RE-ORDER NO. 67-731

FINAL REPORT

to

Jet Propulsion Laboratory
Pasadena, California

Contract No. 951836
with the
University of Southern California
Report prepared by L. Utracki and R. Simha

Study of Solution Properties of Block Copolymers

December 29, 1967

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SUMMARY

The object of this work was to study the solution properties of the di and tri block copolymers of polybutadiene (PB) with polystyrene (PS) and other vinyl aromatic polymers (PVAr). The vinyl aromatic polymers of particular interest to the Jet Propulsion Laboratory were poly 1-vinyl naphthalene, poly 2-vinyl naphthalene, and polyvinyl biphenyl. Their solution properties have seldom been investigated, if at all, and the data therefore are not complete. As it is meaningless to study the copolymers without knowledge of the parent polymers, we found it necessary first to study in detail the solution properties of PVAr's. The results are summarized in the attached abstract entitled "Comparative Studies of the Solution Properties of Vinyl Aromatic Polymers". The paper has been presented at the Third Western Regional Meeting of the ACS in Anaheim in October, 1967. The full text will be submitted to the publisher in the near future.

Due to great difficulties in the copolymerization of PVAr's with PB, we did not receive the samples for the study of block copolymers of this type, and therefore further work was devoted exclusively to the investigation of the solution properties of the PS + PB di and tri block copolymers.

For the study the three solvents chosen were those which at 34.2°C are either good solvents for both the PS and PB block, or a good solvent for one while a near Θ-solvent for the other. The results of these studies are summarized in a paper entitled "The Solution Properties of Polystyrene - Polybutadiene Block Copolymers", which will be presented at the ACS Meeting in San Francisco in March, 1968. The text has been sent to Polymer Preprints, as required.

Finally, as a result of the study of polystyrene - polybutadiene block copolymers we developed a new theoretical approach to the solution properties of block copolymers in general. This new theory is discussed in detail in the last paper,

which is entitled "Polymethylmethacrylate - Polystyrene Block Copolymers in Solution". In the paper we show that the theory is applicable to the system. Comparison of the long range polymer - polymer parameter with the tacticity of the polymethylmethacrylate blocks shows clear correlation. This explains the conflicting reports on the solution properties of this copolymer and ends the long lasting confusion.

COMPARATIVE STUDIES OF THE SOLUTION PROPERTIES OF VINYL AROMATIC POLYMERS**

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ABSTRACT

The solution properties of three vinyl aromatic polymers (PVAr), poly-1-vinylnaphthalene (P1VN), poly-2-vinylnaphthalene (P2VN) and polyvinylbiphenyl (PVB), were studied. The characteristics of the anionic samples are shown in Table I. The M_w's and the heterogeneity ratios M_w/M_n were determined by gel permeation chromatography (GPC) at Stanford Research Institute.

The following experiments were carried out: I. The [η] measurements in benzene in the temperature range of 20-75°C; II. Differential scanning calorimeter thermograms in the temperature range of 0-230°C and scanning rate range of 0.625-80°C/min.; III. The viscosities of low concentration benzene solutions of PVAr and polystyrene samples (PS) in a sealed viscometer in the temperature range of 5-80°C; IV. X-ray diffraction spectra for P1VN and P2VN samples; V. NMR spectra of concentrated CCl_4 solutions of P2VN in the temperature range of 13-80°C.

In a separate series of measurements, the stability of PVAr has been checked. We found that the polymers are relatively stable at room temperature.

** This work was supported by a contract (No. 951836) between the Jet Propulsion Laboratory and the University of Southern California.

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In Table I we show $[\eta]$ and Huggins constant data for all samples. In all cases $[\eta]$ diminishes with T. For P2VN-benzene an upswing of the relation at $t_2 \cong 46^\circ C$ has been noted. In order to study this phenomenon more closely a sealed viscometer has been constructed in which the efflux times of PVAr and PS solutions have been recorded every $5^\circ C$ from $5^\circ C$ up to $80^\circ C$ and back. As the result we found that $(\partial \ln \eta_{sp}/\partial T)_{c=const.}$ changes its value at $t_1 \cong 20$ and $t_2 \cong 50^\circ C$ for all these systems. Next we turned to study the NMR spectra for P2VN-68. The t_1 and t_2 transitions have been recorded here on the plot of spin-spin relaxation time T_2 vs. temperature and on the plot of the ratio of the population of H_α and H_β nuclei to $H_{Aromatic}$. On the basis of these measurements we were able to conclude that the t_1 transition is associated with reconfiguration of large parts of the macromolecule, whereas t_2 is associated with reconfiguration of the relative position of naphthalene rings in respect to the $=CH_2$ groups of adjacent chains. The X-ray diffraction spectra for P1VN indicated spatial distances of 1.94 Å and 4.1 Å, in accord with Natta's[1] 3_1 helix model for this polymer. For P2VN only 1.94 Å spacing was visible as the amorphous band was very strong. The activation energy of the t_2 transition, as calculated from NMR data[2], $\Delta F = 23 \pm 7$ kcal/mol. is of the order of magnitude observed for the order-disorder transition[3]. There are indications in the literature[4] that at temperatures similar to those for PVAr ($t_2 \cong 40$-$70^\circ C$) similar transitions have been observed for a number of polymers, such as polystyrene, polymethamethacrylate, polyethylene, polypropylene, etc. It seems to be reasonable to assume that the t_2 transition is associated with the same energy barrier of the main -C-C- chain, compensated by the thermal energy $R(t_2 + 273)$.

From the $[\eta]$ data using the Stockmayer-Fixman relation[5] we calculated the short and long range interaction parameters A and B and their temperature dependence as well. The plot of A vs. t for all three PVAr systems showed a transition at $t_2 \cong 40\text{-}60^\circ C$. The values of the conformational parameter $\sigma = A/A_f$ (where A_f is a value of the A parameter for a freely rotating model) at t = 30°C are shown in Table II along with the values of the derivative $(d\ln A^2/dt)$ in two ranges of temperature. The B values for P2VN and PVB analyzed according to the relation $B = B_o(1 - \Theta/T)$ gave unreasonably high values for Θ and low values for B_o. Only the parameters for P1VN (shown in Table II) were of the usual order of magnitude. This may be due to aggregation in the P2VN and PVB systems.

Finally, in Table II we show the values for the molecular volume of the pendant group for each of our polymers. It has been observed[6] that the σ's for a homologous series of polymers are a linear function of V_x, and that the slope of this relation $(d\sigma/dV_x)$ is constant for all series. The data presented in Table II follow this rule.

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TABLE I

Intrinsic viscosity $[\eta]$ and Huggins parameter k_1 of PVAr as a function of temperature t.

Sample	$M_w \cdot 10^{3*}$	M_w/M_n*	t = 20		t = 30		t = 45		t = 65		t = 75	
			$[\eta]$	k_1	$[\eta]$	k_1	$[\eta]$	k_1	$[\eta]$	k_1	$[\eta]$	k_1
P1VN-59	155.3	1.14	0.383	0.44	0.379	0.44	0.375	0.45	0.368	0.43	0.361	0.48
P1VN-66	147.3	1.48	0.367	0.38	0.364	0.41	0.358	0.41	0.349	0.44	0.342	0.50
P1VN-88	103.4	1.05	0.271	0.45	0.268	0.48	0.264	0.57	0.254	0.46	0.248	0.60
P1VN-8036	52.2	1.06	0.155	0.46	0.151	0.47	0.146	0.61	0.142	0.75	0.140	0.78
P2VN-44	736.1	1.55	1.073	0.36	1.059	0.36	1.025	0.39	1.011	0.39	1.001	0.39
P2VN-70	563.4	1.88	0.886	0.36	0.864	0.38	0.842	0.40	0.827	0.40	0.808	0.45
P2VN-58	306.1	1.41	0.667	0.34	0.656	0.41	0.633	0.39	0.634	0.32	0.626	0.35
P2VN-48	182.5	1.29	0.456	0.41	0.446	0.43	0.433	0.45	0.434	0.39	0.430	0.34
P2VN-68	64.0	-	0.211	0.47	0.207	0.49	0.196	0.57	0.194	0.43	0.193	0.44
P2VN-61	48.9	-	0.180	0.50	0.177	0.50	0.170	0.58	0.168	0.51	0.165	0.48
PVB-63	1104	2.15	1.342	0.33	1.326	0.36	1.289	0.37	1.262	0.35	1.215	0.36
PVB-41	706.5	2.06	0.927	0.35	0.917	0.34	0.914^{50}	0.36^{50}	0.908	0.36	0.897	0.35
PVB-71	169.4	1.45	0.375	0.56	0.370	0.53	0.369	0.55	0.363	0.50	0.360	0.43
PVB-56	103.0	1.52	0.243	0.48	0.242^{25}	0.53^{25}	0.239	0.52	0.237	0.53	-	-
PVB-51	80.8	1.26	0.217	0.48	0.214^{35}	0.48^{35}	0.213	0.56	0.212	0.39	0.210	0.42
PVB-8036	10.5	-	0.069	0.55	0.070	0.56	-	-	0.070	0.51	-	-

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* GPC data supplied along with samples through the courtesy of Dr. J. Moacanin.

TABLE II

Unperturbed dimensions of PVAr and PS in benzene.

Polymer	σ_{30}	$(d\ln A^2/dt)\cdot 10^3$		$B_o\cdot 10^{27}$ cm^3	Θ °C	V_x
		$t < t_2$	$t > t_2$			
P1VN	2.45	-1.51	-3.21	1.22	-89	137
P2VN	2.39	-1.29	-0.13	-	-	137
PVB	2.62	0.01	1.33	-	-	180
PS	2.20	-1.8 - +0.6	-	4.72	-173	90

THE SOLUTION PROPERTIES OF
POLYSTYRENE - POLYBUTADIENE BLOCK COPOLYMERS[†]

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ABSTRACT

The dilute solution viscosity and osmotic pressure measurements were conducted on polysytrene (PS), polybutadiene (PB), polystyrene-polybutadiene (SB) diblock copolymer and polysytrene-polybutadiene-polystyrene (SBS) three block copolymer. Samples were anionicly polymerized in such a way that the molecular weight of the PS block was kept constant ($\sim$10,000), while the molecular weight of the PB block varied from 18,000 to 450,000. The measurements were carried out at a temperature of 34.20°C. For the study three solvents were selected: toluene, which is a good solvent for PS as well as for PB, dioxane, which is a good solvent for PS and near-Θ- solvent for PB, and cyclohexane, which is nearly a Θ-solvent for PS and a good solvent for PB. In order to check the compositions of SB and SBS, UV spectra were taken of their solutions in $CHCl_3$. The viscosity and osmotic pressure results indicate that properties of SB and SBS are similar. Their intrinsic viscosities and second virial coefficients can be calculated from their chemical compositions, properties of parent polymers, and values of the interaction parameter between styrene and butadiene units ($\overline{\beta}_{SB}$). The magnitude of $\overline{\beta}_{SB}$ varies with the solvent, due to resulting configurational changes of the blocks (i.e., number of intersegmental contacts). The PS and PB blocks are randomly coiled and their domains overlap to a great extent.

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† This work was supported by the Jet Propulsion Laboratory, California Institute of Technology, and sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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POLYSTYRENE - POLYBUTADIENE BLOCK COPOLYMERS†

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INTRODUCTION

Previously reported studies on the solution properties of block copolymers are almost entirely devoted to polystyrene-polymethylmethacrylate (SM) copolymers in various solvents. The results are often contradictory. While some authors[1,2] found that the intrinsic viscosities [η] and chain dimensions of block copolymers are larger than those of homopolymers, others[3-5] made the opposite observation. Inagaki[6] tried to explain this apparent contradiction by showing that if the data for copolymers are grouped into two classes, the first being for samples containing 46-62 wt% of polystyrene (PS) and the second for all other compositions, then a regular change of properties with change of molecular weight within these classes is observed. However his observation cannot be generally valid, since when it is applied to limiting low contents of one of the parent polymers, it gives false results. In spite of the controversy, all authors agree on a very similar model for the configuration of the copolymer molecule in solution; it possesses an overall segment distribution similar to the parent polymer coils, and the domains of chemically different blocks in the coil are separated.

One of the most important parameters which governs the solution properties of block copolymers is the polymer 1 - polymer 2 average or apparent interaction parameter $\bar{\beta}_{12}$. Here again the authors' opinions vary. While most of them[1-4,7] agree on a positive value for this parameter, recently[5] a negative value has been reported as well as[8] $\bar{\beta}_{12} = 0$.

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There are a number of factors responsible for these conflicting observations and conclusions. A copolymer molecule (linear and homogeneous in respect to molecular weight!) is characterized by its molecular weight (M), composition (v) and size of the blocks. From the practical point of view it is very difficult to prepare a large series of samples in which one of the parameters will be constant. Moreover, the only theory[7] of block copolymer configuration in solutions is a generalization of Fixman's theory[9] and in consequence it can be used only when all long range interaction parameters $\beta \to 0$. Unfortunately β_{12} for noncompatible polymers is relatively large[6,10].

The reasons for starting this investigation of the solution properties of PS-polybutadiene (PB) block copolymers were both practical and theoretical. The lack of knowledge of the solution properties of this copolymer eliminated the solution measurements as a method of control of industrial products. Also, it was quite interesting to investigate a system in which the bulky PS chains were connected with flexible PB chains of very low coil density. It has been reported recently[11] that liquid crystals in solutions of PS-PB block copolymers appear at rather high concentration. This would indicate that at infinite dilution this system should behave more regularly than SM, and the theoretical calculations should be more straightforward.

We were fortunate in being able to design our series of samples, taking into account that when PB and polyisoprene are copolymerized with PS of $M_{PS} \gtrsim 10{,}000$, the resulting copolymers exhibit very good mechanical properties[12,13]. The M_{PB} in our series was varied, and of course the composition and the molecular weight of the samples varied along with it.

Toluene, dioxane and cyclohexane were chosen as solvents. Respectively their Mark-Houwink-Sakurada exponents[14] for PS are reported as 0.72 at 30 - 40°C, 0.692 at 34°C, and 0.50 at 34.4°C, and for PB, 0.725 at 30°C, 0.5 at 34°C, and 0.70 at 20 - 40°C. The temperature 34.2°C was chosen for all our measurements as an intermediate between the two reported Θ-temperatures.

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EXPERIMENTAL

The polystyrene-polybutadiene (SB) and the polystyrene-polybutadiene-polystyrene (SBS) samples were kindly synthesized for us by Dr. L. J. Fetters at the National Bureau of Standards. The method of polymerization has been described previously[12] in detail. The samples were dissolved in benzene containing 0.02 wt% N-phenyl 2-naphthylamine (PNA) as antioxidant, filtered under N_2 pressure and precipitated by adding the solution to vigorously stirred MeOH-"dry ice". Subsequently the samples were dried for two weeks at room temperature under high vacuum. They were stored under high vacuum in darkness.

Reagent grade solvents were purified further in a normal way by washing, drying and rectification on a high efficiency packed column. The purity was checked by boiling point and refractive index values. To prevent any possible oxidation of the PB chain during the measurements, PNA was added to all of the solvents (0.02 wt%), and N_2 was used to flush the air out and to move the solutions in the viscometer. Preliminary runs with and without PNA showed no difference in the values of measured quantities.

The $[\eta]$ measurements were carried out in a Hewlett-Packard auto viscometer model 5901B equipped with a constant temperature bath, programmer and printer. Cannon-Ubbelohde dilution viscometers calibrated by means of NBS Standard Viscosity Oils were used.

The determinations of M_n and the second virial coefficient A_2 were made on a Mechrolab high speed membrane osmometer model 503 with adjustable temperature control unit. In order to check the PS content in SB and SBS samples, UV spectra on a Beckman DK-2A spectrophotometer were taken of their $CHCl_3$ solutions. A calibration curve was determined using the 2600 Å band.

RESULTS

The characteristics of the samples are shown in Table I. The PS samples are the same as those measured by McCormick[15] and his values for M_n are included. The slightly smaller values reported here are probably due to the lack of permeation through the membrane of the low molecular weight components in the high speed, compensation type instrument used by us. In column 2 the M_k values refer to the "kinetic M", i.e., to the M calculated prior to the polymerization. For SB and SBS samples M_k's are shown for each block in the sample. From these values the w_k's (wt% PS in the sample) were calculated. Column 3 shows the average M_n values calculated from independent determinations of M_n in three solvents. In column 5 the actual weight percent of PS in the sample is shown. These values were determined by a UV method described by Burnett, Evans and Melville[16] and recommended as the most reliable technique for this purpose[2]. The maximum absorption coefficient $E_{max} = 2.21 \pm 0.02$ calculated from our calibration curve is in excellent agreement with the previously reported[16] values of 2.16 ± 0.07 and 2.20 ± 0.05. With few exceptions the agreement between the predicted w_k and measured w values is very good. From the comparison of w_k with w and M_k with M_n values we conclude that the polymerization ran as desired to produce homogeneous samples as far as molecular weight and chemical composition are concerned. Finally, in the last column of Table I we present the molar fractions of PS in the samples.

The results of osmotic pressure and viscosity meausrements are shown in Table II. The M_n and A_2 values were calculated from the square root plot[17]. The $[\eta]$ and Huggins and Kraemer constants k_1 and k_2 were calculated using a previously published method[18]. Theory predicts that $k_1 + k_2 = 0.5$. The experimental values for this sum as 0.50 ± 0.02, indicating correct experimental and mathematical procedures. Also the M_n values determined in the three solvents show very good reproducibility. The standard deviation in this case is less than 2%.

The $[\eta]$ data from Table II are shown in Fig. 1. According to the Stockmayer -

Fixman equation[19]

$$[\eta]/M_n^{1/2} = \phi(A^3 + 0.51\ B\ M_n^{1/2}) \tag{1}$$

where ϕ is Flory's universal constant at Θ-conditions, and A and B are short range and long range interaction parameters respectively. Eq. (1) was found to hold[20] in the systems where $[\eta]/[\eta]_\Theta \leq 2.8$.

Similarly in Fig. 2 the A_2 values from Table II are plotted according to the equation[21]

$$A_2 M_n^{1/2} = 1.65\cdot 10^{23}\ A^3 + 0.968\cdot 10^{23}\ B\ M_n^{1/2} \tag{2}$$

This relation has limited applicability, as it should not be applied to systems where $[\eta]/[\eta]_\Theta < 2.4$. From the last two equations it is possible to calculate A and B.

DISCUSSION

If the copolymer coils have a random configuration, then eqs. (1) and (2) can be generalized by redefining the interaction parameters. The relations between A and B and their equivalents per unit segment are

$$a_i = A_i M_{oi}^{1/2} \quad \text{and} \quad b_i = B_i M_{oi}^{2}, \quad i = S \quad \text{or} \quad i = B,$$

where M_{oi} is the molecular weight of a statistical segment. Then for randomly coiled[22] copolymer A_{SB} and B_{SB} we have:

$$A_{SB} = [a_S\ x + a_B(1-x)]M_{oSB}^{-1/2} \tag{3a}$$

$$B_{SB} = [\beta_S\ x^2 + \quad 2\ \bar{\beta}_{SB} x(1-x) + \beta_B(1-x)^2]M_{oSB}^{-2} \tag{3b}$$

where $$M_{oSB} = M_{oS}x + M_{oB}(1-x)\ . \tag{3c}$$

The parameter $\bar{\beta}_{SB}$ defines the average interactions between PS and PB segments. If the overall configurations of the PS and PB blocks remain constant, or if the copolymer is statistical, not a block, or if the segments are not bound, the $\bar{\beta}_{SB}$ should have a value independent of the solvent power. In our case configurations of the block are expected to be different from one solvent to another and $\bar{\beta}_{SB}$ should vary accordingly. If we define a new parameter β_{SB} as the interaction parameter for a system in which all units are mutually available for interactions, then $\bar{\beta}_{SB} = X\beta_{SB}$, where X is a fraction of contacts available.

In Table III we show the values of K_0 defined by the relation:

$$[\eta]_\theta = K_\theta M^{1/2} = \phi A^3 M^{1/2}$$

and parameters A_i, a_i, B_i and β_i for PS and PB homopolymers. They were calculated directly from the data of Table II using eqs. (1) and (2). As we stated before, eq. (2) can be applied only to polymer - good-solvent systems. The values of A and B calculated from eq. (2) are consistently larger than those calculated from eq.(1). This was observed by other authors as well[21]. Having established the parameters of parent polymers we calculated values of

$$\Delta\beta = \bar{\beta}_{SB}x(1-x) \tag{4}$$

for each sample. In Fig. 3, the points represent these values, while the curves are drawn according to eq. (4), using the $\bar{\beta}_{SB}$'s shown in the last two lines of Table III. The very good agreement between the experimental results and the results predicted by eqs. (3b) and (4) indicate that the fundamental assumptions of the randomness of PS and PB coils and of the interpenetrations of their domains are correct. In all cases $\beta_{SB} > 0$. Judging from their high numerical values, the fraction X of PS - PB contacts is large. This too must mean that the interpenetration of domains is quite extensive.

Having established the values of $\bar{\beta}_{SB}$, now we can calculate the theoretical molecular weight dependencies of $[\eta]$ and A_2 from eqs. (1) - (3). The broken lines in Figs. 1 and 2 are computed for copolymer molecules with two M_{PS} = 10,000 blocks, the chain line in Fig. 1 was computed for a copolymer with one M_{PS} = 10,000 block in toluene only. The agreement between experimental and calculated values again is very good.

At present it is impossible to predict if the method applied here will be of general use. Even limiting ourselves to the same system, i.e., SB and SBS in the investigated solvent, we cannot answer this question. It should be expected that values of $\bar{\beta}_{SB}$ will change with change in the size of the PS block. The method must break down in the systems where intermolecular precipitation of micella formation[3] occurs.

Nevertheless, eqs. (1) - (3) can be used for interpretation of some MSM - solvent data. For instance it can be shown that the condition for finding a negative value for the polymer-polymer interaction parameter χ_{AB} by Froelich[5] is

$$\bar{\beta}_{SM} < 2(\beta_S + \beta_M) .$$

It is to be expected that this condition will be fulfilled in the systems with separated domains of component blocks.

ACKNOWLEDGEMENT

The authors are indebted to Dr. L. J. Fetters for the synthesis of the samples and to Mrs. V. Schneider for determination of their compositions.

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TABLE I

Characteristics of polymer samples.

Sample	$M_k \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	w_k (%PS)	w (%PS)	x
PS 1	78.1[1]	78	----	----	----
PS 2	147[1]	137	----	----	----
PS 3	222[1]	201	----	----	----
PB 1	∿20	17.8	----	----	----
PB 2	18	28.6	----	----	----
PB 3[2]	95	33.0	----	----	----
PB 4	66	74.4	----	----	----
PB 5	39	75.6	----	----	----
PB 6[3]	∿120	156	----	----	----
PB 7	160	423	----	----	----
SB 1	10+20	43.1	33.3	32.9	0.1131
SB 2	10+65	105	13.3	17.8	0.0533
SB 3	10+93	129	9.71	12.3	0.0352
SB 4	10+400	625	2.44	3.59	0.00956
SBS 1	7.5+18+7	34.8	44.6	45.9	0.1811
SBS 2	10+24+10	44.8	45.5	45.5	0.1783
SBS 3	7.5+28.6+8.8	54.8	36.3	36.6	0.1299
SBS 4	10+49+10	69.8	29.0	30.1	0.1005
SBS 5	10+100+10	117	16.7	20.7	0.06336
SBS 6[2]	14+62+14	141	31.1	40.2	0.1486
SBS 7	10+115+10	170	14.8	11.6	0.03292
SBS 8	10+450+9	517	4.05	4.05	0.01082

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[1] Values reported by H. W. McCormick, ref. 15

[2] Samples extracted from a partially insoluable batch of a branched material.

[3] Crack in the reactor, prior to completion of the polymerization.

TABLE II

Solution properties of homopolymers and block copolymers in toluene, dioxane and cyclohexane at 34.2°C.

Sample	$M_n \cdot 10^{-3}$			$A_2 \cdot 10^4$ (cgs)			[n] (dl/g)			k_1			k_2		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
PS 1	77.8	77.6	78	5.43	5.11	-0.061	0.403	0.383	0.237	0.34	0.34	0.54	0.17	0.16	-0.04
PS 2	139	139	135	4.99	4.73	-0.041	0.601	0.571	0.335	0.33	0.41	0.54	0.18	0.09	-0.02
PS 3	196	196	210	4.46	4.48	-0.071	0.805	0.747	0.384	0.34	0.36	0.55	0.16	0.14	-0.03
PB 1	18.2	17.9	17.4	19.4	3.81	18.3	0.353	0.256	0.353	0.39	0.50	0.42	0.13	0.00	0.09
PB 2	28.5	28.6	27.7	17.2	3.95	15.6	0.499	0.332	0.490	0.39	0.54	0.42	0.13	-0.02	0.11
PB 3	33.0			16.3			0.309			0.51			-0.01		
PB 4	74.4			15.1			1.138			0.38			0.14		
PB 5	76.3	76.3	74.3	14.1	2.85	12.5	0.974	0.593	0.870	0.36	0.53	0.39	0.15	-0.01	0.11
PB 6	155.0		156	12.4		10.5	2.770		2.57	0.35		0.37	0.15		0.13
PB 7	466	434	370	11.5	1.49	9.48	4.38	1.73	3.83	0.38	0.71	0.45	0.13	-0.18	0.06
SB 1	43.0	43.6	42.6	12.6	5.80	10.0	0.566	0.393	0.510	0.37	0.41	0.38	0.14	0.05	0.11
SB 2	104	108	103	11.5	2.72	9.60	1.318	0.736	1.18	0.38	0.54	0.39	0.13	-0.04	0.11
SB 3	129	130	129	11.9	3.41	10.3	1.521	0.838	1.41	0.40	0.52	0.39	0.12	-0.04	0.11
SB 4	625	610	625	8.17	1.64	7.55	6.065	2.59	5.59	0.35	0.59	0.35	0.15	-0.07	0.15
SBS 1	34.6	34.0	35.8	12.5	6.63	10.1	0.442	0.333	0.406	0.43	0.36	0.43	0.11	0.14	0.07
SBS 2	45.5	44.2	44.8	12.7	5.99	9.40	0.546	0.392	0.477	0.36	0.39	0.40	0.14	0.11	0.10
SBS 3	54.9	54.7	54.7	12.0	5.62	9.53	0.665	0.458	0.585	0.35	0.47	0.40	0.15	0.03	0.10
SBS 4	69.0	69.2	71.2	12.3	4.48	10.2	0.861	0.539	0.788	0.40	0.71	0.33	0.11	-0.21	0.15
SBS 5	118	115	118	11.7	3.87	9.64	1.45	0.811	1.33	0.41	0.50	0.40	0.09	-0.01	0.10
SBS 6	141		141	10.2		8.54	1.25		1.03	0.36		0.42	0.13		0.10
SBS 7	173	170	169	11.4	2.16	9.56	1.90	0.983	1.79	0.42	0.48	0.37	0.08	0.03	0.13
SBS 8	516		517	9.57		8.69	7.52		6.72	0.39		0.39	0.11		0.11

1 - in toluene
2 - in dioxane
3 - in cyclohexane

TABLE III

Interaction parameters

Solvent		Toluene		Dioxane		Cyclohexane	
Parameter and method	Polymer	PS	PB	PS	PB	PS	PB
$K_\Theta \cdot 10^3$	(η)	0.920	1.76	0.920	1.76	0.920	1.76
	(π)	1.33	2.54	1.33	----	----	2.54
A (Å)	(η)	0.684	0.830	0.684	0.830	0.684	0.830
	(π)	0.733	0.960	0.733	----	----	0.960
a (Å)	(η)	4.94	3.05	4.94	3.05	4.94	3.05
	(π)	5.29	3.53	5.29	----	----	3.53
$B \cdot 10^{27} (cm^3)$	(η)	1.45	4.87	1.09	1.08	-0.07	4.30
	(π)	3.12	8.87	3.06	----	----	7.31
β ($Å^3$)	(η)	3.91	0.888	2.95	0.197	-0.203	0.784
	(π)	8.44	1.62	8.27	----	----	1.33
$\bar{\beta}_{SB}$ ($Å^3$)	(η)	3.76		2.63		3.49	
	(π)	5.80		----		----	

Note: (η) Parameter values calculated from [η] data.

(π) Parameter values calculated from A_2 data.

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LEGENDS FOR FIGURES

Fig. 1 - Molecular weight dependence of intrinsic viscosity. Full lines represent the experimental data for homopolymers, while points represent data for copolymers. Broken lines are calculated from eqs. (1) and (3) for SBS in three solvents; the chain line for SB in toluene.

Fig. 2 - Molecular weight dependence of A_2. Full lines represent the data for homopolymers.

Fig. 3 - The magnitude $\Delta\beta$ as a function of molecular fraction of PS in the copolymer molecule. Points are experimental. The lines were calculated from eq. (4) using $\bar{\beta}_{SB}$ shown in Table III.

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Fig. 1

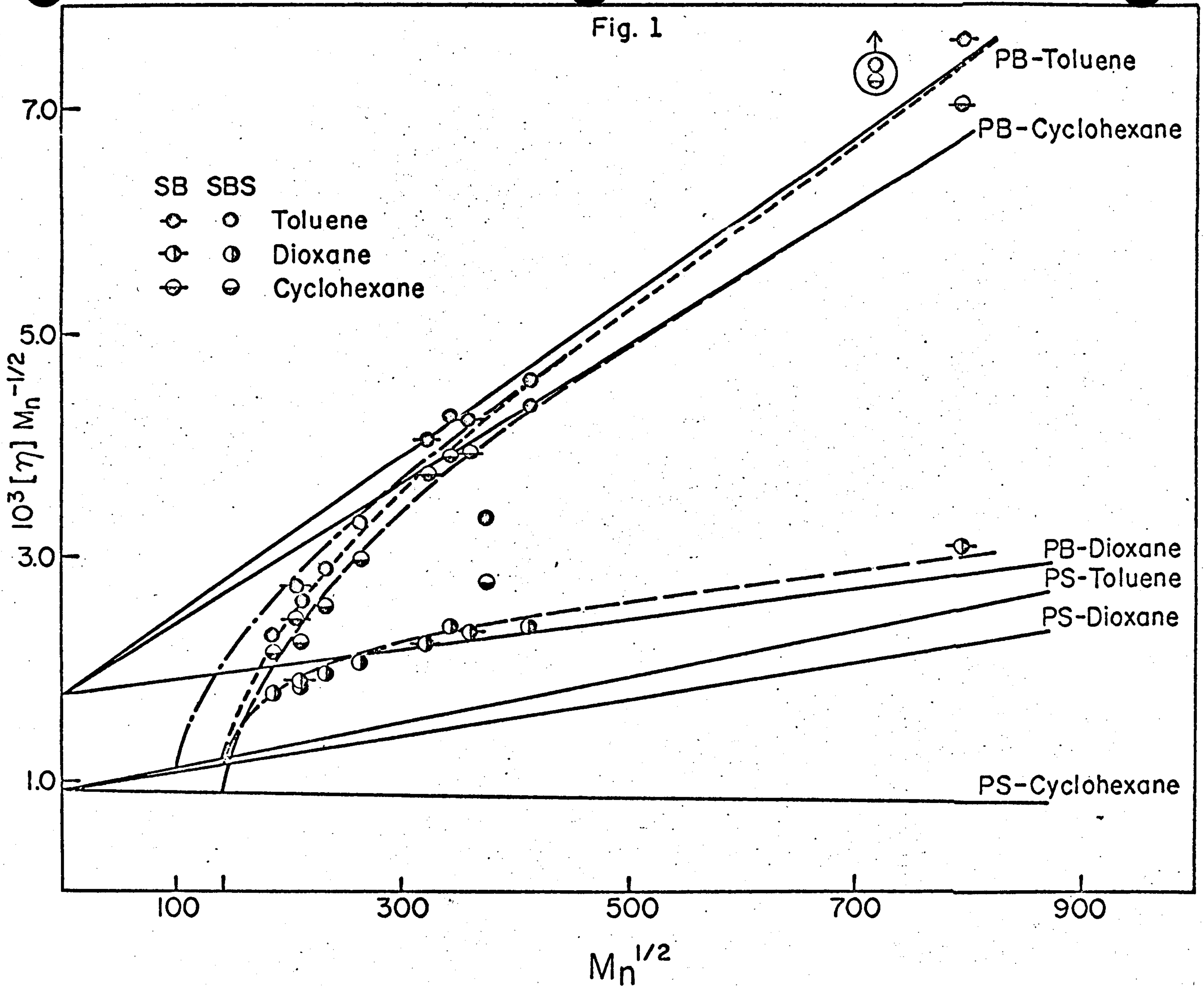
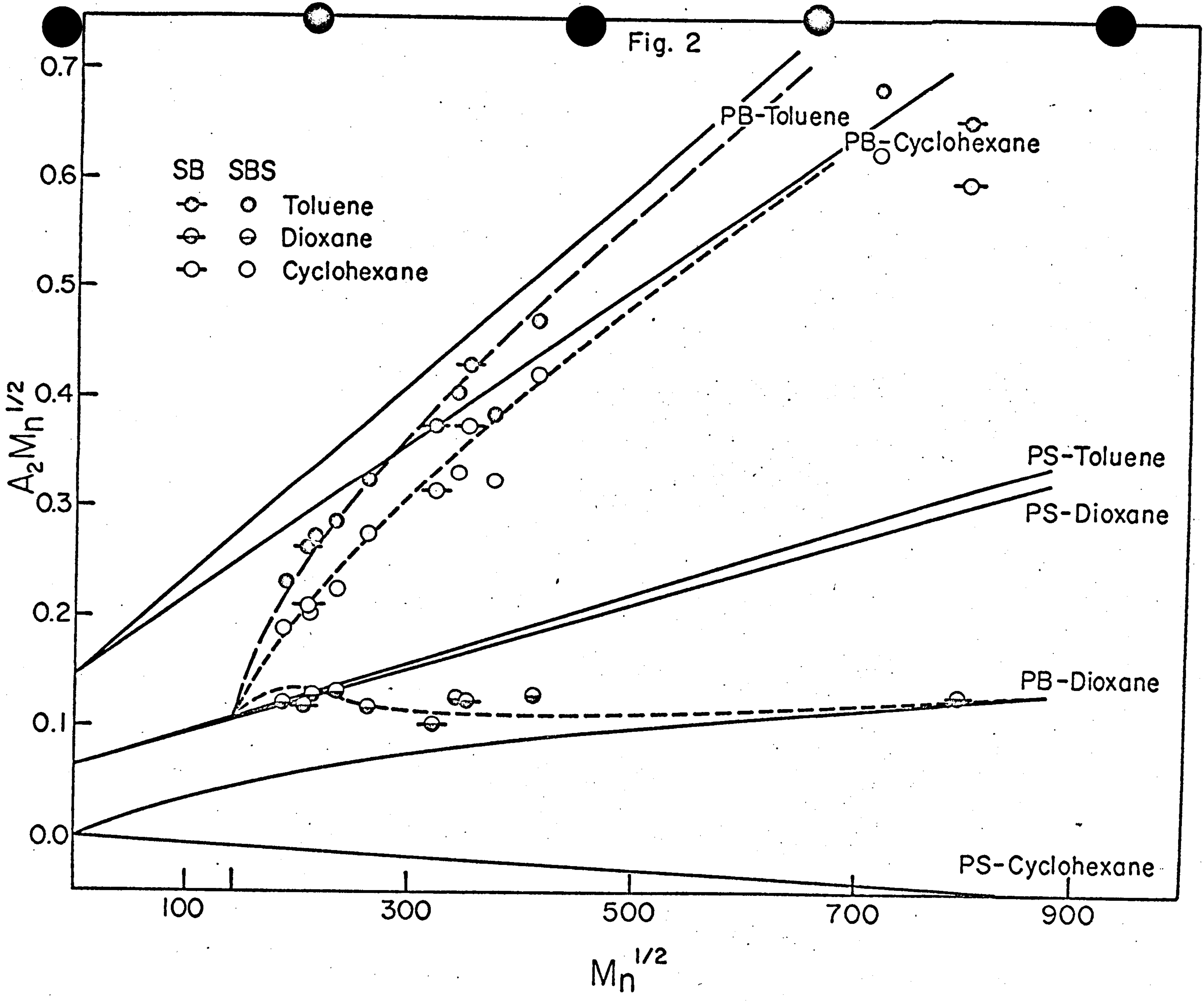
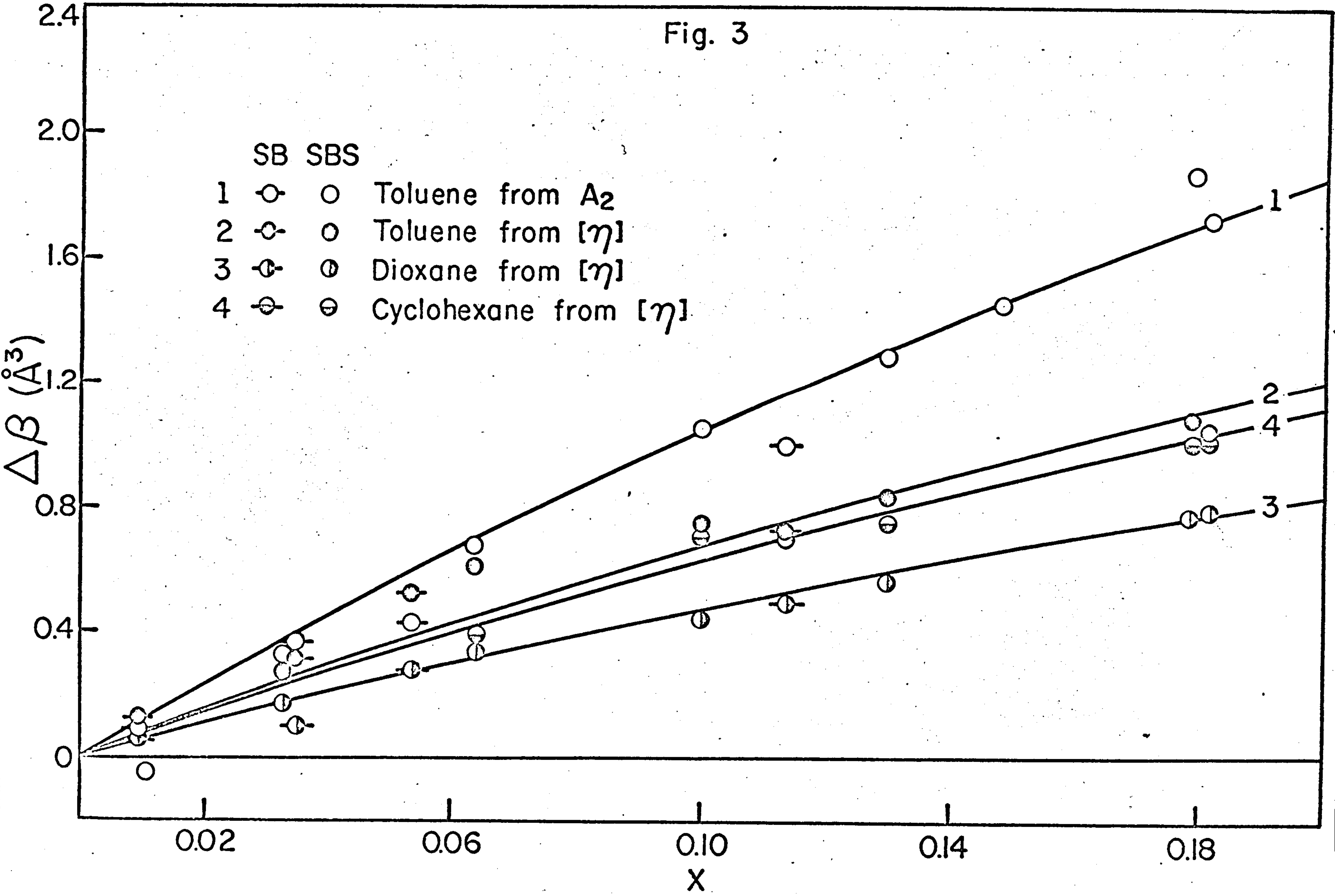

SB SBS
Toluene
Dioxane
Cyclohexane
PB-Toluene
PB-Cyclohexane
PB-Dioxane
PS-Toluene
PS-Dioxane
PS-Cyclohexane
8
7.0
5.0
3.0
1.0
$10^3[\eta]\,M_n^{-1/2}$
100
300
500
700
900
$M_n^{1/2}$

Fig. 2



SB SBS
Toluene
Dioxane
Cyclohexane
PB-Toluene
PB-Cyclohexane
PS-Toluene
PS-Dioxane
PB-Dioxane
PS-Cyclohexane
$A_2M_n^{1/2}$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
100
300
500
700
900
$M_n^{1/2}$

Fig. 3


SB SBS
1 Toluene from A_2
2 Toluene from $[\eta]$
3 Dioxane from $[\eta]$
4 Cyclohexane from $[\eta]$
$\Delta\beta$ (Å^3)
2.4
2.0
1.6
1.2
0.8
0.4
0
0.02
0.06
0.10
0.14
0.18
X
1
2
4
3

POLYMETHYLMETHACRYLATE - POLYSTYRENE BLOCK COPOLYMERS IN SOLUTION[†]

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ABSTRACT

A new method of calculation of the interaction parameters of block copolymers in solution is presented. The method is based on the definition of the θ-condition as that in which all long range interactions vanish. Consequently all the specific properties of block copolymers, i.e., the conformational and configurational characteristics of their chains, are incorporated in the polymer-polymer interaction parameter. Therefore detailed study of this parameter should allow one to deduce the prime characteristic properties of the copolymer molecule.

This new method has been applied to the intrinsic viscosity data of polymethylmethacrylate - polystyrene block copolymers in benzene and toluene. The numerous and conflicting reports on the properties of this polymer in solution have been interpreted by us as resulting from the differences in the tacticity of polymethylmethacrylate blocks. For a series of samples in which the tacticity does not vary much, the polymer-polymer interaction parameter is independent of the composition.

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† This work was supported by the Jet Propulsion Laboratory, California Institute of Technology, and sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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POLYMETHYLMETHACRYLATE - POLYSTYRENE BLOCK COPOLYMERS IN SOLUTION†

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INTRODUCTION

The solution properties of block copolymers have been investigated for fifteen years. The most frequently used copolymers for this study are di- or tri-block copolymers of poly(methyl methacrylate) (PMMA) and polystyrene (PS). When interest in this field arose, the properties of these two polymers were the best known. Parallel to the study of the block copolymers, new methods of synthesis were developed and better defined samples produced. In spite of this, the solution data for copolymers reported by different authors are not less confusing.

While Burnett et al.[1] found that the coil size of the copolymer molecule is always larger than that of either of the homopolymers and passes through a sharp maximum at ca. 56 wt.% of PS, the data of Krause[2] and Inagaki, et al.[8] indicate that the size of copolymer coil is smaller or equal to that of the homopolymers and random copolymer of equivalent molecular weights (M). While most of the authors[1,3,4] found strong repulsive forces acting between PMMA and PS segments, others[2,5,6] reported the effect to be either insignificant or even opposite[7]. Inagaki[9] postulated that if intrinsic viscosity values, $[\eta]$, are plotted according

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to the Stockmayer - Fixman equation[10], all the data can be approximated by two straight lines; one line for the samples with PS content from 46 to 62 wt.%, and the other for all the other compositions. Both lines have lower intercepts and higher gradients than those of the homopolymers. However this observation cannot be generally valid as all the data for samples with low content of either PS or PMMA should fall on the same second line, for which the parameters vary widely from the parameters observed for the respective homopolymers.

Theoretical treatment of the data for block copolymers is very difficult as even the basic thermodynamic parameters are not well defined. For instance, the most frequently used method of determining the unperturbed dimensions of the copolymer coil is to measure the $[\eta]$ at $T = \Theta$, defined by the condition $A_2 = 0$. It has been shown that for block copolymers the Θ-temperature defined in this manner varies with composition[8], with size of the blocks[11] (while the composition and the molecular weight of the samples are kept constant), and with chemical nature of the solvent[12]. It must follow that the Θ-temperature defined as above, even for a given series of samples with constant composition or constant block size of one polymer, must depend on the molecular weight. Ergo, this definition does not permit one to establish a unique, characteristic temperature for a copolymer-solvent system, equivalent to the Θ-temperature of homopolymers. It must yet be decided what we want to call the Θ-temperature and Θ-dimension of a copolymer coil. The Θ-dimensions, as defined by $A_2 = 0$, (i.e., by the condition that the long range interactions in the system are being mutually compensated, will vary with T, M, and composition, w, (wt.%)), will have to be established separately for each sample at its individual Θ-temperature.

On the other hand it is possible to define the Θ-dimensions as equivalent to the sum of the unperturbed dimensions of the blocks in the particular range of temperatures and in the solvent of particular chemical nature. While the first definition demands that the net effect of the long range interactions is zero, the second demands that all the long range interactions are zero.

CALCULATIONS

Recently[13] we applied a new method for calculation of the solution parameters of block copolymers based on the second definition of the Θ-conditions and found it quite adequate for the system. Let us recapitulate the main points of the method. As a consequence of the definition of the Θ-condition we can write that[14]

$$a_{cop}^2 = \sum_i^n x_i a_i^2 \qquad i = 1,2,\ldots,n \tag{1}$$

where n is a number of chemically different polymer blocks in the sample, x_i is a molar fraction of the polymer i and

$$a_i^2 \equiv A_i^2 M_{oi} \qquad \text{and} \qquad A_i^2 \equiv \langle r_\Theta^2\rangle_i / M_i$$

($\langle r_\Theta^2\rangle_i^{1/2}$ is the root mean square of the end-to-end distance), while M_i and M_{oi} are the molecular weight of a polymer i in the copolymer sample and molecular weight of the statistical segment of i-th polymer, respectively. Defining the molecular weight of the statistical segment of the copolymer molecule as follows:

$$M_{o\,cop} = \sum_i^n x_i M_{oi} \tag{2}$$

we can calculate the short range interaction parameter, A_{cop}, for copolymer molecules in a manner similar to that used for homopolymers;

$$A_{cop}^2 = a_{cop}^2 / M_{o\,cop} \tag{3}$$

The above treatment describes the solution properties of a copolymer in the absence of any long range interactions, both solvent-polymer type and polymer-polymer type. This situation is not likely to be found in practice and the long range effect must be taken into account.

Let us define the long range interaction parameter for copolymer in solution in terms of pairwise interactions only as

$$\beta_{cop} \equiv \sum_{i}^{n} \beta_i x_i^2 + \Delta\beta = B_{cop} M_{o\,cop}^2 \tag{4a}$$

where $\beta_i \equiv B_i M_{oi}^2$, B_i being the long range interaction parameter between a statistical segment of polymer i and the solvent. The magnitude $\Delta\beta$ encompasses all the effects of mutual polymer-polymer interactions;

$$\Delta\beta \equiv 2\sum_{i}^{n} \beta_{ij} x_i x_j \qquad i,j = 1,2,\ldots,n \tag{4b}$$

As long as we do not demand that β_{ij} = constant, the above treatment can be applied to any solvent-polymer system. The properties and characteristics of the system will be reflected in the nature and magnitude of the β_{ij}'s. The above equations are valid for polymer mixtures in solution as well as for solutions of copolymers of different types. It is clear that the parameter β_{ij} will depend on two main factors; on the magnitude of the interaction parameter β_{ij}^* between isolated statistical segments of polymer i and polymer j in an ideal contact, and on the fraction of the number of such contacts occurring in the investigated system opposed to the number of all possible contacts, X_{ij}, i.e.,

$$\beta_{ij} = X_{ij} \beta_{ij}^*$$

It must be further expected that both parameters X_{ij} and β_{ij}^* will vary from one system to another. The different geometry of the polymer molecule should be reflected in the changes of X_{ij}, while the temperature and the chemical nature of solvent and polymer blocks will be responsible mainly for changes of β^*_{ij}. Moreover, only if the geometry of the polymer coil is independent of composition x_i, should the X_{ij} be constant. In the case of block copolymers the changes in X_{ij} and in β^*_{ij} should be expected. Changing from one copolymer-solvent system to another, one should expect a different dependence of $X_{ij} = X(x_{ij})$; if the blocks are randomly coiled and the domains of blocks of different chemical nature are separated[2,7,8], then the function will differ from that for the system in which internal precipitation at some x_i occurs[2,12]. Only in the case where the domains are randomly packed and interpenetrated can the β_{ij} be expected to be independent of x_{ij}.

The above method may be compared to the one proposed by Froelich and Benoit[5] (F.-B.). Their result for random copolymer is similar to eq. (4). For the block and graft copolymers the $X_{ij} = X(x_{ij})$ can be evaluated from their proper equations. There are two important differences between the two methods. F.-B. base their calculations on the theoretical calculations of Fixman[15], which are valid only for the near Θ-conditions, i.e., only when β_i and β_{ij} are close to zero, whereas the above method does not require such drastic conditions to be obeyed, and secondly F.-B. assume parabolic dependence of the ratio B/A^3 on the composition, whereas we use different dependences for short and long range interaction parameters.

Knowing the molecular weight of the copolymer sample, its composition and its parameters of interactions we can calculate any of its solution properties. If we limit ourself to the case of solvent-polymer 1 - polymer 2 we would need only one β_{12} interaction parameter besides those for the homopolymers (such parameters are usually available in the literature). In any case we will need a relation between the desired property and the interaction parameters valid in the proper range of conditions. Let us narrow our interest further to the intrinsic viscosities $[\eta]$ of block copolymers.

It has been shown[16] that the Stockmayer-Fixman relation[10]

$$[\eta]/M^{1/2} = \Phi_o(A^3 + 0.51\ B\ M^{1/2}) \quad , \qquad (5)$$

(where $\Phi_o = 2.87 \cdot 10^{21}$ is the Flory constant in θ-conditions and $[\eta]$ is in dl/g) can be used for the calculation of A and B in systems in which $[\eta]/[\eta]_\theta \leq 2.8$. If so, eq. (5) combined with relations (1) - (4) should allow us to calculate β_{12} from the $[\eta]$ of a copolymer of known molecular weight and chemical composition. Furthermore, it should be possible to study the nature and magnitude of this parameter as a function of composition and block structure of the copolymer molecule. As the most numerous data are available for the block copolymer of PS and PMMA, we will limit our computation to this polymer only.

RESULTS

In Table I we present the $[\eta]$'s for PMMA - PS (MS) and for PMMA - PS - PMMA (MSM) di- and tri- block copolymers in toluene and benzene at 25°C and 30°C as reported in the literature. In the sixth column the values of $B_{SM} \equiv \bar{\beta}_{SM} M_o^{-2}{}_{SM}$ are listed for each sample. The dependence of B_{SM} on composition (w in wt.% of PS) is shown in Fig. 1. The values of B_{SM}'s were calculated from eqs. (1) - (5) using the values of M and w shown in Table I and the values of the interaction parameters listed in Table II. These were calculated from the data reported for atactic homopolymers in the indicated solvent and temperature. The B_S parameter for PS in benzene and toluene was found to be the same within the range of experimental error.

In the last line of Table I the B_{SM} for the random copolymer of PS and PMMA in butanone at 30°C is shown. In this case the $[\eta]$'s were replotted according to eq. (5) and then the A_{cop} and B_{cop} were calculated from the intercept and the slope. The intercept value $K_\theta \equiv \Phi_o A^3 = 8.4 \cdot 10^{-4}$ agrees well with the value computed directly from A's for homopolymers ($K_\Theta = 8.5 \cdot 10^{-4}$). The B_{cop} enabled us to calculate the B_{SM} shown in Table I and in Fig. 1; the limits were calculated assuming $M_w/M_n = 1$ for the lower limit, and $M_w/M_n = 1.2$ for the upper. Because in all other cases (except for ref. 2 samples) molecular weights are given as M_n, the upper value rather should be taken into account in further considerations.

DISCUSSION

From observation of the data in Fig. 1, we see that no regular change of B_{SM} with composition can be observed. More detailed comparisons of B_{SM} and size of the block and/or type of copolymer (MS vs. MSM) indicate that these parameters also do not determine the variation of B_{SM}. Similarly the method of computation does not introduce any factor which can be responsible for this behavior. The only possible explanation must lie in the difference of methods for determination of the $[\eta]$'s and M_n's and/or in the differences in the properties of the samples, other than those previously discussed. Judging from the data in Fig. 1, we must conclude that the range of variation of B_{SM} is larger than can be attributed to the usual experimental errors in $[\eta]$ and M.

Differences in the properties of the samples may be of two types; molecular weight distribution and tacticity. Even though sharp fractions were used in all cases, a difference in heterogeneity of the order of 20% could be observed. From the size of the mark in Fig. 1 for random copolymer in butanone, we can see the difference in B_{SM} introduced by a change in heterogeneity of 20%. Again this factor cannot explain the large variation in B_{SM}.

To examine the last possible source of the differences, namely the tacticity, let us look more closely into the mechanism of polymerization of the investigated samples. These are summarized in Table III. It is well known that PS polymerized by radical and/or anionic solution methods has an atactic structure. On the other hand the tacticity of PMMA strongly depends on the method of polymerization and here lies the probable explanation.

The radical polymerization of methylmethacrylate (MMA) at room or at higher temperatures leads to a product containing ca. 5% iso- (i), 38% hetero- (h) and 57% syndio- (s) tactic diads[22,23]. Similar results are obtained if an anionic polymerization is initiated by potassium. In fact the polymerization of MMA at 30°C initiated by K - naphthalene in THF has been recommended as the method of preparation of a "truly atactic" PMMA[24], characterized by an IR index of J = 70 and composition of i = 23%, h = 47% and s = 30%. The same authors report that the polymerization at low temperature (-78°C) under these conditions gives products characterized by J = 71, which indicates a slight increase in the content of syndiotactic isomer. If so, the samples investigated by Dondos, et al.[6] and by Froelich[7] should have a tacticity similar to the radically polymerized samples of Burnett et al.[1] and to those of Inagaki, et al.[8] In effect, the B_{SM}'s calculated for these radical and anionic samples should have similar values. This indeed is observed in Fig. 1. The B_{SM} for these samples vary from $0.87 \cdot 10^{-27}$ to $1.74 \cdot 10^{-27}$, i.e., in the limit quite acceptable in view of differences in structure, solvents, heterogeneity of copolymer samples, and other factors. Two samples, #2 and #3 in Table I, exhibit different properties not only from those of the other "atactic" samples but also from sample #1 of the same authors. As samples #2 and #3 are a fraction of one batch of polymer, while sample #1 is a fraction from another, one can only suspect that these two batches were polymerized in a different manner and the polymers have different structures.

From Fig. 1 we see that Krause's[2] data lead to very low values of B_{SM} consistent within the group. It is known from the earlier work[25] that PMMA, formed under the conditions at which her samples were polymerized, contains large amounts of tactic material (J = 90) and that the size of the syndiotactic blocks is large as indicated by the high value of the gel melting point G = 49°C. If so it is to be expected that under the conditions of thermodynamic equilibrium, PMMA blocks will tend to aggregate[26]. This statement can be further supported by reported[25] gel formation which occurs after 30 minutes of copolymerization of these samples. If the aggregation between copolymer molecules is valid, then the value of M_w determined by the light scattering method must be heavily weighted by the size of the aggregates. On the other hand if the aggregates have only an intramolecular character, M_w will remain unchanged, while the coil volume should diminish. Probably both effects are present, as $[\eta]$'s are smaller than they should be for the established M_w, and as the net result the B_{SM}'s calculated for these samples are much lower than for the others.

Finally let us examine the results calculated from the data of Urwin and Stearne[3]. Their very carefully prepared samples were polymerized anionicly. The polymerization of MMA in THF at -78°C was initiated by living PS. From the conditions specified by the authors one should expect the PMMA block to be highly syndiotactic[24], and the B_{SM} for these samples should be different from those calculated either for "atactic" samples or for the samples in which aggregation occurs.

On the basis of the above analysis we conclude that the differences in the behavior of different samples of MS and/or MSM can be justified as induced by the variation of the tacticity of PMMA blocks. The internal precipitation within the polymer coil observed by Krause[2] can be explained as the effect of intramolecular aggregation[27] of syndio- and iso-tactic parts of PMMA blocks, not as an effect of PS-PMMA interaction. The high values of B_{SM} calculated from the Urwin and Stearne data are probably caused by highly syndiotactic PMMA blocks. As the short range and long range parameters for syndio and atactic PMMA in solution do not differ much[28], the high values of B_{SM} must reflect the true interactions between PS and PMMA segments, which are apparently much stronger for syndio PMMA than iso- and in effect atactic PMMA. This should be expected; the isotactic PMMA chain is much stiffer and more tightly coiled (5_2 helix) than the syndiotactic (10_4 helix). From the conformational and configurational reasons, the number of contacts between PS and i-PMMA must be smaller than for PS and s-PMMA, or smaller for PS and atactic-PMMA than for PS and s-PMMA. It follows that B_{SM} should be smaller in the first case than in the second, which in fact has been observed.

The value of $B_{SM} = 1.2 \cdot 10^{-27}$ (cm^3) calculated for random copolymer in butanone falls very close to the B_{SM} values calculated for the block copolymer with "atactic" PMMA segments. This interesting fact cannot be weighted heavily as we do not know what the solvent effect on B_{SM} is and how polymer-polymer interactions in random and block copolymers are related to one another. One can expect that random copolymer PS-PMMA should have larger B_{SM}'s than those calculated for PS - h-PMMA block copolymer samples. We note that the B_{SM}'s for random and for block PS - "atactic" PMMA copolymers are comparable in magnitude. This may be due to the partial syndiotactic character of the "atactic" PMMA blocks, which increases the values of B_{SM} for block copolymers (see the reported compositions for corresponding PMMA's given above). The important fact is that in both cases the intersegmental PS-PMMA interactions are large ($\beta_{SM} \overset{\sim}{=} 3 \cdot 10^{-24}$), being comparable in magnitude to the polymer - good solvent interactions. This must indicate that the entropic effect of polymer-polymer interaction is large and that the domains of chemically homogeneous parts of the block copolymer are well interpenetrated by one another.

If we accept that the variation of B_{SM} is mainly due to the variation of the tacticity of the PMMA segment, then any meaningful conclusion relating to B_{SM}'s dependence on w can be reached only if one considers a series of samples in which the tacticity of the PMMA segments is constant. From the presented data we see that in this case B_{SM} remains independent of w as well as of block size and/or type of block copolymer within experimental error. This again can be considered as an indication of the absence of any presently detectable domains and/or structures in the copolymer molecules.

The same conclusions have been reached previously[13] for PS - polybutadiene - PS (SBS) block copolymer in three solvents. Recently, through the courtesy of Dr. Keelen of the Shell Chemical Co., Torrance, California, we received data on the measurement of $[\eta]$'s in toluene at 30°C for a series of SBS samples in which M was kept constant while the compositions varied from 13 to 80 wt.% of PS. Here too $\bar{\beta}_{SB}$ was found to be constant. The $[\eta]$'s calculated from eqs. (1) - (5) for this series agreed with the experimental data within ±2%.

The results and discussion presented in this paper are of very preliminary nature. Much more information on well characterized samples is needed before any general conclusions can be reached. The detailed study must show a variation of B_{SM} with composition, with the nature of the solvent, with the size of the blocks and with other parameters as well. Ultimately one should be able to relate B_{SM} (or β_{SM}) to the conformation and configuration of the polymer and to the absolute magnitude of the interaction forces. At the present time it seems fair to state that the proposed method of calculation of the solution data of block copolymers with β_{ij} = constant can be used with good success in many cases. For each system the constancy of the interaction parameter should be carefully checked.

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LEGEND FOR FIGURE

Fig. 1 - Long range interaction parameter B_{SM} vs. PS content. Data from Table I. For details see text.

TABLE I

The intrinsic viscosities of MS and MSM copolymers.

No.	$M_n \cdot 10^{-3}$	w (wt.% of PS)	Solvent and Temp.	$10^3[\eta]/M_n^{1/2}$	$B_{SM} \cdot 10^{27}$ (cm^3)	Ref.
1	229	64	I	1.73	1.40	1[a]
2	259	56	I	2.83	4.38	1[a]
3	316	50	I	2.54	3.21	1[a]
4	368*	72	II	0.93	-1.45	2
5	690*	79	II	1.26	-1.26	2
6	1150*	60	II	1.56	-0.18	2
7	2960*	25	II	0.81	-1.19	2
8	187	48	I	2.05	2.91	3
9	225	62	I	2.18	2.87	3
10	302	70	I	2.32	2.80	3
11	390	85	I	2.40	3.16	3
12	400	65	III	2.11	1.71	6[a]
13	603	52	III	1.97	1.08	6[a]
14	345	51	III	2.03	1.83	7[a]
15	36	46	I	1.09	0.85	8
16	37.4	31	I	1.05	0.89	8
17	36	46	I	1.09	0.85	12
18	317	50	I	1.62	0.97	12
19	509	43	I	2.05	1.50	12
20	530	48	I	2.11	1.50	12
21	Random copolymer*	46.4	Butanone, 30°C	(12 samples)	0.95 - 1.20	4

* M_w, calculated from light scattering.

I - Toluene, 25.0°C; II - Toluene, 30°C; III - Benzene, 30°C.

a MS copolymers (the others MSM type).

TABLE II

The short and long range interaction parameters

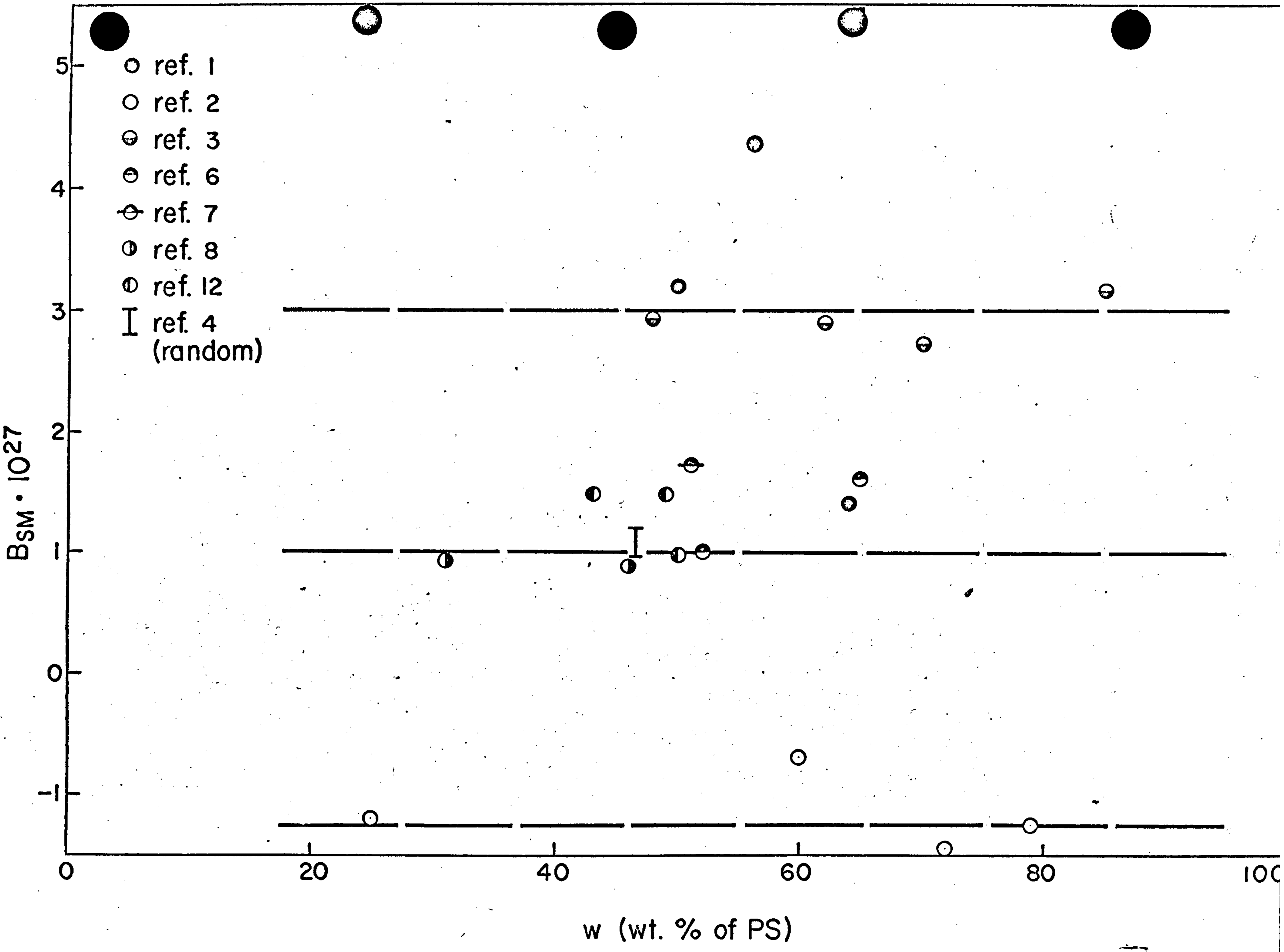
for PS and PMMA in solution.

No.	Polymer	Solvent	Temp. (°C)	A (Å)	$B \cdot 10^{27}$ (cm^3)	Ref.
1	PS	Toluene	25	0.70	1.05	17
2	PMMA	Toluene	25	0.64	0.68	18
3	PS	Benzene	30	0.70	1.05	17
4	PMMA	Benzene	30	0.64	0.91	19
5	PS	Butanone	22	0.70	0.17	20
6	PMMA	Butanone	25	0.64	0.48	21

TABLE III

Polymerization methods of PMMA blocks in MS and MSM samples.

No.	Initiator	Solvent	Temp. (°C)	Copolymerization	Ref.
1	PS-OOH	H_2O (emulsion)	8	PS-OOH purified and dried before second stage of polymerization	1
2	Na-PS-Na (initiated by Na-naphthalene)	THF	-78	MMA added to "living" PS. Gel formed	2
3	Na-PS-Na (initiated by Na-biphenol)	THF	-78	"Living" PS added to MMA. No gel formation reported.	3
4	PS-K (initiated by phenyl isopropyl-K + α methyl styrene tetramere)	THF	-78	MMA added slowly to "living" PS	6,7
5	δδ' azobis(δ cyanopentanol)	DMF	100	Homopolymers purified and dried. Coupling by thionylchloride	8
6	anionic polymerization	?	?	?	12


ref. 1
ref. 2
ref. 3
ref. 6
ref. 7
ref. 8
ref. 12
ref. 4 (random)
$B_{SM} \cdot 10^{27}$
5
4
3
2
1
0
-1
0
20
40
60
80
100
w (wt. % of PS)