[CONTRIBUTION FROM THE GIBBS LABORATORY, DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Association of Polystyrene in Non-polar Solvents[1]

By Q. A. TREMENTOZZI, R. F. STEINER AND PAUL DOTY

A polystyrene sample which had previously been found to exhibit anomalous behavior in osmotic pressure studies has been fractionated and examined by light scattering and viscometric techniques. Pronounced aggregation in non-polar solvents such as toluene is demonstrated. The aggregation is considerably diminished or eliminated in the presence of hydrogen bonding agents. The disappearance of the phenomenon upon acetylation supports the proposal that the association takes place by hydrogen bonding between hydroxyl groups introduced in the course of the emulsion-polymerization.

I. Introduction

Despite the wide utilization of the emulsion method of vinyl polymerization and the extensive industrial use of polymers thereby obtained, relatively little attention has been given to possible modifications of the product by the conditions of polymerization and the resultant influence upon its physical properties. A study of the literature reveals that a certain number of polar groups must be introduced under the usual procedure. Thus $-SO_4$ and $-OH$ groups will probably be present if persulfate is the initiator in an aqueous system and

twice as great a number average molecular weight in toluene as in butanone or dioxane. Moreover the μ-value in toluene was very nearly 0.50 in contrast to considerably lower values generally reported. A recent report[3] that another emulsion polystyrene shows a 20% change in molecular weight with a 50° increase in temperature may represent another aspect of this same phenomenon. In what follows the studies upon the original sample have been extended and evidence obtained which clarifies somewhat the reason for this behavior.

TABLE I

SUMMARY OF LIGHT SCATTERING MEASUREMENTS OF POLYSTYRENE

Parentheses indicate values which are not to be taken quantitatively for reasons mentioned in the text.

Fraction	Treatment	Solvent	M_w	$R(Å.)$	$2B(\times 10^4)$	$[\eta]$
Unfractionated	None	Toluene	4,500,000	(2600)	2.6	
Unfractionated	None	Butanone	1,100,000	(1100)	1.0	
Unfractionated	None	Dioxane	715,000	950	3.8	
1	None	Toluene	20,000,000	(4560)	.96	3.92
1	None	Dioxane	1,670,000	(1460)	(−2.0)	2.76
2	None	Toluene	20,000,000	(4470)	.60	3.20
2	None	Dioxane	1,400,000	(1430)	1.2	2.64
2	None	Butanone	2,630,000	1260	.56	
3	None	Toluene	16,700,000	(3530)	1.7	2.60
3	None	Dioxane	1,300,000	1300	1.9	2.06
4	None	Toluene	4,530,000	(1800)	2.5	1.56
4	None	Dioxane	571,000	600	3.7	1.32
2	None	10% Isopropyl alcohol 90% Butanone	(2,110,000)	(1080)	.07	
2	None	2% Dioxane 98% Toluene	(1,400,000)			
2	None	6% Dioxane 94% Toluene	(1,400,000)			
2	None	2% Dimethyacetamide 98% Toluene	(2,270,000)	(1600)	2.48	
Unfractionated	Acetylated	Toluene	760,000	760	5.6	
Unfractionated	Acetylated	Dioxane	760,000	1060	8.8	

$-OH$ groups if $H_2O_2-Fe^{++}$ is employed. If the polymerization is carried out in the presence of oxygen, other possibilities for the introduction of polar groups arise from its role as a chain terminator.

In a previous publication[2] it has been shown that under certain conditions emulsion polystyrene of distinctly anomalous properties may be obtained.

In particular the sample further investigated in this work (polystyrene E-13) was found to exhibit

II. Experimental

In this work studies were made on the polystyrene sample PS-E-13 which was supplied by the Monsanto Chemical Company. The styrene was polymerized in emulsion in the presence of air using potassium persulfate as the catalyst. The pH of the system before the addition of monomer was adjusted to 11.5 by adding a small amount of sulfuric acid. The soap solution containing 0.1% Rubber Reserve Soap was refluxed for a few minutes. The first catalyst addition (0.08% of the monomer charge) was made and then the monomer was added slowly over a one hour period with the reflux temperature being maintained. The second catalyst addition (0.04% of the monomer charge) was then made

(1) Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., Sept. 5-8, 1950.

(2) Q. A. Trementozzi, J. Phys. Colloid Chem., 54, 1227 (1950).

(3) H. P. Frank and E. H. Innergut, Abstracts of the 119th Meeting of the American Chemical Society, Boston, Mass., Apr. 1-5, 1951.

and the system was refluxed for one additional hour carrying the polymerization nearly to completion. Steam distillation was employed to remove monomer. Further purification was made by the precipitation method employing methyl ethyl ketone as the solvent and methanol as the precipitant. The polymer was filtered and dried at 65°.

The sample was fractionated by adding methanol stepwise to a 1% solution in n-butanone. Methanol was added to the point of incipient phase separation, the solution warmed to redisperse the separating phase, and then allowed to cool slowly and come to equilibrium at a constant temperature. A broad high molecular weight fraction was obtained, which was refractionated into four subfractions. All fractions were separated centrifugally, redissolved in n-butanone and reprecipitated. They were then washed exhaustively with methanol and dried by heating to 60° *in vacuo*.

A Brice–Speiser light scattering photometer was used. The method of calibration has been given elsewhere.[4,5] Prior to light scattering measurements all solutions were freed from extraneous particles by centrifugation in stainless steel tubes at 20,000 g. for several hours. The values of the refractive index increment employed were 0.109 for toluene, 0.221 for butanone and 0.176 for dioxane. These refer to a wave length of 5460 Å. which was used in all this work.

Viscosity measurements were made with Ostwald–Fenske viscometers. Measurements were made in a thermostat at 25.0 ± 0.050.

Eastman Kodak (white label) 1,4-dioxane was used after purification by double distillation from metallic sodium. Other solvents were analytical grade and were redistilled once before using.

Acetylation of the polymer was carried out by the addition of acetyl chloride in excess to a 1% solution of the polymer in dioxane at 0°. The mixture was allowed to stand with stirring for three hours and the polymer then precipitated with methanol. It was then redissolved and reprecipitated.

Results

The values obtained for the molecular weight, root mean square separation of chain ends, virial coefficient and the intrinsic viscosity for the unfractionated polymer and the four fractions in several solvents are tabulated in Table I. Typical data are shown in Figs. 1 and 2 where the results for the unfractionated polymer in dioxane and fraction 2 in dioxane and toluene are plotted. In general the care necessary to ensure the highest accuracy was not used since the magnitude of the effect was so great and the possibility of interpreting the data quantitatively so remote.

Examining the first three entries in Table I it is seen that the observed molecular weight is greater in toluene than in dioxane by a factor of 6.3. In butanone an intermediate molecular weight is observed. In the earlier osmotic pressure work[2] number average molecular weight values of 440,000 in toluene and 250,000 in dioxane were found for this polymer. Thus the ratio M_w/M_n, which is a measure of the polydispersity, is 10 in toluene and 2.8 in dioxane. The very high value for this ratio in toluene compared with a normal value in dioxane suggests that an aggregation is taking place in toluene and that not all of the molecules share equally in this aggregation, that is, some molecules appear to possess more potential points of union than others. Size measurements likewise show an increase in the series dioxane, butanone, toluene. However the size measurements can only be valid for the aggregates if it can be shown that association is end-to-end so that the aggregate has the form of a linear chain. Since it is shown later that the aggregation is not end-to-end only a qualitative significance can be attached to the values of R given for toluene and butanone solutions. Turning to the values of the virial co-
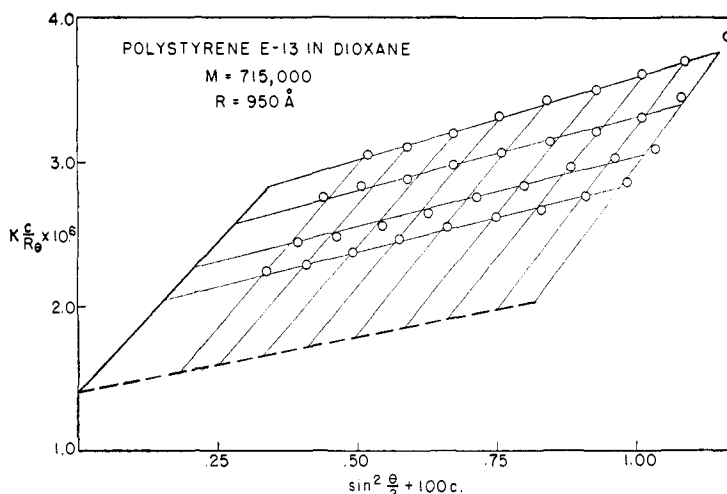

Fig. 1.—Light scattering of unfractionated polystyrene in dioxane solution. Full line of Zimm plot corresponds to zero angle.
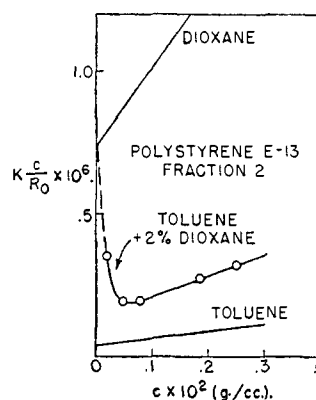

Fig. 2.—Light scattering of polystyrene fraction 2 in dioxane and toluene. Full lines correspond to zero angle.

efficients, B, a comparison with previous measurements[6,7] shows that those in Table I for toluene and butanone solutions are smaller by a factor of about 2. This suggests that a greater intermolecular attraction exists in this sample of polystyrene.

Examining the next entries in Table I showing the results for the four subfractions we note the following: (1) The extent of aggregation in toluene is approximately twice as great as in the unfractionated sample. Since these fractions have a higher molecular weight than the unfractionated material this supports the earlier conclusion that the higher molecular species have a greater capacity for aggregation. (2) The virial coefficients are even lower than in the unfractionated sample, this being consistent with a greater extent of aggregation. (3) Despite a 12-fold greater molecular weight in toluene than in dioxane the intrinsic viscosity is found to increase only about 30%. For end-to-end aggregation the increase should have been about 4-fold. This clearly shows that the association must be very far from the end-to-end type. Indeed the aggregate would appear to be formed from a random association of polystyrene molecules within a volume considerably smaller than that indicated by the values of R derived for a linear coil. In fact the angular data for the aggregate would be better interpreted by using a sphere of constant density as the model. On this basis a diameter of about half that given for R would be obtained for fraction 2.

In order to investigate the origin of this aggregation the effect of the addition of small amounts of polar solvents to the polymer in toluene was studied. Figure 3 shows the

(4) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

(5) B. A. Brice, M. Halwer and R. Speiser, *J. Optical Soc.*, **40**, 768 (1950).

(6) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

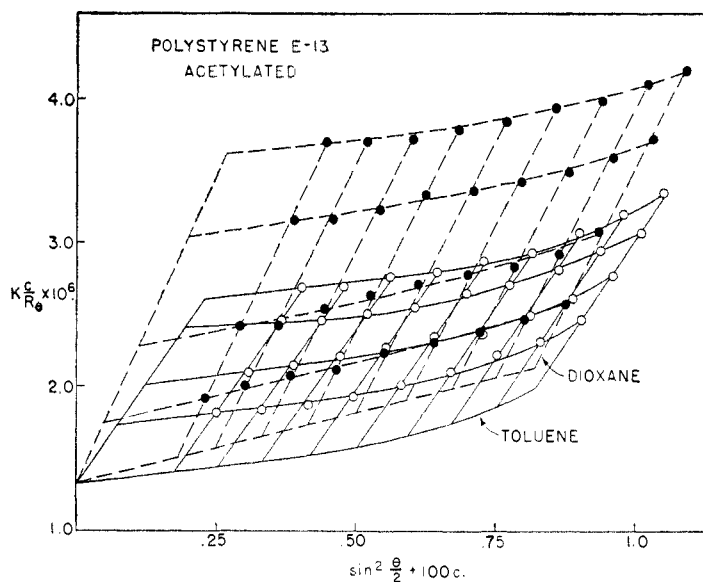(7) P. Doty, W. A. Affens and B. H. Zimm, *Trans. Faraday Soc.*, **42**, 66 (1946).

Fig. 3.—Light scattering of polystyrene fraction 2 in toluene: dioxane (49:1). Points are results of extrapolation to zero angle. Other lines are taken from Fig. 2.

results for fraction 2 in dioxane–toluene mixtures containing 2% dioxane. It is at once evident that the addition of a relatively small amount of dioxane has been sufficient to greatly reduce the aggregation. In addition, as shown by the negative limiting slope, the aggregates present tend to break up upon dilution in a manner consistent with a limiting molecular weight (1,400,000) of the same order as was obtained in pure dioxane. A similar effect was observed with 2% dimethylacetamide. In contrast the addition of small amounts of toluene or dimethylacetamide to dioxane solutions had no effect.

The ability of dimethylacetamide and dioxane in low concentrations to break up the aggregates indicates that only a relatively few labile secondary bonds are involved and that dioxane can competitively combine with the specific groups involved. Since both dioxane and dimethylacetamide are good proton acceptors, this suggests that hydrogen bond-forming groups were present.

An elemental chemical analysis and an infrared absorption spectrum were obtained upon the unfractionated polymer. Neither disclosed any anomalies. It was thus apparent that any hydrogen bond-forming groups must be present in very few numbers, of the order of 0.1% or less.

Chemical methods were then resorted to. The unfractionated polymer was acetylated with acetyl chloride and measurements made upon the product. As shown at the end of Table I and in Fig. 4, the behavior of the acetylated polymer was essentially normal, the molecular weights in toluene and dioxane being essentially the same as that obtained for the non-acetylated polymer in dioxane. Moreover, the values of the virial coefficient have risen to those generally accepted. A control upon another polystyrene sample showed that the acetyl chloride brought about no degradation.

III. Discussion

It was apparent therefore that the bond-forming groups could be effectively blocked or eliminated by acetylation. This would indicate that they were probably hydroxyl groups which participated in hydrogen bond formation. Although one is handicapped by the lack of direct evidence of the nature of the bond-forming group involved, the hydrogen bond hypothesis is supported by the fact that all the agents effective in promoting dissociation, dioxane, n-butanone, dimethylacetamide, are good proton acceptors. Moreover since the only groups likely to be blocked by acetylation are amino or

hydroxyl groups and since no nitrogen containing substance was present in the polymerization mixture, there is good reason to believe that hydroxyl groups are indeed involved. The previous conclusion that the aggregation was more random-like than end-to-end is consistent with the existence of some branching with hydroxyl groups occurring at the ends. Some branching is certainly expected in a polymerization carried to high conversion.

One may therefore tentatively conclude that the introduction of a few -OH groups is sufficient to profoundly alter the solution properties of polystyrene in non-polar solvents and that the introduction of such groups is probably common under the usual conditions of emulsion polymerization.

It would appear that this aggregation is essentially a manifestation in polymer solutions of the well known polymerization of alcohols in non-polar solvents. This type of polymer aggregation stands in marked contrast to that previously demonstrated in polyvinyl chloride solutions.[8] It is now believed that some polar polymers such as polyvinyl chloride can aggregate in poor solvents by the formation of minute crystallites which serve as cross-linkages between chains. The dissociation of the aggregates within a narrow temperature range is consistent with a melting of such crystallites. No such behavior was found with the polystyrene aggregates.
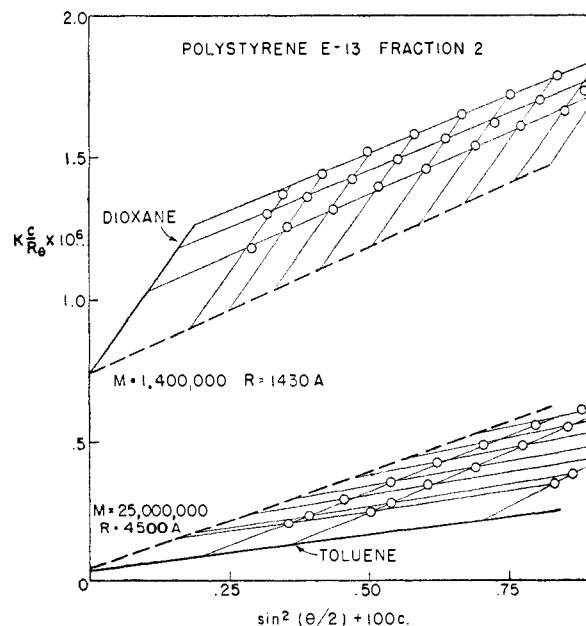

Fig. 4.—Light scattering of unfractionated polystyrene in dioxane and toluene after acetylation.

Indeed the temperature coefficient was found to be very small, thus offering further support for the hydrogen bond hypothesis, since this would be consistent with weak bonds. It is likely that these two cases of aggregation illustrate the two main types of aggregation in polymer solutions to which

(8) P. Doty. H. Wagner and S. J. Singer, J. Phys. Colloid Chem., 51, 32 (1947).

further investigation will add numerous examples.

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Methyl Vinyl Sulfoxide. Copolymerization and Spectra

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Although methyl vinyl sulfoxide retards copolymerization, data with styrene indicate values for the resonance stabilization factor $Q = 0.10$ and for the electrical factor $e = -0.9$. The latter is as expected. The conjugative properties of a sulfoxide group are unexpectedly low, as indicated by the value of Q, by ultraviolet absorption and by infrared spectra.

As reported in a previous publication,[3] the copolymerization properties and ultraviolet spectra of methyl vinyl sulfide and sulfone indicated strong conjugative properties for the sulfide group, very weak conjugative properties for the sulfone group. The evidence was interpreted as supporting the view that the sulfur–oxygen bond is best represented as a semi-polar bond. The purpose of the present investigation was to extend this investigation to methyl vinyl sulfoxide.

Experimental[4]

Methyl Vinyl Sulfoxide. A. From β-Chloroethyl Methyl Sulfoxide.—Although efforts to dehydrohalogenate this chloro sulfoxide with sodium methoxide gave only displacement products, the methoxyl and hydroxyl derivatives,[3] experiments showed that sodium t-butoxide was a satisfactory reagent for dehydrohalogenation. β-Chloroethyl sulfide[5] was oxidized with one equivalent of hydrogen peroxide in glacial acetic acid and the reaction mixture was stripped to 62° at 25 mm. To the residue (161.9 g., 1.28 moles) maintained below 40°, a well-stirred suspension of sodium t-butoxide (122.9 g., 1.28 moles) in 1000 ml. of t-butyl alcohol was added in small portions over three hours. After stirring overnight, the mixture was filtered and the residue distilled, yielding three fractions: (1) t-butyl alcohol, b.p. 81–83°, ca. 1000 ml.; (2) methyl vinyl sulfoxide, b.p. 46–47° (0.8 mm.), n^{25}D 1.4938, 48 g.; (3) β-chloroethyl methyl sulfoxide, b.p. 102–103° (4 mm.), 7.2 g.

Redistillation of fraction 2 yielded 44.5 g. (38.6%) of methyl vinyl sulfoxide, b.p. 43.5° (0.5 mm.), n^{25}D 1.4925. It decolorized bromine in carbon tetrachloride rapidly.

Anal. Calcd. for C_3H_6SO: C, 39.97; H, 6.71; S, 35.57. Found: C, 39.56; H, 6.97; S, 35.16.

B. From Methyl Vinyl Sulfide.—Methyl vinyl sulfide (12 g., 0.16 mole) (prepared in 56% yield according to Brown and Moggridge,[6] b.p. 67.3°, n^{25}D 1.4802) in 25 ml. of methanol was treated with 186 ml. of commercial "Clorox" (a 1.7 N solution of sodium hypochlorite) added so that the reaction mixture was maintained below 5°. After three hours, the homogeneous reaction mixture was extracted with two 100-ml. portions of chloroform. After drying over magnesium sulfate, the chloroform was removed and the residue distilled through a small Vigreux column.

Methyl vinyl sulfoxide (4.6 g., 32%) was collected at 52° (3 mm.), n^{25}D 1.4921.

Anal. Found: C, 39.70; H, 6.77; S, 35.80.

Copolymerization experiments with styrene and methyl methacrylate were carried out by the previously reported procedure.[3] The sulfoxide seemed to have mild retarding properties, especially evident in the copolymerization experiments with methyl methacrylate. The results are summarized in Tables I and II.

TABLE I

COPOLYMERIZATION OF STYRENE (M_1) WITH METHYL VINYL SULFOXIDE (M_2)

$M_2{}^a$	Time, hr.	Conversion, %	Percentages S	C	H	$dM_2{}^b$ (S)	$dM_2{}^c$ (C)
0.125	3.5	3.18	0.94	91.10	7.75	0 0.30	0.026
.250^d	5.0	1.13	1.90	89.84	7.87	.059	.053
.375^d	6.0	1.83	2.27	88.78	7.43	.073	.077
.500^d	7.6	0.42	2.80	87.70	7.78	.089	.099
.625^d	10.5	.28	3.84	..^{e}	..	.123	
.750	22.0	..	..	...	..		
.875	47.0	..	..	...	..		

^{a} Mole fraction of methyl vinyl sulfoxide in original monomer mixture. ^{b} Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from sulfur analysis. ^{c} Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from carbon analysis. ^{d} Analysis corrected for ash content. ^{e} Yield too small for analysis.

TABLE II

COPOLYMERIZATION OF METHYL METHACRYLATE (M_1) WITH METHYL VINYL SULFOXIDE (M_2)

$M_2{}^a$	Time, hr.	Conversion, %	Percentages S	C	H	$dM_2{}^b$ (S)
0.225^d	3.0	2.42	0.24	59.08	8.04	0.007
.250^d	6.0	0.45	.77	60.98	8.36	.024
.375	45.0	..^{e}	..	...	..	
.500	48.0	..	..	...	..	

^{a} Mole fraction of methyl vinyl sulfoxide in original monomer mixture. ^{b} Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from sulfur analysis. ^{d} Analysis corrected for ash content. ^{e} Yield too small for analysis.

Ultraviolet Absorption Measurements.—The measurements were made using 95% ethanol as the solvent. A Beckman quartz spectrophotometer was employed, the spectrum was examined from 225 to 250 mμ at 1.0 mμ intervals, and from 250 to 320 mμ at 5.0 mμ intervals.

The molar extinction coefficient (ϵ) was calculated from the equation $\epsilon = D/cd$; where D is the density of transmission, d is the length of the cell in centimeters, and c is the concentration of the solution in mole/liter. The concentration of methyl vinyl sulfoxide was 0.0001368 mole/liter in the case of the product from the dehydrohalogenation of β-chloromethyl methyl sulfoxide, and 0.0001497 mole/liter in the case of the product from the hypochlorite oxidation of methyl vinyl sulfide. The curves were identical and showed a maximum at 229 mμ, log ϵ 3.32.

Infrared Absorption Measurements.—The measurements were made using a Beckman spectrophotometer Model IR-2; the spectrum was examined from 6.8 to 8.5 μ, employing the pure compounds (*i.e.*, no solvent was used). The β-chloroethyl methyl sulfoxide was recovered material from one dehydrohalogenation experiment, and it was redistilled and collected at 96° (0.9 mm.), but still had a trace

(1) American Cyanamid Fellow, 1948-1950.

(2) Abstracted from a Ph.D. thesis submitted to the Graduate School of the University of Notre Dame. Presented at the XII International Congress, New York, September 11, 1950.

(3) C. C. Price and J. Zomlefer, THIS JOURNAL, 72, 14 (1950).

(4) Analyses by Micro-Tech Laboratories, Skokie, Ill.

(5) W. R. Kirner and W. Windus, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 136.

(6) R. Brown and R. C. G. Moggridge, J. Chem. Soc., 816 (1946).