extrapolation methods*

In order to calculate the unperturbed dimensions of PDFI, it is necessary to determine K_θ either by direct measurements of LVN in a convenient θ-solvent or by extrapolation of the behaviour in good solvents to θ-conditions by one of the procedures suggested in the literature. In the absence of a convenient θ-solvent, we adopted the latter method following procedures used for polymers of itaconic acid esters [6–10]. In addition to the method of Kurata and Stockmayer, four other extrapolation procedures were tested.

(1) Method of Flory, Fox and Schaefgen (FFS) [14]:

$$[\eta]^{2/3}/\mathrm{M}^{1/3} = K_\theta^{2/3} + 0{\cdot}858K_\theta^{2/3}\Phi_0 B\mathrm{M}/[\eta]. \qquad (4)$$

(2) Method of Kurata and Stockmayer (KS) [14]:

$$[\eta]^{2/3}/\mathrm{M}^{1/3} = K_\theta^{2/3} + B\Phi_0 g(\alpha_\eta)\mathrm{M}^{2/3}/[\eta]^{1/3}. \qquad (5)$$

(3) Method of Stockmayer and Fixman (SF) [15]:

$$[\eta]/\mathrm{M}^{1/2} = K_\theta + 0{\cdot}51B\Phi_0\mathrm{M}^{1/2}. \qquad (6)$$

(4) Method of Bohdanecky (BO) [13]:

$$[\eta]/\mathrm{M}^{1/2} = K_0 + B\Phi_0\mathrm{M}^{0\cdot35}. \qquad (7)$$

(5) Method of Berry (BY) [16]:

$$[\eta]/\mathrm{M}^{1/2} = K_\theta^{1/2} + kB\Phi_0\mathrm{M}/[\eta]. \qquad (8)$$

In these equations, B represents a thermodynamic interaction constant related to the solvent–polymer interaction parameter χ, $g(\alpha_\eta)$ in (5) is a function of the viscosity expansion coefficient α_η and k in (8) a correction factor. Three of the resulting plots are presented in Fig. 3.

The value for K_θ of 20·0 obtained according to the FFS-plot was corrected by multiplication with

$$\Phi(\epsilon)/\Phi_0 = (1 - 2{\cdot}63\epsilon + 2{\cdot}83\epsilon^2) = 0{\cdot}706, \qquad (9)$$

for $\varepsilon = 0{\cdot}130$, according to Ptitsyn and Eisner [17], noting the difference between the viscosity and thermodynamic expansion factors α_η and α, disregarded in (4).

All results for K_θ and B are collected in Table 4.

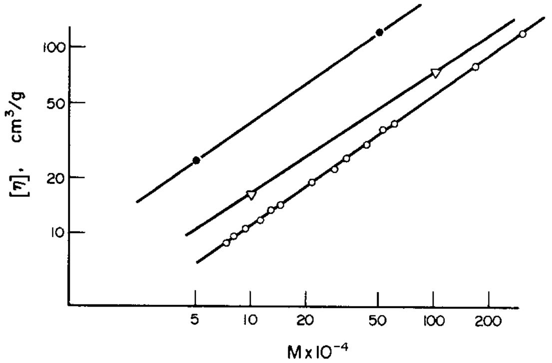

Fig. 2. Double logarithmic plot of LVN vs $\overline{M}_w$ for PDFI (○); poly(styrene) (●) and poly(dicyclohexyl itaconate (▼).

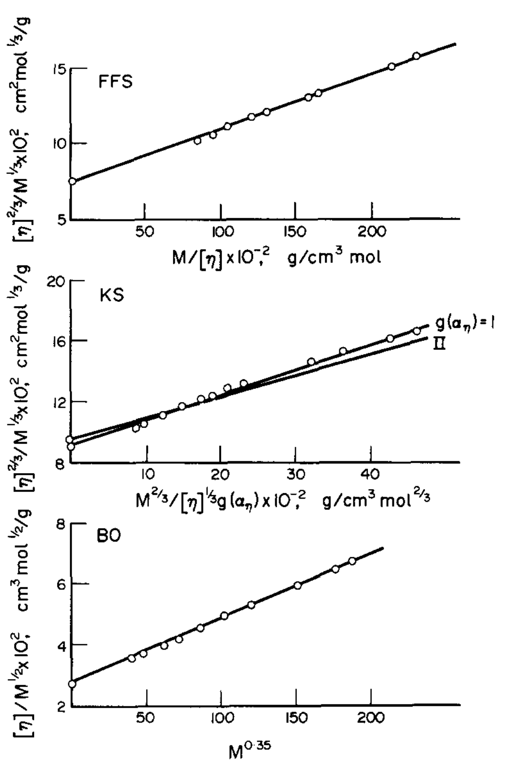

Fig. 3. Extrapolation plots of PDFI for K_θ according to the methods of Flory, Fox and Schaefgen (FFS), Kurata and Stockmayer (KS) and Bohdanecky (BO).

Table 4 shows very good agreement for K_θ obtained according to the first four methods [with correction (9)]; with the method of BY, the value is obviously underestimated. The interaction constant B, obtained from the slopes of the KS- and SF-plots and referring to toluene, is an order of magnitude higher than for poly(styrene) but comparable to B for poly(dicyclohexyl itaconate) [10]. The value of B of $2{\cdot}6 \times 10^{-28}$ quoted is obtained from (3) and refers to *n*-butanone at ambient temperature.

Unperturbed dimensions

In the absence of an absolute criterion for the validity of any of these and other relations presented in the literature, the value of $K_\theta = 28{\cdot}9 \times 10^{-3}$ was adopted for the calculation of unperturbed dimensions. Taking for Φ_0 a value of $2{\cdot}7 \times 10^{23}$ [18] and following exactly the same procedure of calculation as previously [10], the conformation factor of PDFI is:

$$\sigma = (K_\theta/\Phi_0)^{1/3}/(\overline{r^2_{0f}}/M_u) = 2{\cdot}60.$$

The value should be compared with those obtained for two other polymeric diesters of itaconic acid involving alcohols with 6 carbon atoms, viz. poly(dicyclohexyl itaconate) [10] and poly(di-*n*-hexyl itaconate) [6] with σ-values of 2·99 and 2·90, respectively.

Table 4. K_θ and B for PDFI according to various methods

Method	FFS	KS	SF	BO	BY
K_θ(cm³/g$^{3/2}$mole$^{1/2}$) × 10³	20·0	28·9	28·9	28·0	21·5
K_θ × 10³ (corrected)	28·7				
B × 10²⁸		1·4	1·6	2·6	

The lower value of σ for PDFI is in agreement with the smaller volume of the phenyl group, compared with the bulkier cyclohexyl group and the very mobile *n*-hexyl group with numerous configurations. The stiff planar form of phenyl in this case does not seem to be of great significance, as both phenyl substituents of the repeat unit must be far enough from the polymer backbone, being separated from it by an ester and methylene ester group, to influence appreciably the free rotation around carbon–carbon bonds in the main chain. The planar form of phenyl may even contribute to the establishment of stronger interactions between substituents from neighbouring and more remote repeat units of the chain, and between substituents from different molecules in the system, affecting thus the solubility, density and other properties of PDFI.

In a similar investigation of the conformation factors of poly(cyclohexyl methacrylate) and poly(phenyl methacrylate), Hadjichristidis *et al.* [4] obtained values of 2·5 and 2·8, respectively, for σ. In our opinion, the stronger hindrance to free rotation in the second polymer with one phenyl group must at least in part result from the non-aromatic methyl attached to the same carbon atom of the main chain, which is better compatible with cyclohexyl than with phenyl.

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