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SOLUTION PROPERTIES OF ISOPRENE-STYRENE BLOCK COPOLYMERS

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Abstract—Two series of well characterized styrene–isoprene two-block copolymers have been synthesized, with weight fractions 50 and 75 per cent styrene. Their intrinsic viscosities have been studied in a number of solvents and over a wide range of molecular weights. In general the intrinsic viscosities are close to the weighted average of the corresponding homopolymers of equal molecular weight. There is discussion of the implications of these results with regard to the configuration of block copolymers in solution.

INTRODUCTION

THE STUDY of the physical properties of block-copolymers has received much attention in recent years. Phase separation is universally recognized to occur in the solid state(1–4) and in gels(5) but the situation with regard to the individual polymer chain in dilute solution is still not clear. Some authors suggest a segregated structure in which the different units do not interpenetrate(6–8) while others(9) suggest that their data are compatible with a more random interpenetrating structure. Some differences may, of course, be expected according to the type of copolymer. Existing studies have relied on rather a small number of samples in which either the total molecular weight or composition and sometimes both were allowed to change. This complicates interpretation which, even under the most favourable circumstances, is by no means simple.

This work describes the dilute solution properties of two-block styrene–isoprene copolymers. Two series of polymers were prepared each having the same composition but varying molecular weight. The compositions chosen were 75 (series b) and 50 (series a) weight per cent of polystyrene. In order to make an accurate comparison of properties with those of the parent homopolymers, a series of polyisoprenes of the same microstructure was also examined. Ample data on polystyrene exists but, to reduce errors in the comparison, data reported earlier from these laboratories(10) were used and supplemented by additional data. Some molecular weights were remeasured; viscosity measurements were made for a wider range of solvents.

EXPERIMENTAL

The block-copolymers were prepared in benzene solution using standard techniques of anionic polymerization. The initiator was *sec.*-butyllithium, purified by a short path vacuum distillation. The rate of initiation by *sec.*-butyllithium is about 200 times greater than with *n*-butyllithium and is, in benzene, sufficiently rapid to produce almost monodisperse polymers except at very low molecular weights.(11) Styrene monomer was first polymerized and after leaving at least 24 hr, isoprene was distilled in slowly. The polymerization was allowed to go to completion and then the active centres were terminated by a trace of *t.*-butanol. The procedure was carried out under high vacuum conditions in all-glass systems using break-seals to add various components in scaled-up versions of techniques

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described previously.(12) Solvent and monomers were purified as previously reported.(13) Polymers were isolated by precipitation with methanol containing 0·03 per cent of 2–6 di-*t*-butyl-4-methoxyphenol. They were dried to constant weight in vacuum and stored in a vacuum desiccator. The absence of homopolystyrene in the product was checked by density gradient ultracentrifugation as described earlier(14) (< 1 per cent).

Solvents for physical measurements were reagent grade wherever possible. Toluene and cyclohexane were dried over calcium hydride and fractionated in a 100-plate column. Dioxane was refluxed with sulphuric acid, washed and distilled. It was finally fractionated over metallic sodium. Methylisobutyl ketone was dried over drierite, fractionated, treated with activated alumina and subjected to a final distillation. 0·02 per cent of the above antioxidant was added to the solutions of polymers. This was found to be particularly necessary with methylisobutyl ketone which gave evidence of extensive breakdown in a few hours in absence of antioxidant. Solutions in hydrocarbon solvents appear to be quite stable in the absence of antioxidant. Viscosities were determined in Cannon–Ubbelohde semi-micro dilution viscometers known to have negligible kinetic energy corrections. Number-average molecular weights were determined in toluene solution using a Mechrolab 503 rapid membrane osmometer, with Schleicher and Schuell 08 grade membrane filters. Light scattering measurements were made on a Sofica P.G.D. photometer modified so as to allow external thermostating. Details of these determinations are given in another publication.(15) All characterization was carried out at 35°.

RESULTS

The measured physical properties of the polymers are given in Table 1, and the intrinsic viscosity data are presented as a function of molecular weight in Fig. 1. Intrinsic viscosity-molecular weight data of polyisoprenes (particularly of the present microstructure, 71 per cent *cis*, 22 per cent *trans*, 7 per cent 3,4) are not often reported in the literature and it seems worthwhile to quote, the 10^4K and a values: toluene; 1·75, 0·74: cyclohexane; 2·02, 0·73: dioxane; 9·4, 0·53: methylisobutyl ketone; 7·6, 0·56. The intrinsic viscosities are ~6 per cent higher than reported by Beattie

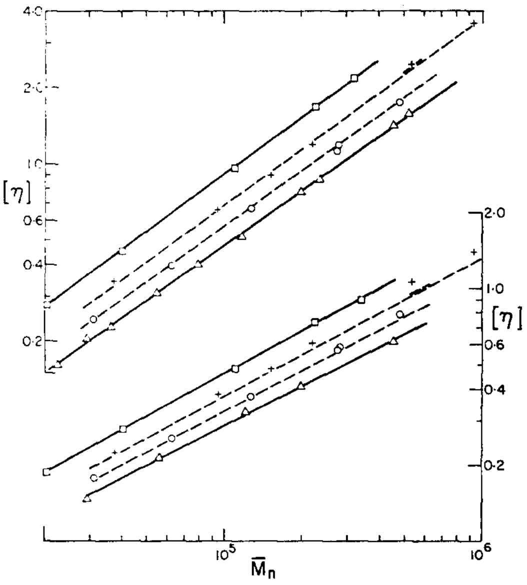

FIG. 1(a). Variation of intrinsic viscosity with molecular weight for homopolymers and copolymers. □ polyisoprene, △ polystyrene, + block copolymers series a (50/50), ○ block copolymers series b (75/25). Upper scale, solvent = toluene; lower scale, solvent = methylisobutyl ketone. The dashed lines are calculated from Eqn. (2). The short dashed line indicates the correction for composition deviation of polymer SI-a-1A.

TABLE 1

Sample	Composition wt % Pst	10^5 $\bar{M}_n$	10^5 $\bar{M}_w$	10^5 $\bar{M}_{Calc}$	$[\eta]_{tol}$	$[\eta]_{Diox}$	$[\eta]_{CH}$	$[\eta]_{MIBK}$
SI-a-4	0·484	0·375	—	0·335	0·345	0·254	0·302	0·226
SI-a-2	0·484	0·947	1·04	0·890	0·654	0·449	0·554	0·383
SI-a-7	0·497	1·52	1·60	1·54	0·90	0·58	0·735	0·48
SI-a-5	0·498	2·21	2·4	2·20	1·195	0·765	0·951	0·601
SI-a-1A	0·45	5·35	—	5·24	2·45	1·361	1·89	1·051
SI-a-6	0·485	—	10·5	8·84	3·60	1·891	2·59	1·39
SI-b-1	0·759	0·31	0·355	0·31	0·244	0·216	0·200	0·179
SI-b-3	0·751	0·626	—	0·61	0·395	0·335	0·295	0·256
SI-b-2	0·747	1·275	1·36	1·215	0·664	0·535	0·456	0·376
SI-b-4	0·760	2·80	3·15	2·76	1·19	0·915	0·73	0·591
SI-b-6	0·754	2·74	2·94	2·70	1·12	0·86	0·709	0·575
SI-b-7	0·741	4·8	5·2	5·0	1·75	1·298	1·050	0·792
PI-5	0	0·202	—	0·18	0·277	0·184	0·286	0·188
PI-2	0	0·401	—	0·365	0·451	0·265	0·464	0·281
PI-1	0	1·10	—	1·00	0·955	0·455	0·985	0·484
PI-4	0	2·26	—	2·28	1·68	0·672	1·72	0·738
PI-3	0	3·19	3·39	2·99	2·18	0·809	2·22	0·899

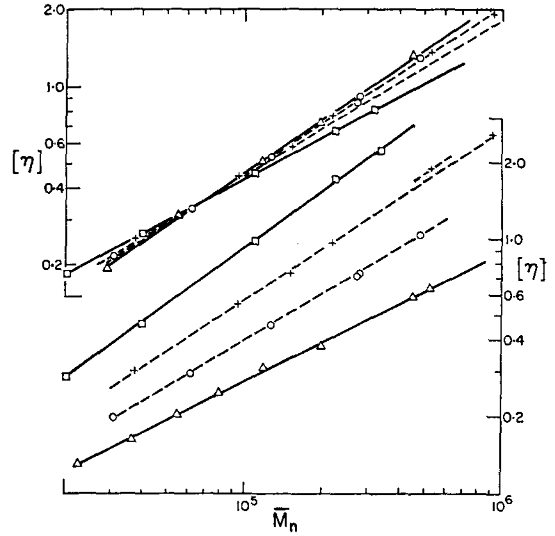

Fig. 1(b). As Fig. 1(a). Upper scale solvent dioxane; lower scale solvent cyclohexane.

and Booth[16] in toluene at 30°. This difference is probably mainly caused by the difference between weight-average and number-average molecular weights as, in both cases, the polymers are sharp-distribution samples produced by butyllithium initiation.

The intrinsic viscosities of the copolymers lie between the values of the corresponding homopolymers of the same molecular weight in the whole range of solvents. In fact they are generally close to the weighted average with occasionally a small deviation in the positive direction. Estimates of K_θ can be obtained from Stockmayer–Fixman plots as illustrated in Fig. 2. As these plots are noticeably curved in good solvents, in determining the intercept most weight has been placed on the data from the two worst solvents. 10^3 K_θ values obtained in this way are 0·87 (polystyrene), 0·97 (series b), 1·10 (series a) and 1·26 (polyisoprene). The value for polystyrene is

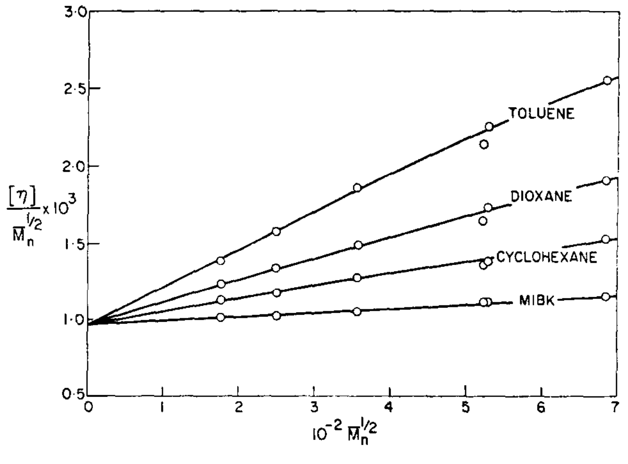

Fig. 2. Stockmayer–Fixman plots for copolymer series b.

close to that quoted in the literature. Some small differences may be caused by the use of number-average molecular weights as the samples must have a small polydispersity. For polyisoprene little information is available and this normally refers to natural rubber with a somewhat higher *cis*-1,4 content. For the latter material, Flory(17) estimated K_θ as $1\cdot19 \times 10^{-3}$ which does not differ greatly from the value quoted above.

Virial coefficients were determined in toluene only and are not reported here, but once again those of the block-copolymers were close to the weighted average of those of homopolymers of the same molecular weight.

DISCUSSION

Although it is clear that with the present copolymers the properties are close to a weighted average of those of the homopolymers, the viscosity results cannot be interpreted unequivocally. As a result, the exact configuration of the polymers in solution cannot be determined from the data. This arises because the inadequacies of dilute solution polymer theory in other than θ-solvents, and particularly that of intrinsic viscosity, are magnified in the case of block-copolymers. Determination of radii of gyration is not possible as the experimentally determined values are apparent ones which are a function of the refractive index increments of the two copolymer components.(18) Some definition of the probability of *a,a b,b* and *a,b* contacts is necessary. Often the dubious but convenient assumption is made that the copolymer consists of a randomly distributed collection of the two types of segment.(9 19) The relative probabilities are then x_a^2, x_b^2 and $2x_ax_b$, where x_a and x_b are segment fractions. Even so, in the definition of a segment, there are problems which are absent in the treatment of homopolymers where an arbitrary definition can be made. In the present case the decision will affect calculations involving the different types of contact. Some authors have defined segments in terms of carbon–carbon links,(9,20) others in terms of mole fractions.(21) The difference is small for vinyl monomers of about the same molecular weight but is large in a copolymer of a vinyl and a diene monomer with quite different molecular weights.

If normal gaussian coil statistics are applicable to our block copolymers under θ conditions,(21)

$$K_{\theta,\,\text{copol}} = [w_a K_{\theta a}^{2/3} + w_b K_{\theta b}^{2/3}]^{3/2} \tag{1}$$

TABLE 2

Solvent/Polymer	Styrene	75/25	50/50	Isoprene
Toluene	1·34	1·82	2·41	3·63
Dioxane	1·25	1·08	0·84	0·265
Cyclohexane	0	0·63	1·63	3·87
Methylisobutylketone	0·088	0·19	0·295	0·455
$10^3\ K_\theta$	0·87	0·97	1·10	1·26
Calc. Eqn. (1)	—	0·965	1·06	—

$10^{27}\ B$ and K_θ [Eqn. (4)]
Calculated using $\phi_0 = 2\cdot66 \times 10^{21}$. Slope $= 0\cdot51\ \phi_0 B$.

where w_a, w_b are weight fractions of the two components. As can be seen from Table 2, the values obtained from the Stockmayer–Fixman plots are in reasonable agreement with those calculated from the equation although the total range of values is, unfortunately, small. In terms of intrinsic viscosities, equation (1) becomes

$$[\eta]_{\text{copol}} = [w_a[\eta_a]^{2/3} + w_b[\eta_b]^{2/3}]^{3/2} \tag{2}$$

where the values of $[\eta_a]$ and $[\eta_b]$ are those of the corresponding homopolymers of the same molecular weight as the copolymer. This equation is strictly valid under θ conditions, but holds surprisingly well for our samples even in good solvents. The values calculated from Eqn. (2) are shown in Fig. 1 as dotted lines. Surprisingly good agreement is found in cyclohexane and toluene but small positive deviations occur in dioxane and methylisobutylketone. Equation (2) will also be a good representation in good solvents if ϕ does not vary appreciably with solvent power and if:

$$\frac{\langle L_c^2 \rangle}{n_c} = x_a \frac{\langle L_a^2 \rangle}{n_a} + x_b \frac{\langle L_b^2 \rangle}{n_b} \tag{3}$$

where n_a, n_b are the number of links in the two units and L represents mean square end/end distance. L^2/n varies with molecular weight in good solvents but the values at molecular weights of the homopolymers equal to that in the copolymer are to be understood. Where Eqns. (2) and (3) apply, qualitatively at least, little coil expansion is caused by heterocontacts and essentially the polymer units are interchangeable. Deviations from this state of affairs are small and essentially confined to methylisobutyl ketone as solvent. These results are not consistent with those reported previously$^{(20)}$ on the same systems where large positive deviations from Eqn. (3) were found even in toluene solutions. This point is evident qualitatively by comparing the intrinsic viscosities which are appreciably higher than shown in Fig. 1 at equivalent molecular weights.

An attempt at more quantitative evaluation of the data by methods used by previous authors (to determine β_{ab} for instance) is less satisfactory. The number of assumptions to be made is rather large. Initially some choice of method for evaluation of β's must be made. The only simple method available is that of Stockmayer and Fixman.$^{(22)}$ The relationship

$$[\eta]/M^{\frac{1}{2}} = K_\theta + 0{\cdot}51\ \phi_0\ BM^{\frac{1}{2}} \tag{4}$$

is certainly not accurate and the β values obtained (BM_0^2, where M_0 is the segmental molecular weight) are not in agreement with those obtained by other methods. The predicted linear relationship is obtained only over a restricted range at low coil expansions.$^{(23)}$ The deficiencies rely principally on the choice of a correct α_η–Z relationship, a subject of great uncertainty at the present time. However, recently it has been suggested$^{(24)}$ that B values better in accord with thermodynamic data can be obtained by using initial slopes of the plots and reducing the constant in Eqn. (4) from 0·51 to 0·287 ($1 < \alpha_\eta^3 < 2{\cdot}5$). This in effect simply multiplies all B values obtained by the normal procedure by 1·8 and does not affect their relative values.

The second assumption commonly made concerns the segment contact distribution, as noted previously often assumed to be a statistical distribution of unconnected segments:

$$\beta_{\text{copol}} = x_a^2\,\beta_{aa} + x_b^2\,\beta_{bb} + 2x_a\,x_b\,\beta_{ab} \tag{5}$$

which leads to a value of β_{ab} obtainable from experimentally observed B values,

$$\beta_{ab} = \frac{M_{0a}\,M_{0b}}{2w_a\,w_b}\{B_{\text{copol}} - w_a^2\,B_{aa} - w_b^2\,B_{bb}\} \tag{6}$$

where M_{0a}, M_{0b} are the segment molecular weights and $M_{0c} = x_a M_{0a} + x_b M_{0b}$. The β_{ab} value obtained will depend on the segment definition via choice of M_{0a}, M_{0b}. Only the ratio $\beta_{ab}/(\beta_{aa}\beta_{bb})^{\frac{1}{2}}$ is independent of this definition. Substitution of values equal to the mean molecular weight per C—C bond will give an equation directly derivable from Utracki and Simha.⁽⁹⁾ Definition of a segment equal in size to the solvent molar volume ($M_{0a} = V_1/\bar{v}_a$ etc.) modifies the equation to one directly derivable from that of Stockmayer *et al.*:⁽²⁵⁾

$$\chi_{\text{app}} = v_a\,\chi_{1a} + v_b\,\chi_{1b} - v_a\,v_b\,\chi_{ab} \tag{7}$$

where v's are volume fractions and the parameter χ_{ab} represents the difference in interaction energy in forming two *ab* contacts from *a,a* and *b,b* contacts. If $\chi_{ab} = 0$, then $\beta_{ab} = (\beta_{aa} + \beta_{bb})/2$.

β_{ab} values from Eqn. (6) can be calculated from the data in Table 2; within experimental error, they are independent of composition but vary, as expected, with solvent (Table 3). The deviation from the arithmetic mean of β_{aa} and β_{bb} depends on the choice of segment. The reasonable agreement (i.e. β_{ab} independent of composition) with a model involving a large number of heterocontacts may be misleading. If we take as model the other extreme structure which involves no heterocontacts at all, then

TABLE 3

Solvent		Toluene	Cyclohexane	Dioxane	MIBK
β_{ab}*	50/50	27	15·7	6·9	5·2
	75/25	26	12·6	7·1	4·8
$\frac{1}{2}(\beta_{aa} + \beta_{bb})$*		26·6	19·3	6·3	3·9
β_{ab}†	50/50	2·06	1·16	0·81	0·28
	75/25	1·98	0·93	0·85	0·26
$\frac{1}{2}(\beta_{aa} + \beta_{bb})$†		1·95	0·56	1·68	0·18

10^{24} β_{ab} (cc) Calculated assuming a statistical distribution of disconnected segments.

* Calculated assuming segments equal in size to the molar volume of solvent.

† Segment fractions calculated as link fractions.

β_{ab} values calculated from the equations of Froelich and Benoit,⁽²¹⁾ which predict moderate diminution in the fraction of *ab* contacts compared with the statistical model, show much greater variation with composition. This occurs even in poor solvents. The fully segregated or statistical contact approximations fit the present data more successfully.

$$\beta_{\text{copol}} = x_a\,\beta_{aa} + x_b\,\beta_{bb} \tag{8}$$

or

$$B_{\text{copol}} = \frac{w_a^2\,B_{aa}}{x_a} + \frac{w_b^2\,B_{bb}}{x_b}. \tag{9}$$

TABLE 4

	Toluene (50/50)	Toluene (75/25)	Cyclohexane (50/50)	Cyclohexane (75/25)	Dioxane (50/50)	Dioxane (75/25)	MIBK (50/50)	MIBK (75/25)
Calc. *	2·41	1·85	1·78	0·85	0·808	1·04	0·258	0·170
Calc. †	2·58	1·98	1·285	0·48	1·373	1·46	0·242	0·156
Exptl.	2·41	1·82	1·63	0·635	0·84	1·08	0·295	0·190

10^{27} *B* values from Eqn. (9).
* † As in Table 3.

Replacement in Eqn. (9) of the appropriate values of segment fractions and experimental B values, allows a check of this equation. Table 4 shows that the agreement between predicted and observed values of B_{copol} is as good as in the previous approach, particularly on the lattice model segment definition. The reason for the lack of distinction between the models is clear. If we assume the random statistical segment distribution model, the experimental results are consistent only with a negligible value of χ_{ab} (experimentally $< \pm 0 \cdot 02$) i.e. β_{ab} is always close to $(\beta_{aa} + \beta_{bb})/2$. Under these conditions, Eqn. (5) simplifies to Eqn. (8) and we have the choice of interpreting the results as $\chi_{ab} \sim 0$ or the number of heterocontacts as negligible. Only if the intrinsic viscosities of the copolymers were much larger than observed here, would one be able to argue in favour of many heterocontacts, as this would correspond to large coil expansions caused by strongly repulsive heterocontacts.

From the present data alone, distinction between the two extreme models would depend largely on the credibility of χ_{ab} values close to zero. A rough indication of the expected magnitude of χ_{ab} can be obtained from cohesive energy densities.(25) These parameters are difficult to determine for polymers, but the most reliable values appear to be $9 \cdot 2$ $(\text{cal/cc})^{\frac{1}{2}}$ for polystyrene(26) and $8 \cdot 0$ $(\text{cal/cc})^{\frac{1}{2}}$ for polyisoprene.(27) These values would lead to a predicted χ_{ab} of close to $0 \cdot 20$, much larger than observed experimentally. Other data exist(15) to indicate that the intermolecular excluded volume of block-copolymers is much larger than is expected from the volume occupied by one type of segment alone. Similar arguments based on virial coefficients(28) have been used for styrene–methylmethacrylate block-copolymers. The segregated structure seems on these grounds more realistic, although it should be emphasized that complete segregation is probably not essential to explain these results. A gaussian or near-gaussian distribution of chains tends to keep the number of heterocontacts small. In poor solvents, small positive deviations in the viscosity curves from the average expected properties could probably be explained by the effect of a small fraction of heterocontacts becoming measurable as the coil size decreases.

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Résumé—On a effectuè la synthèse de deux séries de copolymères séquencés styrène-isoprène bien caractérisés, comportant 50 et 75 pour cent en poids de styrène. On a étudié leurs viscosités intrinsèques dans différents solvants et dans un large domaine de poids moléculaires. En général, les viscosités intrinsèques sont près de la moyenne pondérée des homopolymères correspondants, de poids moléculaire équivalent. On discute les conséquences de ces résultats sur la configuration des copolymères séquencés en solution.

Sommario—Si sono sintetizzati due serie di ben caratterizzati copolimeri a due blocchi di stirene-isoprene con percentuale in peso di stirene del 50 e 75. Si è studiata la loro viscosità intrinseca in diversi solventi e per una larga gamma di pesi molecolari. In generale, la viscosità intrinseca trovata è prossima alla media ponderata dei corrispondenti omopolimeri di eguale peso molecolare. Si discutono le implicazioni di tali risultati per quanto riguarda la configurazione in soluzione di copolimeri in blocco.

Zusammenfassung—Es wurden zwei Serien gut charakterisierter Styrol-Isopren Zwei Blockcopolymerer synthetisiert mit Gewichtsanteilen von 50% und 75% Styrol. Ihre Viskositätszahlen wurden über einen weiten Molekulargewichtsbereich in einer Anzahl von Lösungsmitteln untersucht. Im allgemeinen sind die Viskositätszahlen nahe an dem Gewichtsdurchschnitt des entsprechenden Homopolymeren mit gleichem Molekulargewicht. Die Bedeutung dieser Ergebnisse wird diskutiert im Hinblick auf die Konfiguration von Block Copolymeren in Lösung.