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Dilute Solution Properties of Styrene/Di-n-Alkyl Itaconate Copolymers

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Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

Solution properties of styrene/di-n-butyl itaconate (SDBI), styrene/di-n-hexyl (SDHI) and styrene/di-n-octyl itaconate (SDOI) copolymers from the entire range of copolymer compositions were investigated on series of fractions of uniform composition. Kuhn-Mark-Houwink-Sakurada (KMHS) constants were extrapolated to K_Θ and all results combined with those of styrene/dimethyl itaconate (SDMI) from a previous publication. The σ-parameters describing short range interactions deviate increasingly from the linear summation of parent homopolymer contributions. The excess unperturbed dimensions are correlated with parent homopolymer solubility parameters and discussed in terms of hetero-contacts in the copolymer chain.

INTRODUCTION

Unperturbed dimensions of polymers, resulting from short range interaction only, were investigated in great extent and the results assembled by various authors (e.g. KURATA et al.). Unperturbed dimensions are defined either by the σ-parameter of hindrance to free rotation, or the persistence length C_∞, according to following equations:

$$\sigma = (r_o^2/r_{of}^2)^{1/2} \qquad C_\infty = (r_{of}^2)/nl^2$$

where r_o^2 represents the mean end-to-end distance at Θ conditions, r_{of} refers to a freely rotating polymethylene chain, n is the number and l^2 the mean square of the valence bond length. Investigations on copolymers are unfrequent, both for fundamental and experimental reasons, resulting from composition heterogeneity, apparent mol. weights, limited information on the number and distribution of -AB- heterocontacts and others. Systems investigated so far with great care include copolymers of styrene/methyl methacrylate (STOCKMAYER et al 1955), styrene/acrylonitrile (SHIMURA 1966), styrene/butadiene (HOMMA and FUJITA 1965) and a few other copolymers reviewed by BEKTUROV (1975). Although mostly limited to unfractionated samples of one single composition only, the unperturbed dimensions do not conform to the simple relation proposed

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by STOCKMAYER et al(1955) for any copolymer property P:

$$P_{copol.} = P_A \cdot x_A + P_B \cdot (1-x_A)$$

where x_A represents the weight fraction and P_A and P_B the properties of the parent homopolymers. CHIANTORE et al (1979) recently reinvestigated the styrene/methyl methacrylate system over a broad range of compositions and suggested the introduction of composition variables into the previous relation in order to fit the observed positive deviations of unperturbed dimensions from linearity.Regarding itaconic acid ester copolymers,VELIČKOVIĆ et al.(1969) detected for SDMI only slight deviations practically within experimental error. However,when $-CH_3$ was replaced with n-butyl the deviation became significant(VELIČKOVIĆ and FILIPOVIĆ,prelim.report 1972).

EXPERIMENTAL

The experimental part,including substances,copolymer synthesis,fractionation and treatment of results is essentially the same as described for itaconate homopolymers(VELIČKOVIĆ and VASOVIĆ 1972) and SDMI (VELIČKOVIĆ et al., 1969).

Copolymers were prepared radically with AIBN,terminating the reactions at low conversions in order to obtain a narrow chemical distribution.Comonomer ratios were selected according to copol.constants r_1 and r_2 within limits of 0.25-0.60 according to BRAUN and AHN(1963) and own results for DHI.Fractionations were carried out on a temp.gradient column with benzene/methanol.The chemical composition of bulk copolymers and copolymer fractions were determined by UV and controled occasionally by dn/dc measurements in methylethylketone(MEK).Limiting viscosity numbers (LVN) were measured in a dilution viscometer in toluene at 298 K. M_w values of fractions were determined in MEK solution according to ZIMM(1948) on a Brice Phoenix 2000 instrument.KMHS relations for each copolymer and particular composition were calculated statistically,disregarding head and tail fractions with deviating chemical composition.Unperturbed dimensions: The behaviour in good solvents was extrapolated to Θ conditions according to the relation of KURATA and STOCKMAYER (1963):

$$[\eta]^{2/3}/M_w^{1/3} = K_\Theta^{2/3} + 0.363\ \emptyset_o B g(\alpha_\eta) M_w^{2/3} \cdot [\eta]^{-1/3}$$

where $g(\alpha_\eta)$ is a function of the viscosity expansion coefficient.K_Θ obtained from the intercept was then introduced in the Flory-Fox relation, in order to obtain r_o.

RESULTS AND DISCUSSION

All copolymers were synthetized with 0.1-0.5 wt.% of AIBN at 323,333 or 343 K in order to obtain suitable bulk LVN which ranged from 19.7 to 66.8 cm^3/g.Critical volume fractions of solvent to produce clowdiness, significant for fractionation, are presented in Fig. 1:

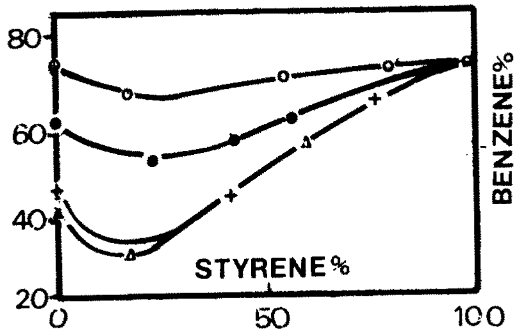


Fig.1 Critical volume fractions of solvent in benzene/ methanol at 293 K, SDMI(+),SDBI(o),SDHI(●),SDOI(Δ).

A typical condensed set of fractionation and fraction characterization for the sample SDHI-4 with 74% styrene and a bulk LVN 40.6 is presented in Table 1.

TABLE 1 Fractionation of 3.0856 g of SDHI-4

No.	weight (mg)	cumulation (%)	LVN (cm^3/g)	Styrene (wt. %)	M_w
2	37.4	2.79	-	74.8	-
3	78.0	5.31	13.2	-	-
5	100.7	13.51	17.6	-	-
6	232.0	21.01	24.4	73.5	55.700
8	372.9	36.82	31.7	72.0	95.800
10	292.3	50.00	37.5	73.0	159.900
12	296.3	64.19	42.6	73.0	167.700
14	299.0	77.04	47.0	73.8	201.100
16	168.1	84.77	58.5	-	241.300
18	143.1	90.90	68.5	73.3	331.800
20	17.8	93.81	-	86.7	-
22	51.2	96.65	96.0	-	-
24	39.2	98.94	-	97.2	-

In all other fractionations also the head and tail fractions had a higher styrene content,but 80-90% of the weight of fractions was uniform in chemical composition, and only this part was considered for further treatment.

Results for KMHS constants, K_Θ and the σ-parameters of all compositions investigated,together with those published previously for PDMI, are collected in Table 2.

TABLE 2 Kuhn-Mark-Houwink-Sakurada constants, K_Θ and unperturbed dimensions of SDMI, SDBI, SDHI and SDOI

Copolymer	Styrene(%)	$K\cdot 10^3$	a	$K_\Theta\cdot 10^3$	σ	$\Delta\sigma$(%)
PS	100	11.45	0.712	78.0	2.17	-
SDMI-1	73.0	10.9	0.69	63.7	2.15	0.5
SDMI-2	70.5	12.8	0.67	63.4	2.15	0.5
SDMI-3	51.0	11.7	0.67	55.3	2.12	0.5
SDMI-4	41.0	9.7	0.67	45.7	2.05	-2.4
SDMI-5	29.9	9.0	0.67	40.3	2.04	-1.9
SDMI-6	25.0	6.6	0.68	35.4	1.96	-5.3
PDMI($^+$)	0	5.15	0.68	30.4	2.02	-
SDBI-1	74.4	13.0	0.69	75.6	2.51	12.5
SDBI-2	63.3	12.1	0.69	72.5	2.69	19.0
SDBI-3	33.0	9.5	0.68	59.2	2.74	15.1
SDBI-4	17.6	8.95	0.67	44.1	2.62	6.5
PDBI	0	6.4	0.68	35.4	2.50	-
SDHI-1	73.5	21.9	0.63	80.2	2.71	20.4
SDHI-2	54.6	17.6	0.65	72.6	2.90	24.9
SDHI-3	41.6	5.8	0.74	62.8	3.01	25.9
SDHI-4	18.2	14.2	0.63	45.1	2.90	12.8
PDHI	0	3.7	0.72	35.4	2.80	-
SDOI-1	78.0	14.3	0.67	72.9	2.64	13.6
SDOI-2	67.1	18.5	0.65	71.6	2.84	24.3
SDOI-3	45.5	19.5	0.63	67.0	3.16	30.6
SDOI-4	33.4	10.5	0.67	54.6	3.13	23.9
SDOI-5	15.9	8.8	0.68	41.8	3.09	17.5
PDOI	0	4.1	0.70	32.7	3.02	-

($^+$) insoluble in toluene. LVN solvent: benzene

All copolymer KMHS relations of the general form $\log[\eta] = \log K + a\cdot\log M_w$ fall within boundaries set by the parent homopolymers in expected sequence according to the decreasing content of styrene.A plot of this kind, indicating also the range of validity of these relations, is presented in Fig.2. A discussion on KMHS constants and unperturbed dimensions of the parent homopolymers has been published before(VELIČKOVIĆ and VASOVIĆ 1972).

The deviation of σ from linearity, i.e. the "excess"unperturbed dimension, was calculated according to the relation

$$\Delta\sigma = \frac{\sigma_{observed}}{\sigma_{PS}\cdot x_{PS} + \sigma_{PDI}\cdot(1-x_{PS})} - 1 ,$$

and results are presented in the last column of Table 2.

σ for SDMI decreases within experimental error monotonously with increasing DMI content, in agreement with the STOCKMAYER additivity relation, but σ values of the other three systems exhibit a clear maximum each. In our opinion Δσ represents the net additional short range interaction caused by the presence of unlike monomer units in the copolymer chain. A more clear picture results when copolymer compositions are expressed on the mole basis, as presented in Fig.3 and Fig.4.

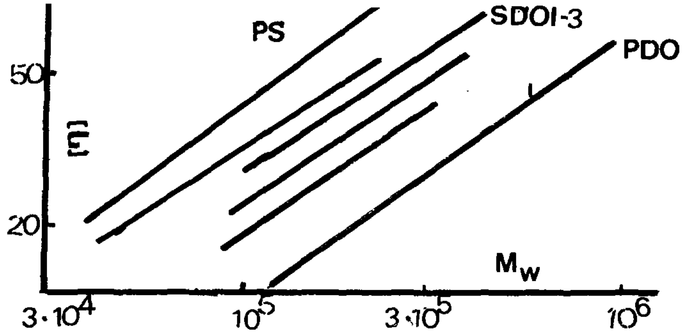


Fig.2 KMHS double logarithmic plots for SDOI compolymers.

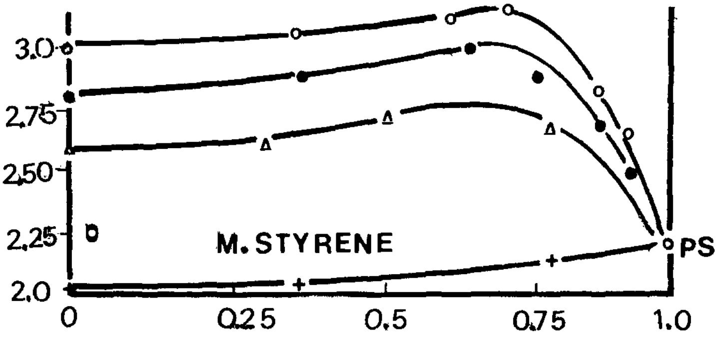


Fig.3 σ-parameters for the copolymer systems SDMI(+), SDBI(o), SDHI(●), SDOI(▲).

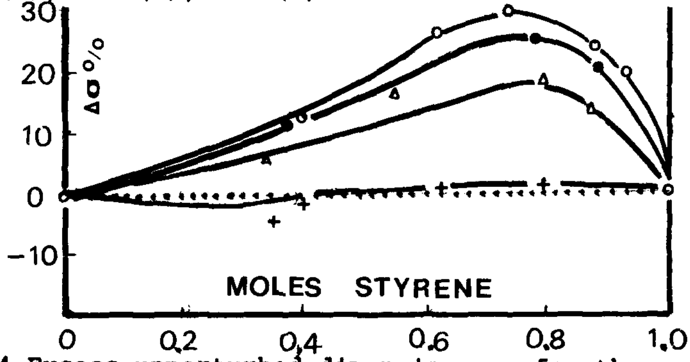
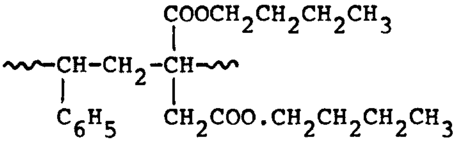


Fig.4 Excess unperturbed dimensions, Δσ for the copolymer systems SDMI(+), SDBI(o), SDHI(●) and SDOI(▲).

The observed excess unperturbed dimensions of the order of 20, 25 and 30% in the region of maxima are well above values reported for other copolymers.Expressed as C_∞ the corresponding deviation from linearity is even 40-60%. In order to explain this phenomenon one should bear in mind the chemical structure of the -AB- heterocontact e.g. in the SDBI system:



$$\sim\sim\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\overset{COOCH_2CH_2CH_2CH_3}{\overset{|}{\underset{CH_2COO.CH_2CH_2CH_2CH_3}{\underset{|}{CH}}}}-\sim\sim$$

The planar nonpolar hydrocarbon phenyl substituent of the styrene residue is expected to be incompatible with any of the two structurally similar highly polar mobile ester substituents of the itaconate unit in the chain. The existing mutual dipole/dipole short range interaction of the latter substituents, or the interaction along -BB- diads or even longer B-segments is being discontinued at the heterocontact site and for steric reasons and other repulsive effects the unperturbed coil is caused to expand.The introduction of the even more voluminous n-hexyl and n-octyl groups increases the steric effect although the strength and positions of the dipoles in relation to the backbone and phenyl do not change. This point of view is supported by the observation that allthree maxima in Fig.4 are positioned at the same approx. 75% mole content of styrene, where the population of -BB- diads or longer sequences is insignificant,although the weight % of B is still high.

It was further assumed that the difference of parent homopolymer solubility parameters δ_p would be a useful guideline to predict the extent of mutual comonomer incompatibility and thus shed more light on the results obtained.Following δ_p values are reported in the literature (VELIČKOVIĆ et al 1970):

PS 19,8
PDMI 19,2 PDBI 18,2 PDHI 17,2 PDOI 16,4 $(J/cm^3)^{1/2}$

From this point of view, the observed difference in solubility parameters of parent homopolymers for SDMI of only 0,6 units indicates a still existing compatibility of A and B units and no increase of unperturbed dimensions in respect to a linear summation of parent homopolymer contribution is observed. $\Delta\delta_p$ for the following three systems is however 1.6, 2.6 and 3.4 units respectively and these criteria of incompatibility are in a fair linear relation with $\Delta\sigma$ defined previously for any copolymer composition in the region of maxima from Fig.4.

In presenting this explanation the authors are aware that it is subject to criticism, as the equality of solubility parameters is a good criterion for the solubility of a polymer in a solvent but necessarily not also for the compatibility of polymer subunits.

The results obtained were also investigated from the aspect of the number of heterocontacts in the copolymer chain. According to HARWOOD and RITCHEY(1964),taking into consideration the copolymerisation constants r_1 and r_2, the so called "run number" 2RN, equal to the fraction of -AB- contacts in the chain,can be calculated for any comonomer composition.Calculations for the systems investigated in this work revealed following highest possible 2RN values: 0.83, 0.72, 0.69 and 0.68, for compositions close to equimolar of the two comonomers.The positions of maxima of deviation of unperturbed dimensions from linearity are however shifted to an aprox. 75 mole % of styrene in the chains, i.e. to a situation where the population of -AB- contacts is still significant, but -BB- and higher segments are practically absent in the system, and therefore any short range attraction resulting from BB dipole interaction vanishes in the system.

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