

Measurement of Molecular Weight of Poly(vinyl Chloride)

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Synopsis

Molecular weights of six bulk-process and five suspension-process PVC samples have been measured as part of a study aimed at developing a technique for gel permeation-chromatographic analysis of this polymer in tetrahydrofuran at room temperature. Osmometric \bar{M}_n values measured in cyclohexanone appear to be valid; the results are insensitive to thermal history or ultrasonic irradiation of the solution. Corresponding measurements in tetrahydrofuran changed with measurement temperature and indicated the presence of stable supermolecular PVC aggregates in this solvent. Such aggregates can be dispersed by ultrasonic treatment of the solution for brief periods. Simultaneous degradation of PVC molecules appears to be prevented by addition of small concentrations of nonionic surfactant to the tetrahydrofuran solutions. Treated solutions are suitable for GPC analyses at ambient temperatures. The results of osmometry, light scattering, and GPC agreed well.

INTRODUCTION

The use of dilute solutions of macromolecules for molecular weight measurements requires the polymer to be dispersed on a molecular level. This state is often not realized with poly(vinyl chloride) (PVC) polymers. Doty and co-workers¹ reported that stable multimolecular aggregates may persist under certain conditions. The aggregation described differs from that observed with many other polymer-solvent systems in that a dynamic equilibrium between clustered and isolated solute molecules does not appear to exist in PVC solutions. That is to say, the concentration and size of PVC clusters are little affected by gross polymer concentration, whereas a dynamic equilibrium shifts toward the disassociated state as the solution becomes more diluted. A pronounced effect of solution thermal history was also noted for mixtures of PVC in dioxane and butanone.

Gautron and Wippler² studied commercial PVC bulk-process polymers similar to some of those in the present investigation. Tetrahydrofuran solutions were reported to contain few agglomerates, but heating of the mixture was noted to result in an increase in association, with a maximum in the extent of clustering at 60°C and disappearance of aggregates at 110°C.

Hengstenberg and Schuch³ studied the behavior of fractionated and whole suspension-process polymers in butanone, tetrahydrofuran, and dimethylformamide. The formation of supermolecular clusters was found to be

influenced largely by solvent, temperature used to effect initial solution, and polymer molecular weight. Concentration was of minor significance in this connection. Macromolecules with very low molecular weights were stated not to form clusters, while a high molecular weight fraction produced a high degree of association in butanone. The clusters could be broken to some extent by application of heat or by ultrasonic radiation. The latter technique is exploited in the study described here.

Pezzin and co-workers⁴ and Nakazawa et al.⁵ have commented on the lack of agreement in Mark-Houwink relations for PVC in various solvents, and this has been ascribed to the existence of stable supermolecular structures, even in good solvents.⁶ Association in tetrahydrofuran has been reported frequently.^{2,7-10} Crugnola and Danusso⁹ observed that heating solutions to 150°C destroyed aggregates in cyclohexanone but not in tetrahydrofuran. This is consistent with the observations of Kratochvil and co-workers⁶ that heating of PVC solutions to 80°C for 1 hr decreased the intensity of light scattered by higher molecular weight polymers. The effect of heating was more pronounced in cyclohexanone than in tetrahydrofuran mixtures, where an increase in molecular weight was sometimes observed.^{2,11}

Measurement of molecular weights of PVC samples is evidently difficult because of the effects described. Such measurements always hinge on the assumption that the polymer molecules exist independently in solution. The influence of concentration-dependent supermolecular entities is eliminated by making measurements in dilute solutions and extrapolating to infinite dilution. These measures cannot be effective, however, if the PVC compositions contain stable aggregates.

The work reported here was undertaken to develop a method for making reliable molecular weight measurements on PVC samples. The existence of aggregates was confirmed, but this study differs from those cited in that the present emphasis is primarily on means of eliminating supermolecular structures, rather than studying their nature. We have attempted to disperse aggregates and so measure molecular weight averages of the entire initial distribution. This differs from other techniques in which large entities are removed from the sample before molecular weight measurements are made.¹²

A particular object of the present work involved the establishment of a procedure for gel permeation-chromatographic analyses of PVC. Tetrahydrofuran (THF) is the most common solvent used in gel permeation chromatography (GPC). Although solvent and temperature changes are possible with this technique, they are not desirable or convenient. An effort was therefore made to establish a GPC measurement method suitable for PVC solutions in THF at room temperature.

The polymer samples studied were commercial polymers, which were analyzed as received. Materials made by bulk and suspension polymerization processes were studied and some differences were noted in the characteristics of these materials.

Exploratory experiments emphasized \bar{M}_n measurement by osmometry because of the convenience of this technique. Conclusions from this pilot study were tested in light-scattering experiments, which yielded \bar{M}_w values. Since \bar{M}_n and \bar{M}_w are the arithmetic means of the normalized differential number and weight distributions, the latter average is evidently more sensitive than \bar{M}_n to the presence of agglomerates. A procedure for GPC in THF at room temperature was based on the results of the light-scattering and osmometry experiments.

EXPERIMENTAL

Materials

Four suspension-process PVC polymers were studied. These included Geons 101EP-F12 and 105EP-F7 (Goodrich) and Opalons 630 and 650 (Monsanto). Five bulk-process polymers^{13,14} examined were Rucons B22, B26, B32, B34, B38, and B41 (Hooker). Superficially, at least, the two PVC types have the same chemical composition, except that suspension resins contain small concentrations of surface-active agents and bulk-process polymers are free of this contaminant. The samples studied by Gauthron and Wippler² were produced by a bulk process. Resins examined by the other workers cited were suspension or solution (surfactant-free) whole polymers or fractions.

It was desirable to add a surfactant to some of the PVC solutions, for reasons discussed below. The material used was Igepal Co 630 (GAF), which is a polyoxyethylene nonylphenol with formula weight 682.¹⁵ A systematic study of effects of other surfactants was not made. The product used was chosen because it is nonionic and is not either very highly soluble or insoluble in THF.

Osmometry

A Hewlett-Packard Model 502 dynamic osmometer was used with gel cellophane membranes. This unit was compared with a conventional static, two-chamber glass Hellfritz osmometer.¹⁶ With Rucon B41 PVC in THF at 27°C, measured \bar{M}_n values were 65,900 and 69,000 with the dynamic and static instruments, respectively. There seems thus to be no systematic error in the high-speed osmometer which would produce results different from static osmometry. It is tempting to expect a difference between the two methods because the lower equilibration time for the dynamic instrument might reduce the amount of diffusion of low polymer through the membrane and hence yield a lower, more nearly correct \bar{M}_n value.¹⁷ Our single comparison showed no significant difference. This is in accord with the more detailed study of Holleran and Billmeyer,¹⁸ who found that a reduction of equilibration time of over two orders of magnitude was not enough to eliminate the effect of diffusion of polyethylenes at 90°C.

The density of cyclohexanone was obtained from the *International Critical Tables*. Tetrahydrofuran densities were measured with a pycnometer and found to be 0.8775, 0.8644, and 0.8617 g/cm³ at 27°, 37°, and 45°C, respectively.

The second virial coefficient was obtained from eq. (1),

$$\frac{\pi}{C} = \frac{RT}{\bar{M}_n} + RT[A_2C + A_3C^2 + \dots], \quad (1)$$

by plotting π/C against C (π is the osmotic head and C is the solute concentration in g/cm³; the units of A_2 are thus (cm³ mole)/g²). Only four concentrations were used in osmometric measurements, and almost all plots of π/C against C were linear. There was thus no advantage in using the more correct $(\pi/C)^{1/2}$ -against- C plot,¹⁹ but the second virial coefficients quoted are less accurate than if a larger number of dilutions had been made. The uncertainty in A_2 values is greater than in the \bar{M}_n measurements.²⁰

Solutions containing 3, 6, 9, and 12 g/l. PVC were prepared by diluting a 20 g/l. stock solution which had been made by dissolving the polymer in tetrahydrofuran or cyclohexanone at room temperature. All solutions were stored under nitrogen.

Results of replicate measurements of \bar{M}_n in tetrahydrofuran are listed in Table I. All repeat experiments were made on different solutions, except as noted in one case. It can be seen that the precision of the method is good except for the highest molecular weight polymers, Rucons B38 and B41.

TABLE I
 \bar{M}_n of PVC Samples in Tetrahydrofuran, 27°C, Osmometric Measurements

Sample	First Series		Replicate Series	
	$\bar{M}_n \times 10^{-3}$	A_2 , ($\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}$) $\times 10^4$	$\bar{M}_n \times 10^{-3}$	A_2 , ($\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}$) $\times 10^4$
Rucon B 22	33.5	19.3	32.6	18.6
Rucon B 26	38.7	26.2	38.7	22.1
Rucon B 32	60.1	20.0	60.0	19.3
Rucon B 34	55.7	18.0	61.4	11.7
Rucon B 38	65.4	17.3	90.6	13.8
Rucon B 41	79.4	18.6	79.5	19.0
			78.3	18.6
	69.0 ^a		68.8 ^a	
Geon 101EP	79.0	18.6		
Geon 103EP	65.1	20.7		
Geon 105EP	49.5	21.4		
Opalon 630	52.5	20.8	52.7	22.1
Opalon 650	51.6	13.5	57.9	16.2
			55.2	15.2

^a This is the only value measured with a static osmometer. The solution is the same as that which yielded an \bar{M}_n value of 65,900 with the high-speed osmometer.

This is not entirely unexpected, in view of the conclusions of Hengstenberg and Schuch² that solution history affects the extent of clustering, particularly at higher molecular weights.

The second virial coefficients listed in Table I are comparable to those reported by Bajjal and Kaupilla²¹ and by Kratochvil.²² Any trend in A_2 values with molecular weight changes is obscured by the scatter in second virial coefficient values.

Results of osmometry measurements at 27°, 37°, and 45°C in THF are given in Table II. The measured \bar{M}_n values of all polymers examined tend to exhibit minima at 37°C. These results are reminiscent of the report of Gautron and Wippler² in which an increase in aggregation is shown in THF at 60°C and higher temperatures. These authors confined their study to a single bulk polymer of \bar{M}_w 100,000, which would be about the same as our Rucon B32 sample. Their conclusion that the molecular weight is essentially invariant in THF at temperatures below 50°C is not entirely consistent with our study of a larger number of samples.

Also included in Table II are results of \bar{M}_n measurements on three PVC samples of unknown manufacture which are available commercially (Pressure Chemical Company, Pittsburgh) as molecular weight standards. The \bar{M}_n values in tetrahydrofuran are again higher at 45° than at 27°C, and the differences are particularly significant with higher molecular weights. Our results disagree with the supplier's data for PVC 400-3, and, to a lesser degree, for sample 400-2. This may be an instance of the effect of solution history on solute aggregation.

TABLE II
Tetrahydrofuran Effect of Temperature, Osmotic Measurements

Sample	27°C		37°C		45°C	
	\bar{M}_n $\times 10^{-3}$	A_2 $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$	\bar{M}_n $\times 10^{-3}$	A_2 $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$	\bar{M}_n $\times 10^{-3}$	A_2 $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$
Rucon B 22	33.5	19.3	24.5	13.2	30.7	19.2
Rucon B 26	38.7	26.2	31.5	15.1		
Rucon B 32	60.1	20.0			97.7	37.7
Rucon B 34	55.7	18.0	50.0	15.8		
Rucon B 38	65.4	17.3	54.2	17.4		
Rucon B 41	79.4	18.6	68.5	17.1	102.5	25.6
Geon 101EP	79.0	18.6			99.3	23.6
Geon 105EP	49.5	21.4				
Geon 103EP	65.1	20.7	30.3	29.6	57.4	24.3
Opalon 630	52.5	20.8				
Opalon 650	51.6	13.5				
PVC 400-2*	36.0				32.9(28.4)	
PVC 400-3*	76.4	—			81.2	
PVC 400-4*	54.5	—			73.6	

* Suppliers \bar{M}_n data ($\times 10^{-3}$): PVC 400-2, 25.5; PVC 400-3, 41.0; PVC 400-4, 54.0.

TABLE III
 Osmometry in Tetrahydrofuran and Cyclohexanone

Sample	Tetrahydrofuran 27°C		Tetrahydrofuran 37°C		Cyclohexanone 27°C	
	\bar{M}_n $\times 10^{-3}$	A_2 , $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$	\bar{M}_n $\times 10^{-3}$	A_2 , $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$	\bar{M}_n $\times 10^{-3}$	A_2 , $\left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2}\right)$ $\times 10^4$
Rucon B 34	55.7	18.0	50.0	15.8	52.3	13.3
	61.4	11.8				
Rucon B 38	65.4	17.3	54.2	17.4	59.5	24.0
	90.6	13.8				
Rucon B 41	79.4	18.6	68.5	17.1	71.2	12.6
	78.3	18.6			73.2	13.3
					69.4 ^a	12.6
Geon 101EP	79.0	18.6			69.4	11.5
Geon 103EP	65.1	20.7	30.3	29.6	58.8	11.5
Opalon 630	52.5	20.8			28.3	5.2
	52.7	22.1			28.3	5.0
					30.1	14.7
Opalon 650	51.6	13.5			28.3 ^a	5.2
	55.2	15.2			37.3	4.4
	57.9	16.2				

^a Solutions held at 80°C for 1 hr before being cooled to 27°C.

Cyclohexanone is known to be a stronger solvent than THF for PVC, and osmotic pressure measurements were therefore also made in cyclohexanone at 27°C; \bar{M}_n and A_2 values for this solvent are compared to corresponding figures for THF solutions at 27° and 37°C in Table III.

The three bulk-process polymers studied (Rucons B34, B38, and B41) gave equivalent \bar{M}_n figures in cyclohexanone at 27° and in THF at 37°C. At 27°, cyclohexanone \bar{M}_n figures were markedly lower than THF values for the Opalon samples and slightly lower for the Geon polymers. The A_2 figures in cyclohexanone are generally less than in THF, in agreement with Kratochvil's observations²² and contrary to the general rule that solvent power parallels the magnitude of the second virial coefficient.

Heating the cyclohexanone solution at 80°C for 1 hr before subsequent osmotic pressure measurements at 27°C had no significant effect on \bar{M}_n of Rucon B41 or Opalon 630. In the light of the references cited above and general coincidence of THF values at 37° and cyclohexanone \bar{M}_n figures at 27°, this observation suggests that the number-average molecular weights in cyclohexanone are not seriously affected by polymer aggregation, at least for our samples.

It is interesting that a pronounced difference in \bar{M}_n figures at 27°C in the two solvents studied is shown only by Opalon resins. This suggests that the solvent resistance of binding forces in aggregates may reflect the details of the polymer manufacturing process in some way.

The data in Table III might also be taken to indicate that agglomeration in THF is not serious at 27°C. Subsequent experiments described below show that this is not true. The reason for this misleading conclusion possibly reflects the fact that \bar{M}_n is the average molecular weight least affected by clustering. Any uncertainty in \bar{M}_n will be accentuated in measurements of \bar{M}_w by light scattering or of \bar{M}_w and \bar{M}_z by GPC. (\bar{M}_z is not very sensitive to the existence of agglomerates if they are less solvated than isolated macromolecules.¹)

Ultrasonic Treatment

Although the preliminary experiments described above indicated that THF might provide suitable solutions at 37°C, operation of many GPC units is not practical or convenient at other than ambient temperatures. The data quoted also imply that the measurement and solution temperatures might be quite critical and might depend to some extent on the process used to manufacture a particular PVC polymer. Attention was therefore directed to other techniques which might permit use of THF solutions at room temperature, for accurate molecular weight measurements.

Following Hengstenberg and Schuch,³ the application of ultrasonic radiation was studied in cyclohexanone and tetrahydrofuran solutions. The device used was a 200-watt 20-KC (nominally) laboratory ultrasonic cleaner. The apparatus has the virtue of being relatively inexpensive but does not provide monochromatic frequencies. The only experimental variable was the duration of ultrasonic treatment. A possible mechanism involved in ultrasonic degradation of supermolecular PVC clusters is discussed below. Osmotic measurements were made immediately after polymer solutions were removed from the sonic cleaner bath.

The effects of such treatment on \bar{M}_n in both solvents are listed in Table IV. There are several interesting features in these results. \bar{M}_n in cyclohexanone did not change appreciably (for one bulk-process and two suspension process polymers) after 5 min of ultrasonic irradiation. This observation and the absence of thermal history effects (Table III) reinforce the suggestion that \bar{M}_n figures measured in cyclohexanone at 27°C might be accurate values.

In tetrahydrofuran solutions, 15 min ultrasonic treatment reduced \bar{M}_n of Opalon samples markedly, but not to the levels measured in ordinary cyclohexanone solutions. It will be recalled that these polymers seemed to be particularly subject to aggregation in THF at 27° (Table III). Reduced osmotic pressure-concentration plots are shown in Figure 1.

Five minutes of ultrasonic treatment in THF at 27°C had little effect on measured \bar{M}_n values of the Rucon bulk polymers, although A_2 figures generally decreased. The bulk polymers exhibited markedly lower \bar{M}_n values, however, after irradiation for 15 min in this solvent. These results are shown in Figure 2. The reasons for the deviation of some of the lowest concentration points in Figure 2 were not investigated, as they are not likely to be germane to the main aims of this study.

TABLE IV
Effect of Ultrasonic Treatment on \bar{M}_n

Sample	Cyclohexanone 27°C		Cyclohexanone 27°C, 5 min, ultrasonic		Tetrahydrofuran, 27°C		Tetrahydrofuran, 27°C, 5 min, ultrasonic		Tetrahydrofuran, 27°C, 15 min, ultrasonic	
	$\bar{M}_n \times 10^{-3}$	$\left(\frac{A_s}{g^2} \times 10^4\right)$	$\bar{M}_n \times 10^{-3}$	$\left(\frac{A_s}{g^2} \times 10^4\right)$	$\bar{M}_n \times 10^{-3}$	$\left(\frac{A_s}{g^2} \times 10^4\right)$	$\bar{M}_n \times 10^{-3}$	$\left(\frac{A_s}{g^2} \times 10^4\right)$	$\bar{M}_n \times 10^{-3}$	$\left(\frac{A_s}{g^2} \times 10^4\right)$
Rucon B 22			33.5	19.3	31.3	15.9				
Rucon B 26			38.7	26.2	36.5	20.7				
Rucon B 32			60.1	20.0	56.8	18.0				
Rucon B 34	52.3	13.3	55.7	18.0	53.7	10.0	32.2*	8.3		
Rucon B 38	59.5	24.0	65.4	17.3	76.6	12.0	38.6*	9.7		
Rucon B 41	71.2	12.6	79.4	18.6	63.7	15.9				
Geon 101EP	69.4	11.5	79.0	18.6						
Geon 105EP			49.5	21.4						
Geon 103EP	58.8	11.5	65.1	20.7						
Opalon 630	28.3	5.2	52.5	20.8					43.6	17.9
Opalon 650	37.3	4.4	51.6	13.5					45.5	11.7

* Evidence of degradation.

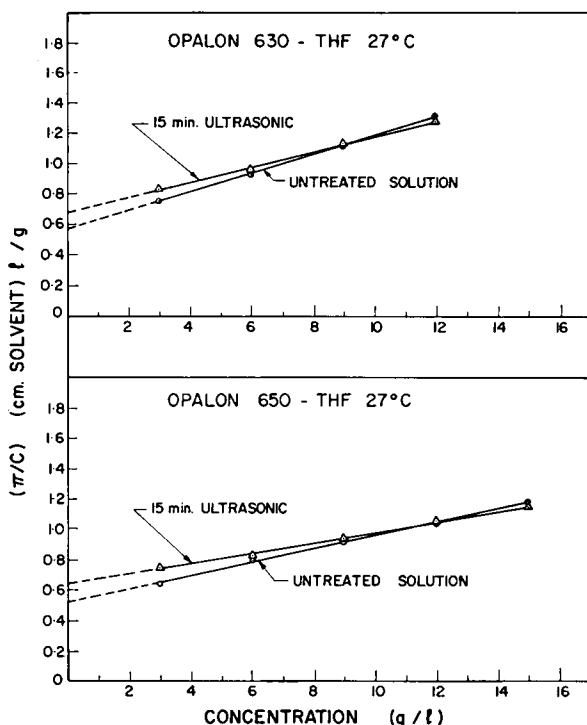


Fig. 1. Reduced osmotic pressure-concentration plots of suspension-process PVC.

Figures 1 and 2 reveal a clear difference in behavior of bulk Rucon and suspension Opalon polymers on prolonged ultrasonic irradiation. We ascribe this to molecular degradation of the bulk process PVC, since the 15-min treatment plots in Figure 2 are shifted to higher π/C values at all concentrations. The reduced osmotic pressure plots in this figure are typically those obtained from chemically identical polymers of different molecular weights. The plots in Figure 1 and the 5-min and untreated lines in Figure 2 coincide at higher concentrations. (The plots differ from those characteristic of concentration-dependent association, in which the intercepts ($1/\bar{M}_n$) coincide, but agglomeration produces a lower A_2 and deviations at higher concentrations.²³) Results of experiments with added surfactant described below support the conclusion that molecular degradation is essentially absent in ultrasonically treated suspension polymer solutions.

Effect of Ultrasonic Energy

It is pertinent at this point to consider possible reasons for the different behavior of the suspension- and bulk-process polymers during ultrasonic treatment in solution. The only difference evident *a priori* between the two PVC types is the presence of small concentrations of surfactants in the suspension polymers, and we ascribe the difference in reaction to sonic en-

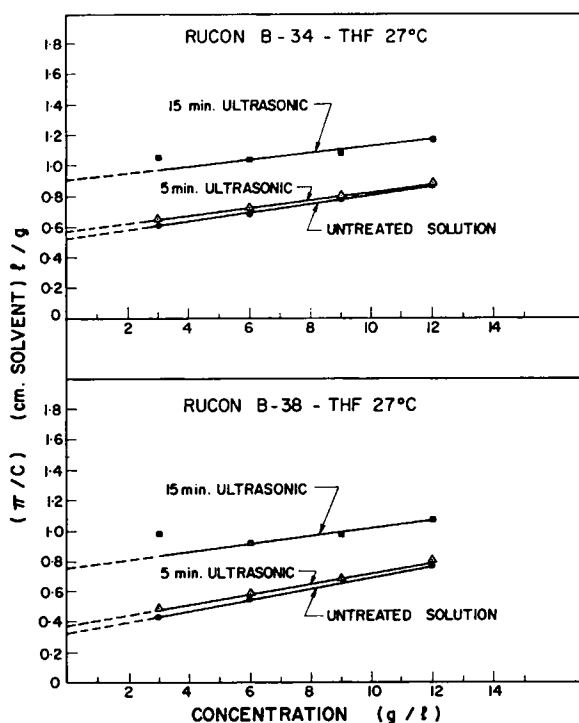


Fig. 2. Reduced osmotic pressure-concentration plots of bulk-process PVC.

ergy to this cause. The arguments presented here are largely circumstantial, but the subsequent experimental work described below produced results which are consistent with this reasoning. The surfactants present are unlikely to have moderated the sonic intensity in the system, but it is probable that the stress exerted on dissolved polymers may have been reduced by the action of adsorbed layers of surfactant molecules.

The occurrence of chemical reactions and dispersion of aggregates in an ultrasonic field are closely connected with the phenomenon of cavitation, wherein voids are formed in the fluid. When these voids collapse, localized motion of the liquid phase will exert forces on dispersed particles. Degradation of macromolecules does not occur in the absence of cavitation,^{24,25} and emulsification, which involves breaking up and dispersion of aggregates, is also closely associated with cavitation.²⁶ It is appropriate, therefore, to consider the different behaviors of Rucon and Opalon polymers in relation to cavitation.

The theory of the growth and collapse of a cavity in a fluid due to Noltingk and Neppiras^{27,28} shows that the variables affecting cavitation are the sonic frequency, the static pressure in the liquid, the amplitude of the pressure waves, and the initial radius of the cavity (or nucleus) R_0 . It can be shown that a cavity will not collapse unless its initial radius satisfies the inequality

$$R_0 > \frac{4S}{3(P_0 - P_a)} \quad (2)$$

where P_0 is the pressure amplitude, P_a is the static pressure, and S is the surface tension of the liquid. A similar expression can be derived for the case when the cavity consists of a spherical solid. In either event, cavitation will occur on smaller nuclei in the presence of a surfactant which lowers S . The intensity of cavitation, as determined by the velocity with which cavities collapse, can be shown to be inversely proportional to S/R_0 and to R_0^3 . Thus, with a given nucleus, addition of a surfactant which decreases the surface forces between the nucleating particle and the solvent will result in more intense shock waves from collapse of the cavities generated. This conclusion is consistent with the observation that cavitation is induced more readily at glass-water interfaces by the introduction of substances that lower the strength of the interfacial forces.²⁹

The presence of surfactants on the Opanol polymers is thus likely to increase the intensity of cavitation and lead to more degradation of the polymers, rather than less, as observed, if all the other factors are equal. It seems reasonable, however, that a surface layer of surfactant on dissolved polymers will moderate the action of cavitation shock waves.

The polymer degradation mechanism proposed by Gooberman³⁰ is based on the assumption that the stresses set up in a macromolecule by the collapse of a cavity are due to the shock wave (rapid pressure rise followed by a sharp pressure drop) radiated from the cavity when it reaches its minimum radius. During the pressure rise, the solvent will be compressed, and, assuming that macromolecular conformation changes little in this brief time interval, the number of solvent molecules within the volume enclosed by the polymer will be greater at the peak pressure than at atmospheric pressure. During the subsequent pressure drop, these entrained solvent molecules flow out of the macromolecule, and this flow sets up stresses within the macromolecule. On this basis there will be a velocity gradient across a macromolecule and hence a stress difference. Gooberman's expression for the total stress, τ , acting on the center bond of the macromolecule is

$$\tau = 0.67fGbn^{1.5} \quad (3)$$

where f is the friction coefficient between solvent and polymer and G is the velocity gradient across the macromolecule which is assumed equivalent to a random coil of $2n + 1$ segments, each with length b . A plausible reason for the lower extent of ultrasonic degradation of suspension polymers in tetrahydrofuran is a reduced frictional coefficient with solvent because of adsorbed surfactant on the PVC. Such layers will have lower strengths than chemical bonds; they can be sheared asunder by flowing solvent which would break the macromolecular chain under other circumstances.

Another factor which may be of secondary importance concerns the stabilization of dispersed components of aggregates. An aggregate is effectively larger than its component molecules and is the most likely of all species to

be broken by shock waves resulting from cavitation, since the stress difference across the larger particle will be greater. Presumably, some bond breaking can occur in this process, depending on the strength of the aggregation forces and the location of the aggregate relative to the collapsed liquid cavities. It seems reasonable that a molecule of given size is less likely to be degraded by sonic stresses if it is isolated than if it forms part of an associated complex. Surfactants in solution may reduce the net aggregate concentration by adsorbing on macromolecules and hindering re-aggregation immediately after such groups are disrupted.

The considerations mentioned led to experiments described below in which surfactants were added to bulk polymer solutions before ultrasonic irradiation.

Osmometry of Polymer-Surfactant Solutions

The surfactant (Igepal Co 630) concentration in the preliminary experiments reported here was 0.1% (weight/volume of solution) or 5% (w/w of polymer) unless noted otherwise. Solutions were irradiated sonically in the laboratory cleaner bath for stipulated times at room temperature and quickly transferred to the osmometer.

Figure 3a shows reduced osmotic pressure plots for Rucon B34 bulk

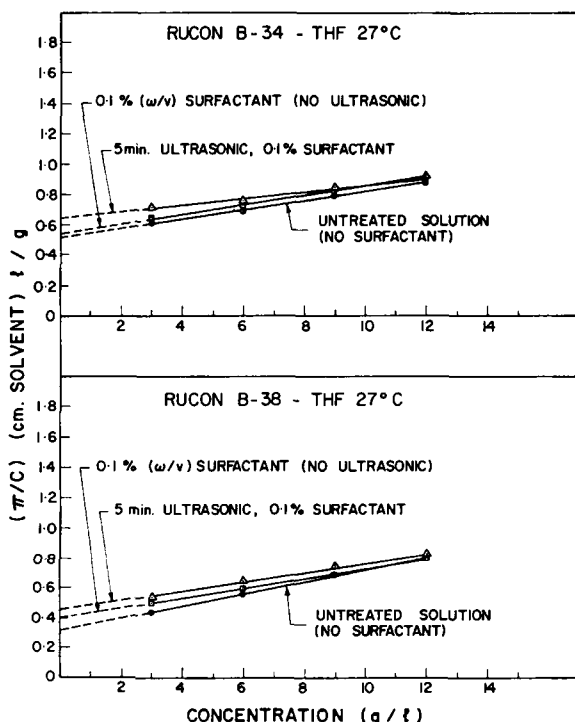


Fig. 3. Effect of added surfactant on reduced osmotic pressure-concentration plots of bulk-process polymers.

polymer in THF untreated, with 0.1% (w/v) surfactant, and with this concentration of surfactant after 5 min of ultrasonic treatment. Addition of 5 wt-% low molecular weight material would be expected to lower the \bar{M}_n of the total solute, but this average was 55,700, which is the same as that quoted in Table IV for solutions of this polymer alone in THF. The application of 5 min of ultrasonic radiation reduced \bar{M}_n to 48,300, with no evidence of degradation in the osmotic pressure plot in Figure 3a. Again, comparing with the data in Table IV, this \bar{M}_n is close to that obtained with the polymer alone in cyclohexanone. These observations indicate a slight effect of aggregation in this polymer (although \bar{M}_n is not very sensitive to clustering) and the existence of the surfactant as micelles with molecular weights much higher than the formula weight of Igepal Co 630.

Figure 3b shows similar plots for the higher molecular weight bulk polymer Rucon B38. Here, addition of surfactant lowered the apparent \bar{M}_n from 90,550 to 72,400, and subsequent application of ultrasonic energy reduced the \bar{M}_n of the mixture to 60,400, which compares closely with the value measured for the polymer alone in cyclohexanone at 27°C.

In THF solution without surfactant, the \bar{M}_n of the lowest molecular weight bulk polymer, Rucon B22, changed from 60,000 (untreated) to 56,800 (5 min of ultrasonic treatment). This result is as expected, since the extent of degradation depends inversely and the degree of clustering depends directly on the molecular weight of the polymer. The addition of 5 wt-% surfactant (on polymer) decreased the apparent \bar{M}_n to 53,700, and ultrasonic treatment of the surfactant-Rucon B22 solution dropped this value to 47,300, with no apparent molecular degradation. Apparently, then, aggregates are broken up more effectively in the presence of surfactant. As mentioned above, this may be due to hindrances to reaggregation because surfactant adsorbs onto the isolated polymer molecules.

Osmotic pressure measurements on surfactant solutions of Rucon B41, the highest molecular weight bulk polymers, showed little difference between the \bar{M}_n values after 5 and 15 min of ultrasonic treatment. In view of this, it was decided to restrict this treatment to 5 min, to minimize possible molecular degradation during longer irradiation times. The indications of this experiment were confirmed by light-scattering measurements described below.

Addition of surfactant to the polymer-solvent system alters the effective \bar{M}_n of the solute, and this change must be compensated in calculating \bar{M}_n of the polymer. Since the surfactant can be expected to aggregate into micelles, an aggregate formula weight for this material is required in the calculations. This can be estimated by comparing the apparent \bar{M}_n of the solute with and without added surfactant, without ultrasonic treatment. It seems likely that simple addition of surfactant will not change the state of aggregation of the polymer. Equation (4) can therefore be applied:

$$(\bar{M}_n)_A = \left[\frac{w_s}{\bar{M}_s} + \frac{w_p}{(\bar{M}_n)_p} \right]^{-1} \quad (4)$$

where w_s and w_p are weight fractions (of solute) of surfactant and polymer, respectively; \bar{M}_s is the mean molecular weight of surfactant micelles; $(\bar{M}_n)_p$ is the number-average molecular weight measured with the solution of polymer alone; and $(\bar{M}_n)_A$ is the corresponding value of the polymer-surfactant mixture. An example, for Rucon B26, is: $w_p = 0.95$, $w_s = 0.05$, $(\bar{M}_n)_p = 38,700$, $(\bar{M}_n)_A = 37,150$, and $\bar{M}_s = 21,700$.

Surfactant effective molecular weights calculated in this manner are listed in Table V. Data for Rucon B38 are not included because the scatter in $(\bar{M}_n)_p$ figures was too great to permit reasonable calculations. The mean \bar{M}_s figure is 22,100, corresponding to an average micelle containing 32 surfactant molecules. This aggregation number is the same order of magnitude as those observed for other nonionic surfactants in organic solvents.³¹

The effect of surfactant concentration was studied with Rucon B41 solutions in THF. The data are also summarized in Table V. The aggregation number of the surfactant is evidently reduced at lower concentrations from 32 molecules at 0.1% (w/v) to 4-5 molecules at concentrations of 0.01-0.02%.

We use the mean \bar{M}_s figure to correct $(\bar{M}_n)_A$ of ultrasonically treated samples for surfactant effects. This reduces the accuracy of the corrected polymer \bar{M}_n because of the uncertainty in \bar{M}_s . The surfactant concentration is 5 wt-% on the polymer in the exploratory osmotic pressure experiments reported here. In the final procedure recommended below, the surfactant concentration is only 1 wt-%, and the assumption of a mean value for \bar{M}_s will have slight consequences. At this concentration, the effect of surfactant on \bar{M}_w and higher averages is negligible. Equation (4) is used with the mean \bar{M}_s value estimated above to calculate the true \bar{M}_n of the polymer after ultrasonic treatment in the presence of surfactant. This requires the assumption that the sonic pulses break polymer aggregates but do not change the size of the average surfactant micelle. This reasoning must refer in any case to "excess" surfactant, since material

TABLE V
Apparent \bar{M}_n of Surfactant in Tetrahydrofuran

Polymer	Igepal Co 630 concentration		$(\bar{M}_n)_A$ (polymer and surfactant) $\times 10^{-3}$	$(\bar{M})_p$ (polymer mean values) $\times 10^{-3}$	\bar{M}_s [eq. (4)] $\times 10^{-3}$
	% w/v on solution	% w/w on polymer			
Rucon B 26	0.1	5	37.2	38.7	21.7
Rucon B 32	0.1	5	53.7	60.1	17.8
Rucon B 34	0.1	5	55.7	58.0	28.9
Rucon B 41	0.1	5	65.5 ^a	74.3	20.0
Rucon B 41	0.02	1	56.8	78.3 ^b	2.0
Rucon B 41	0.01	1	70.7	78.3 ^b	3.5

^a Mean of four different solutions.

^b Same stock solutions.

adsorbed on polymer will not change the osmotic pressure. Validation of the calculation rests ultimately on the internal consistency of the \bar{M}_n figures derived and is not critical in the final procedure, for reasons mentioned above.

A few osmotic pressure measurements were made with Opalons 630 and 650 and Rucon B41 dissolved in cyclohexanone containing 0.1% (w/v) surfactant after 5 min of ultrasonic irradiation. The \bar{M}_n figures did not change significantly from those measured in cyclohexanone alone, after correction for the presence of surfactant. The aggregation number of Igepal Co 630 in cyclohexanone was found to be about 7–8 molecules, compared to the 32 mentioned above for THF solutions. This reflects the fact that cyclohexanone is the better solvent for Igepal Co 630. This surfactant is insoluble in Stoddard solvent, which has a solubility parameter around 7 (cal/cm³)^{1/2}, and soluble in the range of solubility parameters between 8.8 (xylene) and 14.6 (cal/cm³)^{1/2} (ethylene glycol).³² THF has a solubility parameter of 9.1, near the lower end of this range, while the better solvent cyclohexanone has a solubility parameter of 9.9 (cal/cm³)^{1/2}. The invariance of \bar{M}_n under these conditions provides more circumstantial support for the hypothesis that cyclohexanone solutions provided true number-average molecular weights.

All osmometric \bar{M}_n values quoted below for ultrasonically treated polymer-Igepal solutions have been corrected for surfactant effects by the method described above.

Light Scattering

Light-scattering measurements were made in THF with a Brice-Phoenix photometer, at 20°C using 4358 Å light. The specific refractive index increment is 0.1124 ± 0.0044 ml/mg.³³ All solutions were filtered through 0.22 μ “glass fiber” filters, and no solution was older than 10 hr at the time of examination. Angular light-scattering measurements were made at 45°, 70°, 90°, 110°, and 135° to the incident light beam, with solutions containing 1.0, 0.5, 0.25, and 0.125 wt-% polymer. Samples were stirred magnetically for 10 min and then allowed to stand for 10 min, to release air bubbles, before each measurement.

No correction was made to solvent refractive index or refractive index increment for solutions containing surfactant. The good agreement of \bar{M}_w data from light scattering and gel permeation chromatography indicates that this potential complication could be ignored in this case.

Zimm plots were constructed as shown in Figure 4 for Rucon B38. Zero concentration lines were redrawn to a larger scale, as shown in the insert in this figure, to estimate \bar{M}_w and \bar{M}_n . Calculation of \bar{M}_w is straightforward in such plots from the lowest-angle scattering. Large-angle scattering theoretically^{34,35} conforms to the equation

$$\lim_{c \rightarrow 0} \left[\frac{K_c}{R_\theta} \right] = \frac{1}{2\bar{M}_n} \left[1 + \frac{16\pi^2}{\lambda^2} \langle R_G^2 \rangle_n \sin^2 \frac{\theta}{2} \right] \quad (5)$$

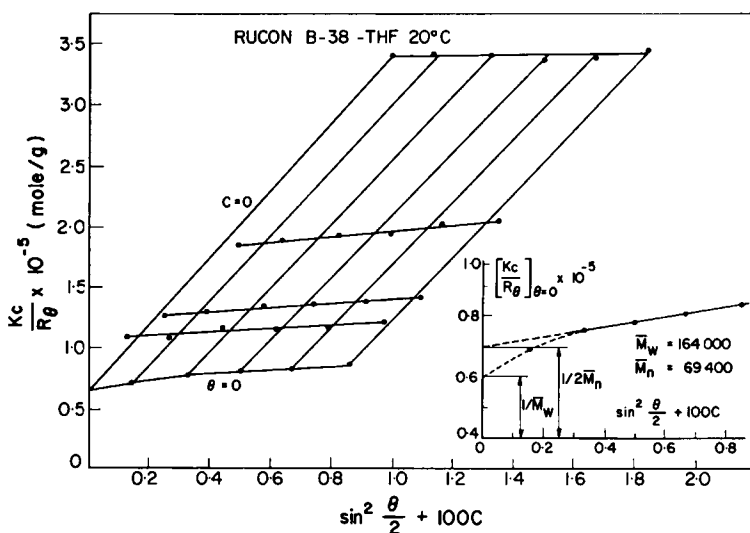


Fig. 4. Zimm plot, Rucon B 38 in THF.

where K is the familiar optical constant used in light scattering, R_θ is the reduced scattering intensity at angle θ to the incident beam, λ is the wavelength of incident light in solution, and $\langle R_G^2 \rangle_n$ is the number-average r.m.s. radius of gyration of the scatterers. The extrapolation of the zero concentration line in the Zimm plot at high values of θ to the ordinate yields an intercept equal to the reciprocal of $2\bar{M}_n$. Equation (5) is derived for linear Gaussian polymer molecules and high scattering angles. It should not be applicable to the data reported here. A surprisingly good agreement was, however, found between \bar{M}_n values from light scattering and osmometry, and it seemed worthwhile to record these results below, with the caution that this coincidence cannot be expected to be general.^{36,37}

Zimm plots for many samples were distorted and involuted. This has been noted frequently with PVC solutions. Freeman and Manning³³ have attributed this anomalous scattering to small quantities of water-soluble dispersing agents present in commercial polymers, but the weight of current evidence indicates that the distorted Zimm plots are caused by entities comparable in size to that of the light used.^{12,38}

The procedure of van Wijk and Staverman⁴⁴ was used to unravel involuted Zimm plots. This involves use of a negative multiplying factor for the concentration term on the abscissa, as shown in Figure 5, for a Rucon B26 solution. Addition of surfactant and ultrasonic treatment did not generally produce more orthodox Zimm plots, so the negative concentration factor was usually used. This observation suggests that the very large entities involved in anomalous lower-angle scattering may include individual molecules as well as clusters which are held together by secondary forces. Giant molecules could easily be formed in this system, since PVC polymer is not soluble in its monomer.

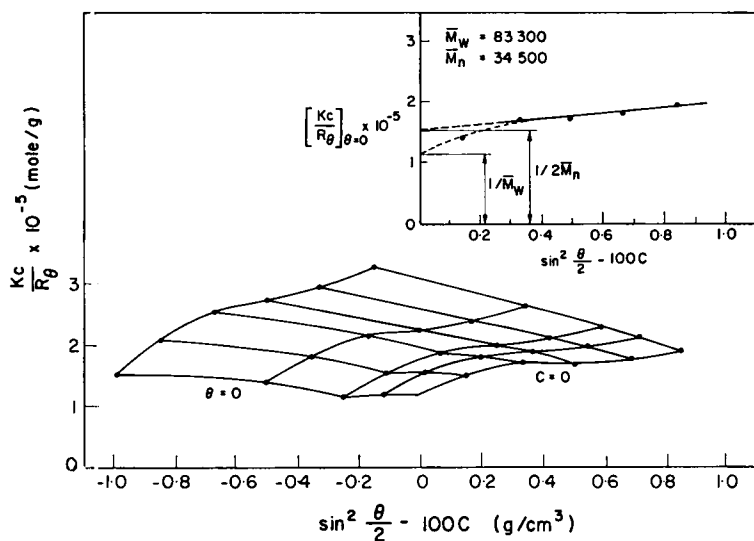


Fig. 5. Zimm plot, Rucon B 26.

A light scattering measurement was made with a Rucon B41 solution in THF containing 0.1% (w/v) surfactant, without ultrasonic treatment. The apparent weight-average molecular weight of the PVC-Igepal mixture, $(\bar{M}_w)_A$ is

$$(\bar{M}_w)_A = w_p(\bar{M}_w)_p + w_s(\bar{M})_s \quad (6)$$

where the meaning of the symbols is apparent from the discussion following eq. (4). The calculated \bar{M}_s in this case was 10,000, which is the same order of magnitude, but lower than the figures listed in Table V, from osmometry. A 5% uncertainty in the \bar{M}_w measurement is more than sufficient to account for this difference.

Measured \bar{M}_w values were not corrected for surfactant because its effect is small compared to the uncertainties in the light-scattering technique.³⁹

Ultrasonic treatment of Rucon B41-0.1% (w/v) Igepal Co 630 solutions for 5 and 15 min gave light-scattering \bar{M}_w values of 143,000 and 149,300, respectively. This reinforces the conclusion from osmometric measurements that the shorter treatment time was satisfactory. It also indicates that the surfactant protects the polymer from molecular degradation.

Results of light scattering and osmometric measurements in THF are listed in Table VI. Note that surfactant was added only to Rucon solutions, before ultrasonic treatment. The suspension polymers (Opalons and Geons) were treated as received, since the preliminary osmometry experiments did not indicate a need for added surfactant. The technique used to disperse agglomerates clearly decreases \bar{M}_w sharply. The significance of aggregation is indicated to depend directly on the polymer molecular weight, as expected from reports of other workers.^{3,6}

TABLE VI
Light-Scattering (20°C) and Osmometric Measurements (27°C) in Tetrahydrofuran

Sample	Surfactant concn, % w/v	Ultrasonic treatment, min	Light Scattering			Osmometry	
			$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3a}$	$A_s \left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2} \right) \times 10^4$	$\bar{M}_n \times 10^{-3a}$	$A_s \left(\frac{\text{cm}^3 \text{ mole}}{\text{g}^2} \right) \times 10^4$
Rucon B 22	—	—	68.9	32.6	4.6	33.5	19.3
Rucon B 26	—	—	83.3	38.7	3.3	38.7	26.2
Rucon B 26	0.1	5	75.2	34.3	6.3	34.6	19.3
Rucon B 32	—	—	143	60.0	9.0	60.1	20.0
Rucon B 32	0.1	5	100	41.3	11.4	50.4	15.2
Rucon B 34	—	—	189	67.5	10.3	55.7	18.0
Rucon B 34	0.1	5	125	55.9	11.3	51.5	9.0
Rucon B 34	—	5	138	59.0	11.8	—	—
Rucon B 38	—	—	164	69.4	8.4	65.4	17.3
Rucon B 38	—	5	130	57.0	15.0	—	—
Rucon B 38	0.1	5	105	60.5	18.2	66.0	9.3
Rucon B 41	—	—	205	75.8	10.5	79.4	18.6
Rucon B 41	—	5	211	62.5	15.5	—	—
Rucon B 41	0.1	5	143	62.4	9.0	62.3 ^b	—
Opalon 630	—	—	133	50.0	9.0	52.5	20.8
Opalon 630	—	5	100	46.0	17.0	43.6	17.9 ^c
Opalon 650	—	—	166	50.0	10.7	51.6	13.5
Opalon 650	—	5	100	43.4	10.0	45.5	11.7 ^c
Geon 101EP	—	—	198	70.7	11.5	69.4	11.5
Geon 101EP	—	5	140	50.0	10.7	—	—
Geon 103EP	—	—	149	62.0	12.2	65.1	20.7
Geon 103EP	—	5	110	38.4	7.1	—	—
Geon 105EP	—	—	100	49.5	20.6	49.5	21.4
Geon 105EP	—	5	71.4	31.2	17.3	—	—

^a Values quoted for solutions containing Igepal Co 630 are corrected for the presence of surfactants.

^b Mean of three readings.

^c 15 min of ultrasonic irradiation.

Number-average molecular weights from light scattering and osmometry agreed very well, for untreated and treated solutions. It should be noted in this connection that fresh solutions were used for each measurement for which results are listed in Table VI.

Gel Permeation Chromatography

A Waters four-column apparatus was used, with 0.2% (w/v) polymer concentration and 1-min injection time into THF eluant pumped at a rate of 1 ml/min. All solutions were prepared at room temperature and filtered through glass fiber filters under nitrogen pressure. No sample was older than 3 hr at the time of measurement.

Bulk process polymer solutions were also made up with 0.01 weight fraction of Igepal Co 630 (on polymer). That is, the concentration was 0.2 g PVC and 0.002 g surfactant in 100 ml THF. The concentration of Igepal is one fifth that used in osmometry and light-scattering measurements. Surfactant-polymer solutions were filtered, placed in the ultrasonic cleaner bath for 5 min, and then quickly injected into the GPC apparatus. Opalon and Geon solutions were treated similarly, except that no surfactant was added. The procedure described by Coll and Prusinowski⁴⁰ was used to translate the standard polystyrene curve into a PVC calibration curve. It is assumed that flexible coil macromolecules with the same radius of gyration will have equivalent elution volumes in given GPC columns operating under standard conditions. The log M -elution volume curve for polymer B can be obtained from that for polymer A by

$$\log M_B = \frac{1}{1 + \alpha_B} \log \frac{K_A \phi_B}{K_B \phi_A} + \frac{1 + \alpha_A}{1 + \alpha_B} \log M_A \quad (7)$$

where the α and K terms refer to the Mark-Houwink coefficients for each polymer in THF at the experimental temperature, the ϕ terms are obtained from⁴¹

$$\phi = \phi_0 (1 - 2.6\epsilon + 2.86\epsilon^2) \quad (8)$$

$$\epsilon = (2\alpha - 1)/\alpha \quad (9)$$

and ϕ_0 is a constant which cancels out. Taking polymer A as polystyrene and polymer B as PVC, the appropriate constants for use in eqs. (7) to (9) are⁴²

$$\alpha_A = 0.682, K_A = 1.905 \times 10^{-2} \text{ dl/g}, \epsilon_A = 0.1213$$

and

$$\alpha_B = 0.6486, K_B = 5.012 \times 10^{-2} \text{ dl/g}, \epsilon_B = 0.09973.$$

Use of Mark-Houwink coefficients to shift the GPC calibration curve from that of polystyrene is evidently open to suspicion if, as seems very likely, the coefficients for PVC may have been determined with samples for which the absolute molecular weights were not accurately measured.

This calibration curve does yield results which agree fairly well with those from light scattering and osmometry. This may be explained by the fact that supermolecular structures are more dense and less solvated than individual polymer molecules, so that solution viscosity is not strongly affected.^{1,3}

Molecular weight averages were computed from GPC refractograms without attempts to compensate for axial dispersion of the polymer during its transit through the apparatus. It is interesting that \bar{M}_n , the molecular weight average which is usually affected most by such manipulations, agreed nicely with corresponding values from light scattering and osmometry.

Results of GPC measurements are listed in Table VII. Clearly, ultrasonic treatment with added surfactant, where necessary, results in a proportionately greater change in the higher mean molecular weights than in \bar{M}_n . The effect is always greater the higher the molecular weight of the sample.

That large species, presumably aggregates, are being broken up is shown by the decreased skewness of the molecular weight distribution

TABLE VII
Gel Permeation Chromatography Results, Tetrahydrofuran

Sample	Treatment ^a	\bar{M}_z $\times 10^{-3}$	\bar{M}_w $\times 10^{-3}$	\bar{M}_n $\times 10^{-3}$	$Sn \times$ 10^{-4b}	$Sw \times$ 10^{-4c}	Bn^d	Bw^d
Rucon B 26	Nil	268	82.3	30.5	4.0	12.4	7.9	4.9
Rucon B 26	S-us-5	192	71.3	29.3	3.5	9.3	6.2	3.9
Rucon B 32	Nil	494	146	55.3	7.1	22.6	8.5	5.1
Rucon B 32	S-us-5	302	105	36.5	5.0	14.4	6.7	3.7
Rucon B 34	Nil	575	181	62.0	8.6	27.6	7.6	4.0
Rucon B 34	S-us-5	446	137	52.4	6.6	20.6	8.0	4.5
Rucon B 38	Nil	621	197	88.9	9.8	28.9	8.0	5.3
Rucon B 38	S-us-5	437	158	60.4	7.7	21.0	6.3	3.6
Rucon B 41	Nil	679	217	91.7	10.7	31.6	7.8	4.4
Rucon B 41	S-us-5	475	171	61.9	8.2	22.8	6.4	3.4
Opalon 630	Nil	318	111	49.2	5.5	15.2	6.9	4.5
Opalon 630	Us-5	300	104	36.4	4.9	14.3	6.7	3.8
Opalon 650	Nil	682	194	86.2	9.6	30.8	9.4	5.5
Opalon 650	Us-5	417	148	57.9	7.2	20.0	6.6	3.8
Geon 101EP	Nil	658	209	90.6	10.3	30.6	7.9	4.8
Geon 101EP	Us-5	479	174	62.3	8.3	23.0	6.2	3.3
Geon 103EP	Nil	484	143	53.2	6.9	22.0	8.4	4.3
Geon 103EP	Us-5	302	105	36.5	5.0	14.4	6.6	3.7
Geon 105EP	Nil	325	115	50.0	5.7	15.5	6.8	4.4
Geon 105EP	Us-5	302	105	36.5	5.0	14.4	6.6	3.7

^a $S = 0.002\%$ (w/v) Igepal Co 630; us-5 = ultrasonic irradiation for 5 min.

^b $Sn =$ Standard deviation of number distribution $= (\bar{M}_w \cdot \bar{M}_n - \bar{M}_n^2)^{1/2}$.⁴³

^c $Sw =$ Standard deviation of weight distribution $= (\bar{M}_z \cdot \bar{M}_w - \bar{M}_w^2)^{1/2}$.⁴³

^d $Bn =$ Skewness of number distribution; $Bw =$ skewness of weight distribution. Skewness is measured as the ratio of the third moment of the distribution about the mean and (standard deviation)³.⁴³

after ultrasonic treatment. The weight distributions are affected more than number distributions, as expected. These observations are consistent with molecular degradation as well as with dispersion of aggregates. The good agreement between \bar{M}_n from GPC in THF after ultrasonic treatment and \bar{M}_n from untreated cyclohexanone solutions (Table IV) shows that molecular degradation is not involved. The cyclohexanone values are considered to be close to the true figures because ultrasonic treatment and heating had no significant effect, as shown above.

DISCUSSION

The \bar{M}_w and \bar{M}_n values from GPC, light scattering, and osmometry in THF are compared in Table VIII. All values compare well for untreated solutions, but there is some tendency for \bar{M}_w of higher molecular weight polymers to be greater in GPC measurements than in light scattering. Rucon B38 and Rucon B41 are examples in the bulk process class. The surfactant concentration in the light-scattering and GPC solutions was 0.1 and 0.002% (w/v), respectively, and the concentration used in GPC may not be quite high enough to facilitate break-up of aggregates with high molecular weight polymers.

The suspension resins contained no added surfactant. Ultrasonic

TABLE VIII
Comparison of Molecular Weight Measurements in Tetrahydrofuran

Sample	Treatment*	GPC data			Light scattering		Osmometry, \bar{M}_n $\times 10^{-3}$
		\bar{M}_z $\times 10^{-3}$	\bar{M}_w $\times 10^{-3}$	\bar{M}_n $\times 10^{-3}$	\bar{M}_w $\times 10^{-3}$	\bar{M}_n $\times 10^{-3}$	
Rucon B 22	Nil	—	—	—	68.9	32.6	35.5
Rucon B 26	Nil	268	82.3	30.5	83.3	38.7	38.7
Rucon B 26	S-us-5	192	71.3	29.3	75.2	34.2	35.6
Rucon B 32	Nil	497	146	55.3	143	52.0	60.1
Rucon B 32	S-us-5	302	105	36.5	100	41.3	50.4
Rucon B 34	Nil	—	181	62.0	189	67.5	55.7
Rucon B 34	S-us-5	—	137	52.4	125	55.9	51.5
Rucon B 38	Nil	679	197	88.9	164	69.4	65.4
Rucon B 38	S-us-5	475	158	62.0	105	60.5	66.0
Rucon B 41	Nil	—	217	91.6	250	75.8	79.4
Rucon B 41	S-us-5	—	171	61.9	143	62.3	62.3
Opalon 630	Nil	318	111	49.2	133	50.0	52.5
Opalon 630	Us-5	300	104	36.4	100	46.0	43.6
Opalon 650	Nil	682	194	86.2	166	50.0	51.7
Opalon 650	Us-5	417	148	57.9	100	43.4	45.5
Geon 101EP	Nil	658	209	90.6	198	70.7	69.4
Geon 101EP	Us-5	479	174	62.3	140	50.0	65.1
Geon 103EP	Nil	484	143	53.2	149	62.0	65.1
Geon 103EP	Us-5	302	105	36.5	110	38.4	—
Geon 105EP	Nil	325	115	50.0	100	49.5	49.5
Geon 105EP	Us-5	302	105	36.5	71	31.3	—

* For explanation of symbols see footnotes to Table VII.

treatment of THF solutions of Opalon polymers in particular may not have eliminated all agglomerates, as judged by comparisons of \bar{M}_n in cyclohexanone and in treated THF solutions. It would appear that slight amounts of surfactant should also be added to suspension resin solutions to ensure aggregate elimination without molecular degradation on ultrasonic treatment.

The weight of evidence presented shows that the technique described is likely to permit accurate molecular weight measurements of PVC resins in THF solution at room temperature. The method may require some further detailed refinement for polymers of different manufacture, but it seems to be conveniently applicable to GPC, as intended.

Supermolecular structures in PVC are often described almost synonymously as aggregates or microgel. This work indicates that both types exist in commercial polymers, in the sense that giant entities are held together by secondary valences (aggregates) or primary valence bonds (microgel). The former material can be dispersed by ultrasonic treatment in the presence of surfactant, but the latter type persists as shown by distorted Zimm plots of ultrasonically treated solutions. Estimates of the true molecular weight distribution of a sample should count the microgel but not the aggregates. The technique presented here seems to permit this distinction. The existence of both kinds of large structures is plausible in view of the small extent of stereoregularity of commercial PVC and the tendency for polymer precipitation out of solution in monomer during the manufacturing process.

Our observations are in general agreement with those of previous workers cited above. The very high second virial coefficients measured by many groups in THF are anomalous and deserve further study. The A_2 values recorded in Table VI from light scattering on ultrasonically treated surfactant-bulk polymer solutions are closer to conventional magnitudes and generally lower than osmometric second virial coefficients in cyclohexanone. Peculiar virial coefficients may be a useful indicator of the persistence of supermolecular clusters in PVC solutions. The Opalon suspension resins are a case in point in this work. The ultrasonic deagglomeration technique seems not to have succeeded with these polymers in the absence of added surfactant.

Light-scattering and osmometry methods were used in this work primarily as exploratory tools, to define an acceptable solution preparation procedure for GPC. The most convenient and unsophisticated techniques were used so far as possible. Another factor in the selection of simple characterization methods involves the questionable value of detailed studies of molecular weight distributions of commercial materials with unknown variations in batch-to-batch manufacturing history. It is probably fortuitous that osmometric measurements could be reproduced with only four polymer concentrations and that \bar{M}_w measurements at five light-scattering angles down to 45° agreed fairly well with GPC data. This agreement was nevertheless close enough to satisfy the primary aim of this

study and discourage elaboration of the molecular weight measurement techniques.

Light-scattering \bar{M}_n values were always obtained from a linear extrapolation through the four highest angle data points in the Zimm plots, as in Figures 4 and 5. The \bar{M}_w datum was always derived by curvilinear extrapolation through the 45° angle point in such plots. This rudimentary procedure was selected initially because the results were required primarily for comparisons of different solution pretreatments. The precision and consistency of data from different molecular weight measurements was a rather unexpected benefit. This should not be construed, however, as a recommendation of the osmometric and light-scattering methods reported here for other than exploratory work. Studies focused on characterization of polymer samples as a main goal require more extensive data.^{45, 46}

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