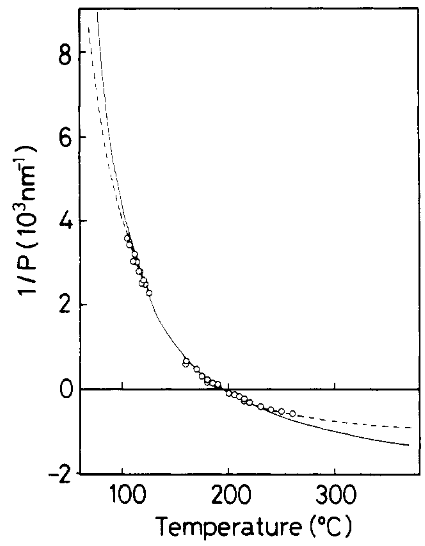

Figure 7. Comparison of the observed data (given by the circles) with the calculated curves. The solid and dashed curves are due to the calculations according to eq 8 and 9, respectively.

understanding of it seems to need further collection of data for other kinds of thermotropic polypeptides. The study is in progress.

Registry No. BD-1-58, 111291-00-0.

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Synthesis and Characterization of Hydrophobically Associating Block Polymers

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ABSTRACT: The influence of polymer composition and architecture on solution rheological properties of hydrophobically associating polymers was explored. The water-soluble block polymers were synthesized in two steps involving anionic polymerization of poly(*tert*-butylstyrene-*b*-styrene) followed by selective sulfonation of the styrene block. Viscometric measurements in distilled water clearly identified viscosity enhancement due to the presence of the hydrophobic *tert*-butylstyrene groups in a block architecture, while the presence of the same functionality in a random copolymer produced little effect on the solution properties. The block polymer solutions were also observed to solubilize toluene with a marked increase in the solution viscosity. These results were interpreted in terms of polymer intermolecular association through the hydrophobic blocks similar to micellization of surfactants.

Introduction

Block and random polymers comprised of *tert*-butylstyrene and styrenesulfonate as the hydrophobic and hydrophilic or water-soluble blocks, respectively, were synthesized to study the effects of polymer molecular architecture on aqueous solution behavior. All of the water-soluble, sulfonated polymer systems, including homopolymers, random and block polymers, were synthesized by functionalization via sulfonation of hydrocarbon-soluble polystyrene or poly(*tert*-butylstyrene–styrene) copolymers. Their aqueous solution behavior was studied as a function of hydrophobe block size, polymer molecular weight, molecular architecture of the polymer (block versus random configurations), and other solution effects such as hydrocarbon solubilization.

Viscosification of an aqueous solution can be achieved with linear ultrahigh molecular weight polymers.[1] The presence of ionically charged monomers along a randomly coiled polymer chain will expand the coiled polymer by charge repulsion (polyelectrolyte effect),[2] thereby increasing the effective hydrodynamic volume. However, the repulsions can be largely screened by salts in the aqueous solution ultimately lowering the viscosity.

An alternative approach to ultrahigh molecular weight and chain expansion for aqueous viscosification by polymers involves intermolecular aggregation in solution through hydrophobic association. Landoll reported[3] on the behavior of hydrophobically modified cellulosic ethers wherein the solution properties were explained in terms of interchain polymer associations resulting in aggregate

Table I
Copolymer Compositional Data

	composition, wt % (mol %)			mol wt	
polymer	TBS	styrene	TBS	$10^{-5}M_w$	$10^{-5}M_n$
		Block			
D5-TBS-S1	5 (3.3)	95 (96.7)		1.4	1.3
D5-TBS-S2	5 (3.3)	95 (96.7)		2.8	2.7
D5-TBS-S3	5 (3.3)	95 (96.7)		5.2	4.9
D5-TBS-S4	5 (3.3)	95 (96.7)		7.2	6.9
D5-TBS-S5	5 (3.3)	95 (96.7)		10.0	9.4
D11-TBS-S	11 (7.4)	89 (92.6)		4.7	4.4
T5-TBS-S	2.5 (1.65)	95 (96.7)	2.5 (1.65)	6.1	5.7
		Random			
R5-TBS-S	5 (3.3)	95 (96.7)		4.8	4.6
R10-TBS-S	10 (6.7)	90 (93.3)		5.0	4.6

formation. Selb and Gallot[4-7] studied the solution behavior of block copolymers of styrene and vinylethylpyridinium bromide. They concluded that the hydrophobic blocks associate in aqueous solution resulting in micelle-like aggregates of polymer molecules.

A series of block polymers was synthesized to explore this concept of hydrophobically associating polymers to provide enhanced viscosification. A two-step synthesis involved, first, the anionic polymerization of a hydrocarbon-soluble block polymer. This polymer was then functionalized to selectively convert one block to a water-soluble moiety. Thus, these polymers had a water-soluble and a water-insoluble portion in analogy to surfactants. The block polymer systems used in this study consisted of *tert*-butylstyrene, TBS, as the hydrophobic block and sulfonated styrene as the water-soluble block. The major component of these polymers was the styrenesulfonate block to ensure water solubility. This paper describes the synthesis and solution characterization of these polymers.[8]

Experimental Section

***tert*-Butylstyrene–Styrene Polymers.** A number of block and random polymers of *tert*-butylstyrene, TBS, and styrene were synthesized by anionic polymerization techniques.[9-11] The block polymers were prepared by polymerization first of the TBS block using *sec*-butyllithium as initiator followed by the addition of styrene to the living TBS polymer to give the styrene block. The polymerization was then terminated by the addition of methanol to give diblock polymer. Triblock polymer was synthesized by adding a second portion of TBS following the styrene addition and prior to termination with methanol. The random copolymers were prepared from the appropriate mixture of TBS and styrene monomers. The compositional data for the polymers are presented in Table I. The molecular weight data were obtained by gel permeation chromatography using a Waters 150C instrument with a six-column u-Styragel arrangement that covered a porosity range of 10^6–10^2 Å. Tetrahydrofuran was the mobile phase used at a flow rate of 1.0 mL/min at 30 °C.

***tert*-Butylstyrene–Styrenesulfonate Polymers.** Conversion of the copolymers to water-soluble polymers was done via selective sulfonation of the styrene portion of the molecules.[12-14] The general procedure was to place 0.2 equiv of triethyl phosphate, TEP, dissolved in 1,2-dichloroethane, DCE (2 g of TEP/100 mL of DCE), into a dry reactor fitted with a mechanical stirrer, two dropping funnels, and thermometer. The solution was cooled to 0 °C and 1.0 equiv of polymer dissolved in DCE (5 g of polymer/100 mL of DCE) was placed in one dropping funnel and 1.1 equiv of SO_3 in DCE in the other dropping funnel. The SO_3 solution, followed by polymer solution, was added alternately in small portions while the reactor was maintained at 0 °C. The sulfonated polymer precipitated from solution and was washed with pentane. The polymer was dissolved in methanol and neutralized with sodium methoxide to pH 7 (the pH of aliquots diluted with water was measured) and was then isolated by evaporation as the sodium sulfonate polymer. Polystyrenesulfonate homopolymers, SS1 and SS2, were prepared in an analogous manner from polystyrene homopolymers.[15] The analytical data are presented in Table II.

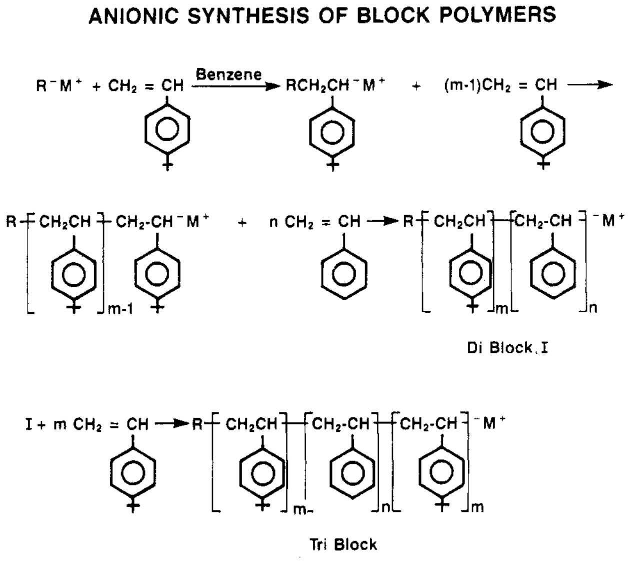

Figure 1. Synthesis of *tert*-butylstyrene–styrene block polymers.

Table II
Molecular Weight and Elemental Analysis of Sulfonated Polymers

		elemental anal., wt %				
		calcd		found		sulfonate content,[a]
polymer	$10^{-5}M_w$	S	Na	S	Na	%
		Block				
D5-TBS-SS1	2.4	15.3	10.88	16.16	10.1	106
D5-TBS-SS2	4.7	15.3	10.88	13.78	9.54	91
D5-TBS-SS3	9.0	15.3	10.88	15.47	10.4	102
D5-TBS-SS4	12	15.3	10.88	12.58	8.19	83
D5-TBS-SS5	17	15.3	10.88	12.88	9.11	85
D11-TBS-SS	7.4	14.63	10.51	14.38	9	98
		Random				
R5-TBS-SS	8.3	15.3	10.88	15.79	10.6	104
R10-TBS-SS	8.5	14.71	10.57	14.20	10.5	96
		Homopolymer				
SS1	6.5	15.53	11.16	13.68	10.10	88
SS2	20	15.53	11.16		11.50	

[a] Sulfonate content, [S(found)/S(calcd)] × 100, is a measure of sulfonate groups per styrene unit.

Rheological Measurements. The polymers were dissolved in doubly distilled water at 2500 ppm concentration under mild agitation conditions (magnetic stirrer) at room temperature. The rheology of solutions of desired concentrations in terms of viscosity–shear rate profile was obtained by using a Contraves LS-30 Couette viscometer at 25 °C. The shear rates investigated ranged from 0.02 to 120 s^{-1}.

Results and Discussion

Block Polymer Synthesis. The synthesis sequence to the block polymer systems containing *tert*-butylstyrene and styrenesulfonate began with the anionic polymerization of *tert*-butylstyrene followed by addition of styrene monomer to continue polymerization on the living anion polymer. As shown in Figure 1, all polymerizations were initiated with *sec*-butyllithium to form the *tert*-butylstyrene anion. Additional *tert*-butylstyrene was added to give the desired length of that block followed by addition of styrene only for diblock polymer preparation. Chain termination was accomplished by the addition of an alcohol to the reaction mixture to protonate the anionic chain end functionality. The preparation of triblock polymers with end blocks of *tert*-butylstyrene was done sequentially, again, starting with initiation of *tert*-butylstyrene by

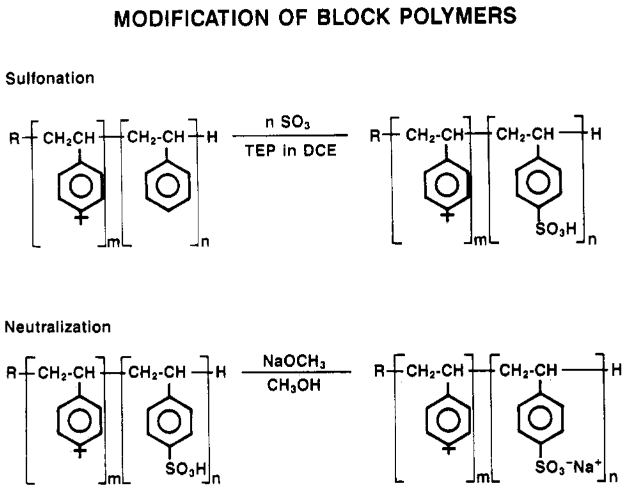

Figure 2. Synthesis of *tert*-butylstyrene–styrenesulfonate block polymers.

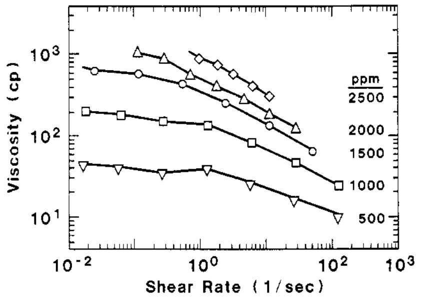

Figure 3. Solution viscosity as a function of shear rate of a diblock polymer.

sec-butyllithium. After addition of styrene to form the midblock, *tert*-butylstyrene was again added to complete the triblock synthesis.

Sulfonation of the styrene block, shown in Figure 2, utilized sulfur trioxide (SO_3) complexed with triethyl phosphate (TEP) as the sulfonating agent. The solvent medium was dichloroethane (DCE) chosen because the *tert*-butylstyrene-*b*-styrene polymers were soluble, but the sulfonated analogues were not. This combination of solubility properties allowed for facile isolation of the desired sulfonated polymers. Only the styrene block was sulfonated since the preferred para position of the *tert*-butylstyrene block was already occupied. Therefore, after neutralization of the sulfonic acid to the sodium salt, the polymers then consisted of a hydrophobic block, *tert*–butylstyrene, and a water-soluble block, sodium styrenesulfonate.

The various analytical and compositional data for the sulfonated polymers are presented in Table II. The weight average molecular weights, M_w, listed in this table are calculated values based on the M_w of the polymer precursor and the extent of sulfonation. The extent of sulfonation of the styrene block was determined from the sulfur elemental analysis by ratioing the measured sulfur content to the calculated value.

Aqueous Solution Properties. The viscosity in distilled water of a diblock polymer with 3.3 mol % *tert*-butylstyrene, D5-TBS-SS3, is presented in Figure 3 as a function of shear rate at concentrations ranging from 500 to 2500 ppm at 25 °C. As can be observed, at or above 2000 ppm, the log–log plots show a decrease in viscosity with shear rate. This pseudoplastic behavior can thus be represented by a simple power law relationship. At concentrations of 1500 ppm and below, a Newtonian or shear rate independent viscosity can be observed at low shear rates. The viscosity of more concentrated polymer solutions could not be obtained at shear rates below ~0.1 s^{-1} because of the shear stress limitations of the instrumentation. For these samples, the viscosity–shear rate data were fitted to an Ellis model[17] to predict the low shear or Newtonian viscosity. This so-called zero shear viscosity was used to construct reduced viscosity–concentration plots providing information on the hydrodynamic volume of the polymer in solution.

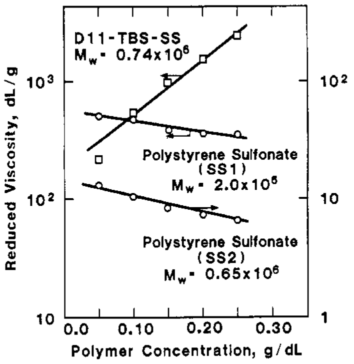

Figure 4. Reduced viscosity versus polymer concentration plots for a diblock polymer and homopolystyrenesulfonates.

The reduced viscosity–concentration curves for a 7.4 mol % *tert*-butylstyrene diblock polymer, D11-TBS-SS, and two polystyrenesulfonate homopolymers, SS1 and SS2, are shown in Figure 4. The block polymer exhibits a reduced viscosity at least 1–2 orders of magnitude higher than the homopolymer, SS1, of similar molecular weight. Although block polymer, D11-TBS-SS, had a molecular weight some three times smaller than homopolymer, SS2, its viscosity was greater at concentrations above ~0.1 g/dL. Thus, the presence of a relatively small amount of hydrophobic groups significantly enhanced the viscosification efficiency of these polymers.

The opposite slope of the reduced viscosity curve for the block polymer as compared to the homopolymers is indicative of fundamental mechanistic differences in viscosification. The decrease of reduced viscosity with increased polymer concentration for the homopolymers is a result of a decrease in effective polymer size from coiling. This is due to a reduction of charged group repulsions by shielding of the anionic charge because of the proximity of other polymer molecules. With the block polymer, it is postulated that the reduced viscosity increases with increasing concentration because of polymer hydrophobe association. It is envisioned that the *tert*-butylstyrene blocks associate into aggregates due to their incompatibility with the aqueous medium. As the polymer concentration increases, the size and/or number of these aggregates increases. This results in enhanced interaction and, hence, solution viscosity. Conversely, in dilute solution (<0.1 g/dL) wherein polymer molecule interactions are minimized, molecular weight becomes the controlling factor. Consequently, the reduced viscosity of the block polymer is less than the homopolymer, SS2, in the dilute concentration region because of its lower molecular weight.

To define the effect of molecular weight on intrinsic viscosity, diblock polymers, D5-TBS-SS, with 3.3 mol % *tert*-butylstyrene were prepared having weight average molecular weights from 240 000 to 1.7 million. It can be seen from the plot in Figure 5 that a power law relationship, described by the Mark–Houwink–Sakurada equation ($[\eta] = kM^a$) exists between the molecular weight and intrinsic viscosity for this series of block polymers in distilled water. The exponent, a, was determined to be 1.0 which was in good agreement with $a = 0.93$ reported[16] for poly-

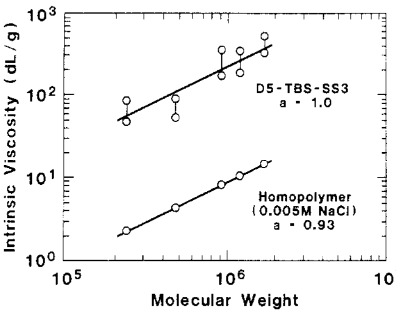

Figure 5. Effect of polymer molecular weight on solution viscosity.

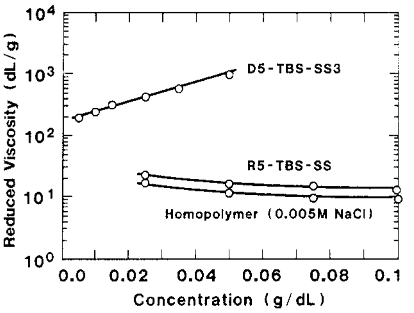

Figure 6. Effect of hydrophobic group distribution on solution viscosity.

styrenesulfonate in 0.005 M sodium chloride solution. The lower plot in Figure 5 represents the literature data. Therefore, the influence of molecular weight on the hydrodynamic size of the block polymers in solution was similar to what was observed for the homopolymer analogues. The block polymers have intrinsic viscosities an order of magnitude higher than those of the homopolymers due to the aggregation of several polymer molecules via the association of the hydrophobic blocks.

In dilute solution, the reduced viscosity of a ionically charged polymer increases upon dilution because of the polyelectrolyte effect.[2] As the charge centers along the backbone become deshielded by dilution, the polymer hydrodynamic size increases due to electrostatic repulsion. Surprisingly, the polyelectrolyte effect was not observed with the block polymers, most likely due to the association of polymer molecules. Polymer concentrations as low as 50 ppm were used with no apparent upturn in reduced viscosity with decreasing concentration. Apparently, block polymer aggregation is present to very low concentrations which maintains a locally effective shielding of the sulfonate anions within the aggregate. Alternatively, individual block polymer molecules may assume a collapsed coil conformation in dilute solution such that the hydrophobic TBS block is surrounded by the styrenesulfonate block to isolate it from the aqueous medium. This type of conformation would counter chain expansion due to charge repulsion of the sulfonate groups with no polyelectrolyte effect as was observed. As of yet we have not made direct measurements of the hydrodynamic size of these polymers or their aggregates in solution using light or neutron scattering techniques, for example, to be able to determine the validity of the above postulates.

A comparison of the reduced viscosity as a function of concentration for the block polymer, D5-TBS-SS3, and the random polymer, R5-TBS-SS, having 3.3 mol % *tert*-butylstyrene content and M_w's of 9.0×10^5 and 8.3×10^5, respectively, is shown in Figure 6. It can be seen that the random polymer is very similar in rheological behavior to the homopolymer and significantly different than that of the associating block polymer. The *tert*-butylstyrene hydrophobic groups are not aggregating in the random polymer due to the hydrophilicity and steric bulk of their styrenesulfonate neighboring groups.

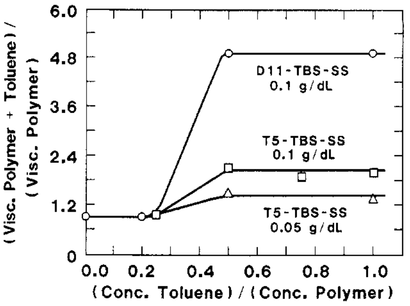

Figure 7. Solubilization of toluene in block to polymer solutions.

The analogous nature of these block polymers to surfactant molecules led to the investigation of hydrocarbon solubilization[18] in their aqueous solutions.[19] Toluene was selected as the hydrocarbon to be added to the aqueous solutions because of the solubility of *tert*-butylstyrene in aromatic solvents. A plot of the relative zero shear viscosity of a polymer solution with toluene to that without toluene is given in Figure 7 as a function of the ratio of toluene to polymer. When the toluene to polymer ratio was less than 0.2, toluene did not effect solution viscosity. Between 0.2 and 0.5 the viscosity increased significantly, and beyond 0.5, no further increase was observed. The viscosity responses involve size, shape, and/or number density changes in the polymer aggregates.

Conclusions

A series of water-soluble block polymers was synthesized in two steps involving anionic polymerization of poly(*tert*-butylstyrene-*b*-styrene) followed by selective sulfonation of the styrene block. Rheological studies of solutions of these polymers in distilled water clearly identified viscosity enhancement due to the presence of the hydrophobic *tert*-butylstyrene end blocks. Comparison with homopolymer and random copolymers of similar composition and molecular weight demonstrated the increased viscosification with the block configuration. The block polymer solutions were also observed to solubilize toluene with a marked increase in the solution viscosity. These results are interpreted as the result of polymer intermolecular association through the hydrophobic blocks similar to micellization of surfactants.

Acknowledgment. We wish to acknowledge Dr. L. J. Fetters for the synthesis of the various *tert*-butylstyrene–styrene block and random polymers done at the University of Akron. D. Griffin and S. Zushma carried out the sulfonation of the polymer precursors, and W. Gallagher and S. J. Pace performed the rheological measurements.

Registry No. Toluene, 108-88-3.

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Some Unsolved Problems on Dilute Polymer Solutions

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ABSTRACT: In contrast to the prevailing notion, our understanding of polymer behavior in dilute solutions still leaves much to be desired. This fact is illustrated here by discussing some typical unsolved problems regarding the following subjects: intrinsic viscosity, hydrodynamic factors, second virial coefficient, and the onset of the excluded-volume effect on the statistical radius.

It is misleading to consider that polymer behavior in dilute solutions has been worked out so thoroughly in the past decades that few problems of fundamental importance on this subject remain unsolved or unexplored. If we study the existing literature somewhat carefully, we will soon come across many important experimental results which are waiting for adequate theoretical explanations in terms of molecular parameters. The aim of the present paper is to illustrate this fact by discussing some unsolved problems regarding four typical subjects: intrinsic viscosity, hydrodynamic factors, second virial coefficient, and the onset of the excluded-volume effect on statistical radius. In so doing, we will confine our object to the behavior of monodisperse flexible linear polymers in a single solvent, except in the last subject which is concerned with semiflexible polymers.

Intrinsic Viscosity

The Houwink–Mark–Sakurada Relation. One of the most surprising generalities observed in polymer systems is that the intrinsic viscosity $[\eta]$ of a series of polymer homologues increases with the polymer's molecular weight M following a simple power law usually called the Houwink–Mark–Sakurada (HMS) relation, i.e.,

$$[\eta] = KM^{\nu} \tag{1}$$

where K and ν are constant for a given polymer + solvent system. A vast amount of experimental data[1] indicates the empirical rule that ν in Θ solvents where the second virial coefficient A_2 of the solution becomes zero is always 0.5, while it is found between 0.5 and 0.8 in non-Θ solvents where A_2 is positive. Generally, this index for a given kind of polymer is larger for a better solvent which is conveniently defined as one giving a larger second virial coefficient.

When data for log $[\eta]$ of a series of polymer homologues are graphed as a plot of log $[\eta]$ against log M, we seldom see a discernible curvature, sometimes it is seen in the region of relatively low molecular weight, and as a rule the slope of the plot is steeper for a better solvent, as sketched in Figure 1. This is another version of what was stated in the preceding paragraph explaining the HMS relation.

The upper bound of M accessible to experimental work is limited, implying that the asymptotic behavior of $[\eta]$ at indefinitely large M is beyond the reach of our measurement. What can actually be done is to make an estimation guess of it from experimental data obtained over a limited range of M, and for a surer estimate it is desirable to acquire data extended up to M so high that polymer behavior is considered to obey an asymptotic law. Recently, such data were obtained by Einaga et al.[2,3] for narrow-distribution polystyrene (PS) in benzene and by Meyerhoff and Appelt[4] for PS in toluene; the highest molecular weight of PS studied was as large as 6×10^7 for the former and 4×10^7 for the latter. Interestingly, for both systems, the log $[\eta]$ versus log M plots were perfectly linear over the range of at least 2 decades up to these M values. It is difficult to suspect that even in the region of such "ultrahigh" molecular weights the viscosity behavior of a linear polymer in dilute solution does not yet become asymptotic; i.e., the HMS relations established by the above authors will fail to hold if the measurement is extended to "superhigh" molecular weights. If this is the case, it would virtually be impossible to approach by experiment the asymptotic polymer behavior at high M, and theoretical calculations with infinitely long chains would become a matter of mere mathematical interest. On the basis of the vast amount of available experimental information, the author maintains the opinion that once found valid over a sufficiently broad range of M, say more than 2 decades, the HMS relation should be valid up to any higher molecular weights and that this should be taken as the fact or truth that has to be explained by molecular theory.

Theoretical Predictions

Polymer transport properties in dilute solutions have so far been formulated on the basis of the Kirkwood–Riseman integral equations[5] or the Kirkwood generalized diffusion equation.[6] Despite the great many efforts of theoreticians no exact solution to these equations is as yet found for flexible polymers. Thus, some typical theoretical predictions for $[\eta]$ described below are based on approximate solutions whose accuracy is not easily assessed.

Θ-Solvent Systems. Theories of $[\eta]$ and other transport properties such as the diffusion coefficient are greatly simplified when we are concerned with Θ-solvent systems in which the complications due to excluded-volume effect are considered to disappear. In what follows, $[\eta]$ in such a system is given a subscript Θ.

In 1948, Kirkwood and Riseman (KR)[5] and independently Debye and Bueche (DB)[7] presented the first mo-

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