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Preparation and Properties of Polydimethylsiloxane and Its Block Copolymers with Styrene

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ABSTRACT: A series of polydimethylsiloxanes and two-block copolymers with styrene of reasonably narrow molecular weight distribution has been prepared using the monomer hexamethylcyclotrisiloxane. The initiator was *sec*-butyllithium. Evidence was found for a low level of side reactions which results in the molecular weight distributions becoming broader at very high molecular weights. Similarly block copolymers with $M > 2 \times 10^5$ were contaminated with both homopolymers. Purification methods to remove the homopolymers are described. The solution properties of polydimethylsiloxane agreed in general with earlier studies which used fractions produced by polymerization of octamethylcyclotetrasiloxane. The intrinsic viscosities of the block copolymers are, unlike those of styrene–isoprene two-block copolymers, greater than the average of those of the homopolymers. This suggests greater segregation of the two types of segment. The optical properties of the block copolymers are rather unusual. Refractive index increments of the two types of segment are markedly different and in toluene opposite in sign. The overall refractive index increment can therefore be rather small and the P_θ function under these conditions greater than unity at finite angles. Zimm plots of unusual form are then observed. These effects are explained in terms of the Benoit theory of light scattering from block copolymers.

The catalyzed ring opening polymerization of octamethylcyclotetrasiloxane (D_4) to form high polymers is a well-known reaction.[2a] The polymerization is of the equilibrium type and besides linear polymer, cyclic structures of which the monomer (D_4) is a major constituent exist in solution. A recent communication[2b] has stressed the use of hexamethylcyclotrisiloxane (D_3) as monomer. It is claimed that under certain conditions it polymerizes to give linear polymer of negligible cyclosiloxane content at a much more rapid rate. A suitable initiator is butyllithium which can be mixed with D_3 in hydrocarbon solvents to form $Bu{\cdot}Si{\cdot}(CH_3)_2OLi$.[3] No polymerization occurs even in the presence of excess D_3 until a donor solvent such as tetrahydrofuran is added, when a reasonably rapid polymerization starts to give near monodisperse polymers.[2b] Equilibration reactions do occur[4] but these are slow compared with the polymerization rate and so can be minimized by termination of the reaction before complete conversion. Block copolymers can be prepared by the replacement of butyllithium with polystyryllithium.[5-7]

This investigation describes the preparation and characterization in solution of a series of homopolymers and block copolymers of polydimethylsiloxane. Extensive studies of solution properties of styrene–methyl methacrylate and styrene–diene block copolymers can be found in the literature. In some respects the styrene–dimethylsiloxane polymers would be expected to possess interesting properties but a detailed description has not until now been disclosed.

Experimental Section

D_3 obtained from Pierce Chemical, Aldrich Chemical, or supplied by Dr. P. Juliano, General Electric Co., was first zone refined over 40 cycles. The top 75% of the column was then transferred to a flask containing calcium hydride. The flask was evacuated and benzene was distilled in to form a 40% solution which became slightly viscous after standing overnight. Solvent and monomer were distilled off in vacuo. The residue contained some polymer. A solution of polystyryllithium was added via a break-seal to the D_3–benzene mixture. After 1 hr the latter compounds were sublimed off and the solution was subdivided into break-seals. These had previously been washed with butyllithium in benzene followed by rinsing with the solvent. The purification of benzene and tetrahydrofuran (THF) to the standards required for anionic polymerization has been described in earlier publications.[8,9] 1,2-Bis(2-methoxyethoxy)ethane (Triglyme/Eastman) was twice distilled from sodium metal followed by transferral to the vacuum line where it was treated with sodium–potassium alloy before distillation into ampoules. *sec*-Butyllithium prepared in vacuo from *sec*-butyl chloride and lithium metal was purified by a short path distillation in vacuo, diluted, and subdivided into ampoules. The ampoules for initiator and triglyme were cleaned by the same procedure described above for the break-seals.

All polymerizations were carried out in a sealed vacuum apparatus using conventional break-seal techniques. First the *sec*-butyllithium and D_3 were mixed in benzene at 30° and allowed to react for 3 hr. At this point either an equal volume of tetrahydrofuran or enough triglyme to form a 4% (v/v) solution was added. The initial concentration of D_3 was 5–10%. Polymerization at 30° was allowed to proceed to 50–75% conversion until terminated by the addition of a small amount of chlorotrimethylsilane. The lower conversions were used in the preparation of polymers of higher molecular

Table I
Physical Properties of Polydimethylsiloxanes

Sample	M_n (calcd)[a]	M_n	M_w	$[\eta]_{Tol}^{35°}$	$[\eta]_{CH}^{35°}$	$[\eta]_{MEK}^{20°}$	$[\eta]_{BCH}^{28°}$	$\langle S_0^2\rangle_z^{BCH} \times 10^{12}$
H3		16,800	17,300	0.117	0. 127	0.099	0.089	
12a	24,400	24,500	(25,200)[b]	0.156	0.178	0.127	0.115	
9	45,600	46,300	46,400	0.240	0.278	0.186	0.169	
7b	94,000	89,200	92,200	0.388	0.462	0.259	0.239	
11	199,000	178,000	205,000	0.665	0.81	0.390	0.357	
21b	342,000		372,000	1.026	1.255	0.543	0.484	3.0
22b	374,000		444,000	1.16	1.44	0.585	0.532	3.7
23b	700,000		886,000	1.91	2.41	0.865	0.752	8.5

[a] Calculated from initiator and monomer consumed. [b] Estimated using $M_w/M_n = 1.03$.

weight to keep broadening of the distribution to a minimum. The resultant solutions were freeze dried, redissolved in benzene containing sodium bicarbonate, and precipitated in methanol. The bicarbonate was found to be necessary since traces of HCl formed in methanol by hydrolysis of excess terminating agent caused some broadening of the molecular weight distribution. Polymers were finally dried in vacuo at 50° to constant weight.

Block copolymers were prepared by first polymerizing styrene with *sec*-butyllithium in benzene. Eighteen hours were allowed at 30° to complete the polymerization. THF was then added to form a 0.1 *M* solution followed by D_3 solution. The absorption band of polystyryllithium at 335 nm disappeared completely within 10 min. More THF was then added to give a 50% solution (or 4% triglyme). At about 50% conversion of D_3, polymerization was terminated and the polymer was isolated as described above. The purity of the block copolymers was analyzed by density gradient ultracentrifugation. A 60/40 v/v mixture of cyclohexane and carbon tetrachloride was used to detect homopolystyrene contaminant and a 78/22 mixture of toluene and bromocyclohexane for homopolydimethylsiloxane content. The presence of about 1% of polystyrene or 3-5% of polydimethylsiloxane could be detected by this technique.

Measurements of solution properties of the polymers were carried out as described earlier,[10-12] the Fica-50 instrument alone being used for light scattering studies. Gel permeation chromatography determinations were made using a Waters 301 instrument equipped with eight 3-ft columns of nominal pore size 60, 500, 3×10^3, 10^4, 3×10^4, 10^5, 3×10^5, 10^6 Å. The solvent used was toluene. Both columns and detector were thermostatted at 35°. Samples (4 mg) were injected via a 2 ml loop. Cyclohexane, cyclohexene, and toluene were purified as described earlier.[12,13] Methyl ethyl ketone was dried over K_2CO_3 and subsequently fractionated in a 100-plate column. Bromocyclohexane was dried over Na_2SO_4 followed by fractionation at 20 mm of pressure. Both the latter solvents showed negligible quantities of impurities in gas chromatographic analysis.

Results

(a) Homopolymers. It was established by isolation and weighing of the polymers at various times of reaction that D_3 disappears according to a first-order law at least up to 95% conversion. Half-lifetimes were about 2 hr in the 50% THF solutions and 4 hr in the triglyme experiments. A plot of the first-order constants thus obtained against stoichiometric lithium concentration shows that the reaction order in active centers is fractional, and of the order of 0.25 to 0.35. A more detailed kinetic study would be required to assess the order more exactly. This behavior is obviously connected with self-association of the active centers. A noticeable decrease in solution viscosity is produced by addition of the terminating reagent. It is known that *tert*-butoxylithium is highly associated in hydrocarbon solvents ($n \sim 6$) and even in ether solvents the degree of association is about four.[14] The chemically similar lithium silanates would be expected to show similar degrees of association. It is possible that the mechanism suggested for polymerization of polystyryllithium in benzene applies[9] and that the true active species is the small amount of dissociated product.

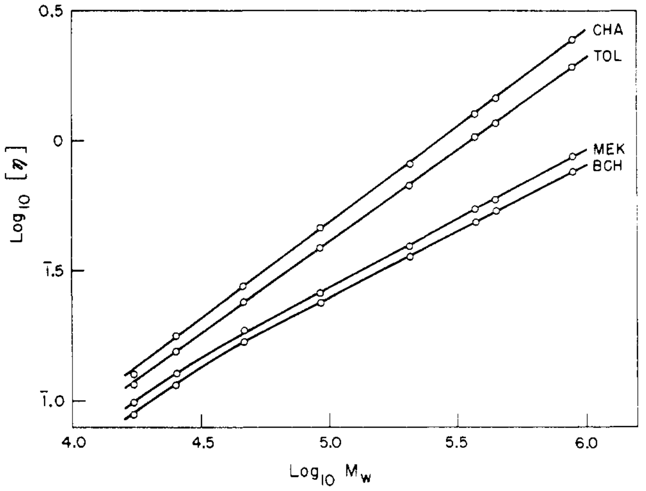

Figure 1. Intrinsic viscosity-molecular weight relationships for polydimethylsiloxane in (top to bottom) cyclohexane (35°), toluene (35°), methyl ethyl ketone (20°), and bromocyclohexane (28°).

Gel permeation chromatography of the homopolymers produced gives apparent M_w/M_n values (uncorrected for instrumental broadening) of around 1.1 in the molecular weight range 20,000-100,000 rising to about 1.2 at a molecular weight of 400,000. The highest molecular weight sample showed a ratio of almost 1.3. For comparison, polystyrenes produced by *sec*-butyllithium initiation in benzene give apparent M_w/M_n values which vary from 1.08 at the low end of the range to 1.15 at molecular weights close to 10^6 under the same experimental conditions. The polydimethylsiloxane polymers are therefore quite monodisperse up to $M = 200{,}000$ but some side reaction in the polymerization causes broadening which is more important the higher the molecular weight.

Molecular weight data and viscosities of polydimethylsiloxane in bromocyclohexane ($\theta = 28°$), cyclohexane and toluene at 35°, and methyl ethyl ketone at 20° are given in Table I. The viscosity results are plotted in Figure 1. In bromocyclohexane the experiments give $K = 7.9_5 \times 10^{-4}$ and $\alpha = 0.50$ for the molecular weight range 4×10^4-10^6. The intrinsic viscosities of the polymers of molecular weight less than 30,000 fall progressively more below the θ line as the molecular weight is reduced. Methyl ethyl ketone at 20° showed the same phenomenon but in addition was found not to be a θ solvent as previously reported having K and α values of 6.4×10^{-4} and 0.525. On the other

Table II
Physical Properties of Polystyrene–Polydimethylsiloxane Block Copolymers

Sample	M_n (calcd)[a]	M_n	M_w	x[b]	$[\eta]_{\mathrm{Tol}}^{35°}$	$[\eta]_{\mathrm{CH}}^{35°}$	$[\eta]_{\mathrm{MEK}}^{20°}$
13	18,500	17,800		0.535	0.135	0.130	0.117_5
14	32,600	34,000	36,000	0.568	0.211	0.190	0.174
15	90,000	87,000	100,000	0.471	0.430	0.386	0.306
5	143,000	156,000	185,000	0.735	0.684	0.474	
8	209,000	195,000	213,000	0.596	0.729	0.570	0.479
25			555,000	0.665	1.50	1.03	0.914
26			730,000	0.583	1.82	1.36	1.03

[a] Calculated from initiator and monomer consumed. [b] Weight fraction styrene.

hand the data in cyclohexane and toluene maintain the α value (0.735 and 0.703, respectively) down to the lowest molecular weights examined. The corresponding K values are 1.02×10^{-4} and 1.25×10^{-4}. Similar behavior was described by Brzezinski and coworkers.[15] A possible experimental cause for the behavior in bromocyclohexane could be an increase in the refractive index increment as molecular weight decreases. An appreciable effect of this type was described by Haug et al.[16] We were unable, however, to confirm this, the value determined (0.094 at 4358 Å) remaining constant within experimental error in the molecular weight range 1.7×10^4 to 4×10^5.

(b) Block Copolymers. The purity of the block copolymers formed is sensitive to the techniques used in their preparation. A critical point arises in the addition of D_3 to polystyryllithium. If instead of adding a little THF and D_3 to the polystyryllithium as described earlier the THF is omitted, then although a rapid disappearance of the polystyryllithium occurs at first, it slows down before complete conversion. A yellow color associated with an absorption band at 360 nm is still visible after 3 hr. This is not the normal absorption of polystyryllithium. In addition the isolated block copolymers even of low molecular weight contain about 20% of homopolystyrene and show an absorption band at 294 nm. With the procedure actually adopted, block copolymers of molecular weight up to about $M = 2 \times 10^5$ can be prepared essentially free of homopolymers. The ones of higher molecular weight unfortunately are not pure. Both homopolystyrene and homopolydimethylsiloxane are present in roughly equal amounts. This is probably caused not in the cross-over reaction but by subsequent side reactions of the growing siloxane chain.

The two copolymers of highest molecular weight were therefore purified. Homopolydimethylsiloxane is easily removed (at least for copolymers up to 70% siloxane content) by stirring a suspension of the block copolymer in *n*-hexane for 24 hr. The homopolydimethylsiloxane dissolves. This procedure is best repeated after an intermediate settling and centrifugation. Polystyrene is less easily removed. In this case, the polymer was dissolved in distilled dioxane containing 0.1% 4-methyl-2,6-di-*tert*-butylphenol to give a 1.3% solution. This was titrated with a 50/50 mixture of water and methanol until it became cloudy. After stirring for several hours the polymer was allowed to settle overnight. The supernatant was then decanted. The extraction process was repeated twice. These methods, in which the block copolymer forms the solid phase, were found to be superior to those described in the literature[5] involving precipitation of the homopolymer impurity. The high surface activity of solutions of siloxane containing polymers leads to difficult separations under these conditions.

After the above extractions the copolymers of high molecular weight were found to contain polystyrene and polydimethylsiloxane concentrations at or below the detectable limits. The schlieren patterns in the density gradient ultracentrifugation experiments still however showed the presence of an impurity of higher styrene content than the block copolymer itself as judged by its apparent density. It is clear that in fact in both the homopolymerization and copolymerization reactions there exist side reactions which become noticeable as chain lengths become longer.

The characterization of the block copolymers is summarized in Table II. Molecular weight determinations by light scattering were normally carried out in cyclohexane where the refractive index increment is reasonably high. Viscosity measurements were made in cyclohexane and toluene at 35° and in methyl ethyl ketone at 20°. Because of experimental difficulties (necessity of incomplete conversions, and of removal of homopolymers in some cases) the composition could not be controlled accurately as was possible in the styrene–isoprene case.[11] In toluene, a good solvent for both components, this is not too important, for the intrinsic viscosities of the parent homopolymers are quite close, so that $[\eta]$ of the block copolymers is not sensitive to small composition differences. A similar situation exists for methyl ethyl ketone, a poor solvent for both homopolymers. In cyclohexane the intrinsic viscosities of the homopolymers are widely different, so comparison of data is more difficult. Nevertheless, the intrinsic viscosities of the copolymers are higher than the weighted average of those of the homopolymers in both toluene and cyclohexane and in methyl ethyl ketone even a little higher than the viscosities of homopolystyrenes (Figure 2).

The light-scattering behavior of the block copolymers is somewhat unusual as is shown in Figures 3, 4, and 5. The refractive index increment of polystyrene is positive and that of polydimethylsiloxane is negative in many common solvents. In fact in toluene at 35° and at λ 4358 Å, the values are +0.112 and −0.104, respectively. Thus a block copolymer containing 47.5% styrene should have a zero refractive index increment (Figure 6) and hence would scatter no light at 0°, although some scattering would be expected at higher angles.[17] Even for compositions where dn/dc is small but not zero the amount of light scattered is predicted to increase with angle of observation.[18] As the refractive index increment becomes larger more normal behavior is expected. For copolymer 25, dn/dc is 0.041 in toluene, 0.096 in cyclohexene, and 0.115 in cyclohexane. An apparently negative radius of gyration is observed in toluene which becomes positive in the other two solvents (Figures 3–5).

Discussion

Under θ conditions the observed K_θ value for polydimethylsiloxane is in good agreement with previously determined values in bromocyclohexane[19] and methyl ethyl ke-

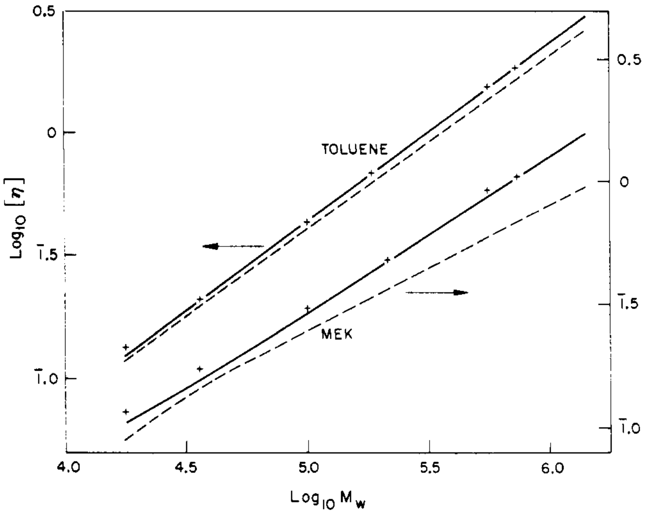

Figure 2. Intrinsic viscosity–molecular weight relationships for polydimethylsiloxane–polystyrene two-block copolymers compared with those for the two homopolymers: (—) polystyrene; (- - -) polydimethylsiloxane. Copolymer results shown as +. Upper, toluene (35°); lower, methyl ethyl ketone (20°). Polystyrene results obtained using the samples described in ref 12 plus two others of lower molecular weight prepared in a similar manner.

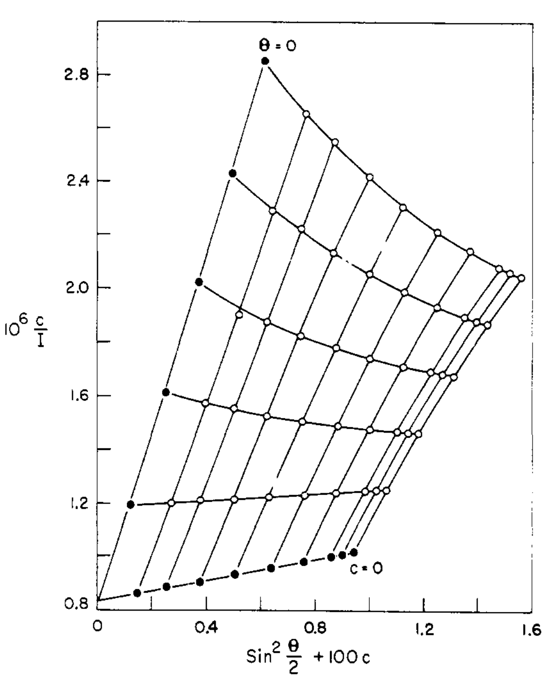

Figure 4. Zimm plot for copolymer 25 in cyclohexene (35°).

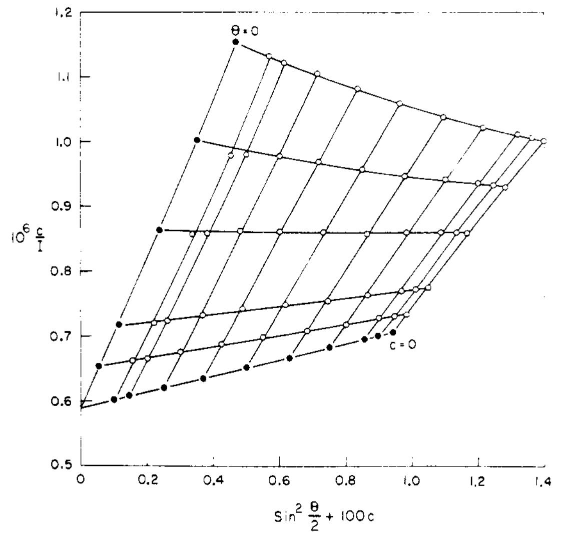

Figure 3. Zimm plot for copolymer 25 in cyclohexane (35°).

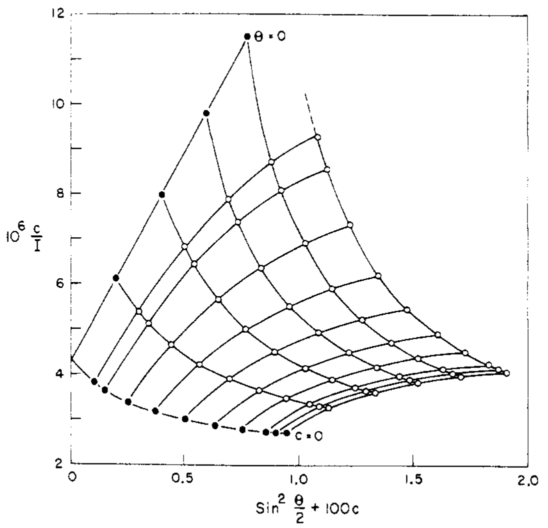

Figure 5. Zimm plot for copolymer 25 in toluene (35°).

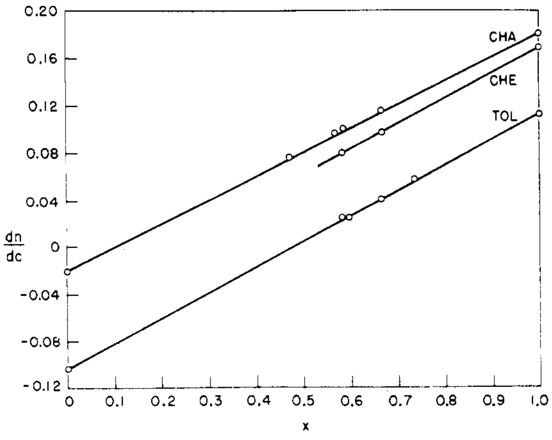

Figure 6. Refractive index increments for the block copolymers and homopolymers as a function of weight fraction of polystyrene. Top to bottom: cyclohexane, cyclohexene, and toluene, wavelength 4358 Å, 35°.

tone.[20] The present sample of methyl ethyl ketone behaved more like a poor solvent at 20° than as a true θ solvent. This behavior can perhaps be traced to differing impurity levels in the respective samples. The sharp decrease in $[\eta]_\theta$ below molecular weights of about 30,000 is unexpected and not usually observed. With polystyrene for example, the θ line of 0.5 slope is maintained at least down to a molecular weight of 15,000. As both the standard hydrodynamic theory and Gaussian-chain statistics of polymer chains become increasingly invalid at low molecular weights, some deviations can be expected which apparently depend on the exact nature of the polymer chain.[21]

Table I contains estimates of $\langle S_0^2 \rangle$ for the three polydimethylsiloxanes of highest molecular weight. These lead to values of $10^{18}\langle S_0^2 \rangle_z / M_w$ of 8.1, 8.3, and 9.5 $\mathrm{cm}^2/(\mathrm{g\ mol})$. The higher value is caused by the greater polydispersity of the sample of highest molecular weight. Its M_w/M_n ratio is probably close to 1.2 (1.27 by GPC) whereas the two of lower molecular weight have an M_w/M_n ratio close to 1.1.

Correction for polydispersity[22] yields a value of $10^{18}\langle S_0^2\rangle_w/M_w$ of 7.7 ± 0.3. This value is somewhat larger than that recorded earlier by Haug and Schulz, i.e., 6.3 ± 0.3,[16] and is very close to that reported for polystyrene[12] (7.9). K_θ is also very similar.

The solution properties of the block copolymers show some differences from those observed previously with styrene–isoprene two-block copolymers. In the latter case, the intrinsic viscosities were surprisingly close to the weighted average of those of the corresponding homopolymers although small positive deviations were noticeable in a poor solvent. The difficulties of interpretation of such results were emphasized.[11] In the present case, the intrinsic viscosities are definitely higher than the average and in the poor solvent methyl ethyl ketone even slightly higher than those of polystyrene of the same molecular weight. The situation seems to approach that observed with random copolymers whose intrinsic viscosities are considerably larger than those of the parent homopolymers due to unlike segment repulsions. The present results argue for a more marked segregation of the two types of segment than is the case for styrene–isoprene block copolymers. The expansion of molecular volume caused by this repulsion can be seen even in toluene for the intermolecular excluded volume as measured from second virial coefficients is higher than that of either homopolymer of the same molecular weight. This again contrasts with the situation observed for styrene–isoprene block copolymers where the virial coefficients were close to the weight average of those of the homopolymers. It is evident that these results are not unexpected since there is a larger difference in cohesive energy density or internal pressure between polystyrene and polydimethylsiloxane than between polystyrene and polyisoprene.[23]

The light-scattering behavior of the block copolymers at infinite dilution confirms the predictions of Benoit and coworkers.[18] In terms of the parameter $y = x\nu_A/\nu$ (where x and ν_A are the weight fraction and refractive index increment of polystyrene and ν the refractive index increment of the block copolymer) as y decreases the apparent radius of gyration should change from a high negative value through zero to positive values. The change-over point should, for equal radii of gyration of the two components, appear at $y = 1.21$. For copolymer 25 it would be closer to 1.3 because of the unequal composition. This assumes $\langle S^2\rangle/M$ in toluene for polydimethylsiloxane is about the same as for polystyrene as is evident from the viscosity results. For this copolymer the y values in toluene, cyclohexene, and cyclohexane are 1.82, 1.165, and 1.04, respectively. In cyclohexane, in fact, the measured radius of gyration is close to the radius of gyration of the polystyrene part of the molecule alone, a situation which applies exactly for $y = 1.0$.

Turning to the situation in toluene, at $x \sim 0.77$ the apparent radius of gyration should be zero. Copolymer 5 ($x = 0.735$) comes close to these conditions and in fact shows an unmeasurably small radius of gyration but this is in part caused by the fact that the true radius of gyration would be rather small ($M_w \sim 200{,}000$). As noted previously, at $x = 0.475$ in toluene the refractive index increment of the copolymer is zero, and no scattering should be observed at 0°, but scattering should increase rapidly at increasing angles to give a negative apparent radius of gyration much greater than the true one. Copolymer 15 comes close to these conditions ($x = 0.471$). We did find some light scattered at 0° of the order of 10% of the scattering from the solvent itself, which did increase rapidly with angle. It is clear however that with presently available techniques it is impossible to purify polymer solutions adequately enough to show exactly zero light scattering at 0°. The scattering envelopes at zero concentration in toluene can be estimated using formulas given by Benoit.[18] On the assumption that the $\langle S^2\rangle$ values for both types of segment are about equal to those in homopolymers of the same molecular weight, the experimental P_θ function can be reproduced qualitatively. For example, estimation of $10^{12}\langle S^2\rangle$ in toluene as 5.4 and 2.4 for polystyrene and polydimethylsiloxane segments in copolymer 25 leads to a predicted monotonic decrease in $1/P_\theta$ to 0.67 at $\sin^2\theta/2 = 1$. The experimental value is 0.64. A 25% increase in $\langle S^2\rangle$ would force an exact fit but the difference is probably within experimental error.

The above considerations concern abnormal *intra*-molecular interferences in block copolymers expected where the refractive index increments of the two components are opposite in sign, producing a net increment which is small. The angular dependence of scattered light at infinite dilution measures these effects. In addition, *inter*-molecular interference effects can be observed which are peculiar to all block copolymer systems. In all solvents (Figures 3–5) at finite concentrations the angular dependence of c/I becomes increasingly more negative in slope as the concentration increases. In cyclohexane and cyclohexene this involves a change in sign from positive to negative, similar to the effect previously noted for styrene–isoprene block copolymers in benzene and chlorobenzene. The expression describing the scattered light as a function of angle and concentration is

$$\frac{Kc}{I_{(\theta)}} = \frac{1}{MP_{(\theta)}} + 2A_2c\,\frac{\Phi_{(\theta)}}{P_{(\theta)}} \qquad (1)$$

where $P_{(\theta)}$ is the function describing *intra*-molecular interference and $\Phi_{(\theta)}$ the *inter*-molecular interference. The other symbols have their usual significance. Normally both $P_{(\theta)}$ and $\Phi_{(\theta)}$ decrease from unity at zero angle as the observation angle increases, more rapidly the larger are the molecular dimensions.

For normal homopolymers partial cancellation in the ratio $\Phi_{(\theta)}/P_{(\theta)}$ produces only a small increase in slope of the angular dependence at higher concentrations (cf. polystyrene in toluene). For block copolymers under conditions where only one component scatters light, the $P_{(\theta)}$ function reflects only the size of this component and stays therefore closer to unity than expected for the total size of the molecule.[10] $\Phi_{(\theta)}$, on the other hand, is determined by the intermolecular excluded volume of the whole molecule and drops much more rapidly below unity at higher angles. This effect will also be magnified for abnormally high excluded volumes. The net result is an exaggerated decrease of the ratio $\Phi_{(\theta)}/P_{(\theta)}$ at higher angles producing the curious Zimm plots observable in Figures 4 and 5 and in more exaggerated form in Figure 2 of ref 10 where the molecular weight is higher.

The styrene–siloxane block copolymers, however, show this effect in toluene solution where both components scatter light strongly. In this case it should be remembered that $P_{(\theta)}$ is even more abnormal, i.e., it *increases* above unity. If the $\Phi_{(\theta)}$ function is normal, i.e., *decreases* below unity at higher angles, the $\Phi_{(\theta)}/P_{(\theta)}$ ratio will drop even more rapidly with angle producing quite strongly abnormal Zimm plots (Figure 5). This analysis assumes normal behavior for $\Phi_{(\theta)}$. Although it is difficult to prove that this should occur, the experiments suggest this behavior of $\Phi_{(\theta)}$. $\Phi_{(\theta)}$ reflects inter-molecular interference in a binary cluster of polymer molecules, and therefore larger average inter-segmental distances than does the function $P_{(\theta)}$. It is known that the gradient of $P_{(\theta)}$ at larger angles and larger inter-segmental distances does change sign.[18] The maximum produced in $P_{(\theta)}$ is not experimentally accessible in our case but would require molecular weights well over 10^6. It is therefore at least plausible that $\Phi_{(\theta)}$ might behave normally.

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References and Notes

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Some Peculiarities of Thermal Polymerization of Styrene in Chloroform–Acetone Mixtures

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ABSTRACT: In this study some peculiarities in relation to the kinetics and especially the chain transfer reactions of the thermal polymerization of styrene in chloroform–acetone mixtures have been investigated. It has been found that the values of $1/\bar{P}_n$, the transfer constant for the solvent, $k_t/k_p{}^2$, and the fractional rate depend on the concentration of solvent. These anomalies are explained by the formation of complexes among the components of the polymerization system. Thereby the effect of the polarity of the medium must not be neglected.

The problem concerning the effect of medium on the rate and mechanism of polymerization has not been solved yet. This is due to the fact that the quantity of available convincing experimental data or theory is not sufficient.

The solvent affects the polymerization rate especially because of its chemical character, polarity, and viscosity.

The effect of chemical character of a solvent manifests itself in the formation of complexes (solvates) among the solvent and other components of the polymerization system (specific solvation). These complexes contain secondary bonds. Moreover, the autoassociation of particles may also have an influence on the polymerization rate.

The reactivity of polymer radicals may be influenced not only by the solvation of an atom with an unpaired electron but also by the interaction of other atoms and functional groups of radical with solvent. The polar structure of the radical may also influence its reactivity.[1]

There are only a few cases in which the effect of the polarity (nonspecific solvation) of the medium on the overall rate as well as the rates of individual elementary processes of radical polymerization can be clearly observed. Together with the effect of polarity the influence of specific solvation can often be observed.

The analysis of literature data shows[1-16] that according to the character of the solvent, monomer, and polymer radical one or another type of complex can prevail and affect the kinetics of polymerization. Complexes usually reduce the reactivity of polymer radical and monomer[1-5,15] but there are cases in which the reactivity increases.[4,6-15] The character of the interaction between a growing radical and medium is not quite clear.[13]

In several cases a binary system monomer–solvent is not enough to obtain full information on the effect of solvent on k_i, k_p, k_t, R_p, and C_s (transfer constant of solvent).

The literature is short on data concerning the change of k_i, k_p, and k_t, and there are few data on the variation of R_p and C_s in binary mixed solvents.

The study of polymerization kinetics in a binary mixed solvent, the composition of which may vary, is advisable. In this case the concentrations of different solvate forms also vary. Such investigations are necessary for the explanation of the effect of solvent on the reactivity of monomer or polymer radical.

This work has been undertaken in order to study some peculiarities concerning the kinetics and mainly the chain transfer reactions occurring in the thermal polymerization of styrene in chloroform–acetone mixtures.

The polymerization of styrene in some commonly used organic solvents has been studied.[15,17-29] The information available on styrene polymerization in solvent mixture is, however, scanty.

The pair of solvents acetone–chloroform was examined for the first time in the radical polymerization of methyl methacrylate and vinyl acetate in a nitrogen atmosphere.[30] This investigation manifest that not only the proportion of both solvents but also other factors affected the transfer reaction in mixtures of solvents. It may be supposed that these factors involve intermolecular interactions, i.e., the