Dilute Solution Properties of Low-temperature Polymerized Polyvinyl Chloride. II. Fractionation and Properties of Fractions

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In a previous paper of this series (hereafter referred to as Part I) we have shown that the solution behavior of a sample of polyvinyl chloride prepared at −15°C differed significantly from that of samples polymerized at higher temperatures. In order to seek the causes of this difference, we have dermined the molecular weight distributions in some samples of this polymer polymerized at different temperatures and have measured representative solution properties of the fractions of these samples. The present paper is intended to describe the results of this study and to discuss their molecular implications.

Experimental

Materials.—Five samples of polyvinyl chloride were studied. They were as follows:

SO968—A whole polymer suspension-polymerized at 48°C.

XF-13—A whole polymer emulsion-polymerized at 5°C.

F-2 — A whole polymer bulk-polymerized at −15°C.

F-5* — A whole polymer bulk-polymerized at −15°C under conditions similar to those used for F-2.

F-5-M—A middle cut of F-5; the 3 wt.% higher molecular weight portion and the 29 wt.% lower molecular weight portion of F-5 were removed by fractional precipitation.

Of the five samples, SO968 and F-5-M were materials treated also in Part I of this series.

As before, tetrahydrofuran was chosen as the solvent; its preparation has been described in Part I.

Density Measurement. — The film of a given polymer sample cast from its 3% tetrahydrofuran solution was soaked in carbon disulfide and then dried in vacuo. Its density was measured at 30°C in a density gradient tube using carbon tetrachloride and *n*-heptane as the density-forming liquids.

Fractionation. — The polymer was dissolved in tetrahydrofuran by refluxing for three hours at the boiling point of the solvent. At 30°C the precipitant, water in the present case, was vigorously stirred into the polymer solution of 0.625∼0.75% until it became turbid. By raising the temperature of the solution to the boiling point of the solvent, again while being vigorously stirred, the once-developed precipitate disappeard. Then the solution was gradually cooled to 30°C and maintained at this temperature until the supernatant became transparent. The precipitate formed was separated and dissolved in tetrahydrofuran. The polymer was recovered from this solution by the addition of excess methanol, and then dried in vacuo to constant weight. This gave the first fraction. The second fraction was obtained by applying the same procedure to the supernatant solution. By repeating this process the desired successive fractions were obtained.

Viscosity, Osmotic Pressure and Light-scattering Measurements. — Details for these measurements were described previously.

Results and Discussion

Fractionation.—For a successful fractionation of a polymeric material, the choice of a solvent and non-solvent is of primary importance. A survey of the literature[1,2] and also our own experience showed that the combination of tetrahydrofuran and water was one of the best for polyvinyl chloride. Preliminary experiments with monohydric alcohols (such as methanol, *n*-propanol and *n*-butanol) as precipitants gave precipitates which were too fine to be separated easily. Therefore, we adopted the system of tetrahydrofuran and water for the present purpose.

Fractionation was made on samples SO968, XF-13, F-2 and F-5; Table I records some related data. For SO968, F-2 and F-5, the fraction number stands for the order in which the precipitates were separated. However, in the case of XF-13, the amount of fraction 4 was so large that it was refractionated into three fractions 4-1, 4-2 and 4-3; moreover,

TABLE I. RELATED DATA OF FRACTIONATION

Sample	Initial concn.	Temp.* °C	Number of fractions	Yield of recovery %
SO968	15 g./2 l.	30	8	93.5
XF-13	25 g./4 l.	30	10	92.5
F-2	30 g./4 l.	20	12	99.7
F-5	50 g./7 l.	20	13	97.1

* Temperature at which precipitate was separated.

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* This was prepared later because the sample F-2 had been exhausted in the early stages of this investigation.

1) M. Imoto and T. Ōtsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **57**, 245 (1954).

2) J. Mencik, *J. Polymer Sci.*, **17**, 147 (1955).

TABLE II. PROPERTIES OF FRACTIONS OF SO968

Fraction	Wt.%	$[\eta]$ ml./g.	M_n $\times 10^{-3}$	M_w* $\times 10^{-3}$	A_2 $\times 10^3$	$\langle r^2\rangle_z^{1/2}$ Å	$\langle r^2\rangle_w^{1/2}$ Å	M_w/M_n
Whole	—	118	46.3	105.6	1.24	462	368	2.44
F-1	8.1	197	85.6	321.2	0.95	778	598	3.75
F-2	14.3	164	93.8	171.0	1.17	515	426	1.83
F-3	23.7	142	64.4	154.2	1.29	484	380	2.40
F-4	7.4	119	62.2	110.0	1.40	324	266	1.77
F-5	13.0	100	55.3	79.5	1.35	283	233	1.44
F-6	16.1	79	48.8	63.4	1.45	207	186	1.30
F-7	13.8	55	33.1	35.3	1.54	125	121	1.07
F-8	3.8	28	—	(7.7)	—	—	—	—

* M_w in bracket is calculated value.

TABLE III. PROPERTIES OF FRACTIONS OF XF-13

Fraction	Wt.%	$[\eta]$ ml./g.	M_n $\times 10^{-3}$	M_w* $\times 10^{-3}$	A_2 $\times 10^3$	$\langle r^2\rangle_z^{1/2}$ Å	$\langle r^2\rangle_w^{1/2}$ Å	M_w/M_n
Whole	—	111	45.0	119.6	0.88	650	510	2.67
F-1	10.5	173	65.6	277.0	1.18	725	534	4.23
F-2	6.5	167	—	277.0	1.05	684	—	—
F-3	15.3	165	68.1	211.2	1.34	680	525	3.10
F-4-1-1	9.9	148	75.6	178.3	1.07	548	436	2.36
F-4-1-2	9.8	124	56.3	125.0	0.97	470	377	2.22
F-4-2	7.9	113	48.4	(104.0)	—	—	—	—
F-4-3	4.6	84	42.5	(56.9)	—	—	—	—
F-5	15.6	80	48.1	61.3	1.18	316	280	1.27
F-6	10.7	55	35.0	(27.8)	—	—	—	—
F-7	9.4	31	—	(9.7)	—	—	—	—

* M_w's in brackets are calculated values.

TABLE IV. PROPERTIES OF FRACTIONS OF F-2

Fraction	Wt.%	$[\eta]$ ml./g.	M_n $\times 10^{-3}$	M_w* $\times 10^{-3}$	A_2 $\times 10^3$	$\langle r^2\rangle_z^{1/2}$ Å	$\langle r^2\rangle_w^{1/2}$ Å	M_w/M_n
Whole	—	108	45.0	84.3	1.22	591	488	1.88
F-1	5.8	132	—	(139.0)	—	—	—	—
F-2	11.8	141	105.6	196.7	0.84	765	632	1.86
F-3	15.5	142	—	(161.0)	—	—	—	—
F-4	13.1	138	93.8	152.6	0.76	535	455	1.63
F-5	4.6	133	—	(142.5)	—	—	—	—
F-6	12.3	120	71.3	105.2	1.22	356	309	1.48
F-7	3.4	86	—	(63.5)	—	—	—	—
F-8	12.9	82	59.4	54.4	1.33	212	—	—
F-9	8.2	53	—	(26.0)	—	—	—	—
F-10	6.3	36	35.6	(12.3)	—	—	—	—
F-11	3.1	24	—	(5.8)	—	—	—	—
F-12	3.1	18	—	(3.3)	—	—	—	—

* M_w's in brackets are calculated values.

fraction 4–1 was separated further into 4–1–1 and 4–1–2. The relative weight and limiting viscosity number, $[\eta]$, in tetrahydrofuran at 30°C of each fraction of these four samples of polyvinyl chloride are listed in Tables II, III, IV and V.

For XF–13, F–2 and F–5, the fractions appearing in the initial stage of fractionation (fractions 1 and 2 for XF–13; up to fraction 4 for F–2; up to fraction 5 for F–5) were obtained in the form of fine powder, in contrast to the case of commercial polyvinyl chloride, where gel-like precipitates are usually obtained. Since such powder-like fractions were difficult to separate in the usual manner, these were specifically precipitated at 20°C (not at 30°C)

TABLE V. PROPERTIES OF FRACTIONS OF F-5

Fraction	Wt.%	[η], ml./g.	d_{30}
Whole	—	102	1.405_6
F-1	2.1	122	—
F-2	6.3	126	1.409_0
F-3	6.1	135	1.406_5
F-4	10.1	141	1.406_8
F-5	9.6	139	1.408_8
F-6	11.1	136	1.404_9
F-7	5.3	128	1.404_3
F-8	8.3	123	—
F-9	7.8	97	1.404_1
F-10	10.0	76	1.403_0
F-11	7.8	57	1.402_8
F-12	5.8	45	1.401_5
F-13	9.8	26	—

and separated by centrifugation at room temperature (which did not differ significantly from 20°C). It was found that the formation of powder-like precipitates in the initial stage of fractionation was characteristic of low-temperature polymerized polyvinyl chloride. Tables IV and V show that, contrary to what is generally observed, the [η] of fractions of these low-temperature polymerized polyvinyl chloride increases with the increase of the fraction number in the initial stage of fractionation, comes to a maximum value, and then decreases in the usual manner. From the results reported in Part I, it was apparent that it would have been desirable to dissolve polymer at as high a temperature as 100°C, but because of the lack of a suitable vessel the original solutions for these fractionations had been prepared at the boiling point of tetrahydrofuran; under these conditions associated particles, or undissociated particles, were present in the solutions of XF-13, F-2 and F-5. Anomalous fractionation data on polyvinyl chloride similar to this have been reported by Mencik[2], who attributed the phenomenon to the association of molecules before the phase separation took place. However, the reason why powder precipitates developed is not clear.

Molecular Weight Distribution.—Figures 1—3 give the integral distributions of (weight average) molecular weight, M_w, for samples SO968, XF-13 and F-2 respectively; the values of M_w for fractions whose M_w were not determined experimentally have been estimated by using the viscosity vs. molecular weight relation described below. The two-stage feature appearing in the data for XF-13 and F-2 seems to be characteristic of polyvinyl chloride polymerized at low temperature. Although any definite conclusion must be left for future work, this feature is likely to be due to the presence of undissociated molecules in the original solution and also to the occurrence of molecular association during the fractionation procedure.

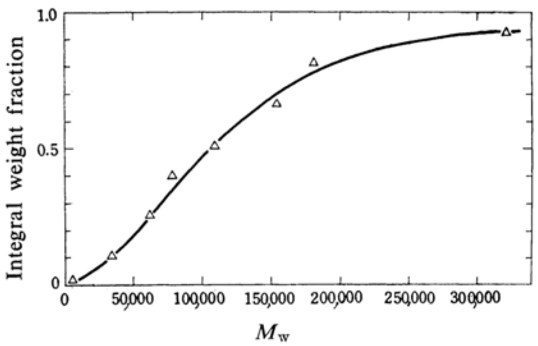

Fig. 1. Molecular weight distribution of SO968.

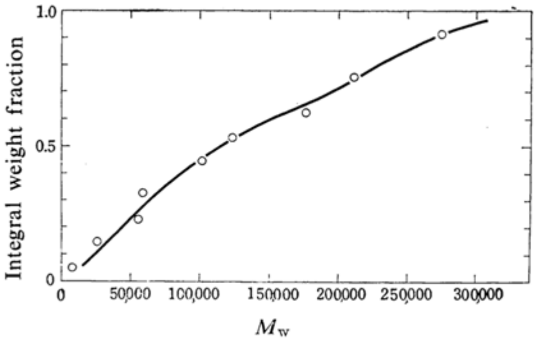

Fig. 2. Molecular weight distribution of XF-13.

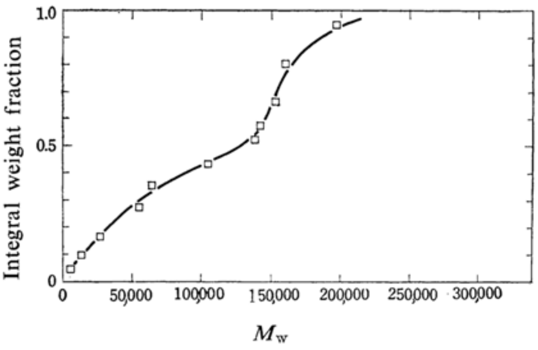

Fig. 3. Molecular weigt distribution of F-2.

Some Physical Properties of Fractions of F-5.—Table V, which gives the densities of successive fractions of F-5, indicates a systematic decrease of the density with the increase of the fraction number. This suggests that the crystallinity or chain regularity is higher for earlier fractions than for later fractions. When the density of each fraction is plotted against its limiting viscosity number in tetrahydrofuran at 30°C, the data for fractions whose fraction numbers are higher than 6 are seen to form a certain order, while those for the remaining fractions are out of this order. Infrared studies[3-5] on polyvinyl chloride indicate that the ratio of the optical density for absorption at 635 cm^{-1}, which is assigned to the crystalline part, to that for absorption at 690 cm^{-1}, which is assigned to the amorphous part, can be taken as a measure of the crystallinity of a given sample. We measured infrared spectra of several fractions of samples SO968 and F-5 by using a Perkin-Elmer model 13 infrared spectrophotometer; the results obtained are listed in Table VI. One can see that the degree of crystallinity of samples F-5, which was polymerized at -15°C, is higher than that of sample SO968 polymerized at 48°C. Table VI also reveals that, although the values of $[\eta]$ for fractions 1 and 8 of sample F-5 are quite similar, the former fraction is more crystalline than the latter; incidentally, this is in conformity with the preceding suggestion from the density data that the later fractions of F-5 are less crystalline than the earlier fractions. From these results one may consider that white powderlike precipitates of polyvinyl chloride will develop in the tetrahydrofuran-water system when the degree of crystallinity or chain regularity of the polymer is higher than a certain limiting value. If this is the case, it is quite likely that the fractionation of samples XF-13, F-2 and F-5 proceeded in accordance not only with the molecular weight but also with the chain regularity. Previous X-ray[6] and also infrared[3-5] studies showed that the chain regularity of polyvinyl chloride increased as the polymerization temperature was lowered, and this was attributed to the increase in the syndiotactic portion[7] of the polymer.

TABLE VI. CRYSTALLINITY OF FRACTIONS OF SO968 AND F-5

SO968

Fraction	$[\eta]$, ml./g.	D_{635}/D_{690}
F-1	197	1.82
F-3	142	1.75
F-6	79	1.77

F-5

Fraction	$[\eta]$, ml./g.	D_{635}/D_{690}
F-1	122	2.29
F-3	135	2.23
F-8	123	2.10

Relations between Limiting Viscosity Number and Average Molecular Weights. — The values of the limiting viscosity number $[\eta]$ (in tetrahydrofuran at 30°C), number-average molecular weight M_n, obtained from osmotic pressure measurements, and the weight-average molecular weight M_w, determined from light-scattering measurements, for fractions of SO968, XF-13 and F-2 are summarized in Tables II, III and IV. Figure 4 illustrates Zimm plots for fraction 4 of F-2. When these data for $[\eta]$ and M_n are combined on a log-log plot, the points, though quite scattered, fall within the range of the literature's data[8-11]. The corresponding plots for $[\eta]$ vs. M_w are given in Fig. 5, which shows that even if the polymerization temperature is different, the relation between $[\eta]$ and M_w for polyvinyl chloride in tetrahydrofuran remains practically the same.

The relation between the limiting viscosity number and the molecular weight, M, of a polymer generally obeys an empirical equation of the form:

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

where K and α are constants characteristic of

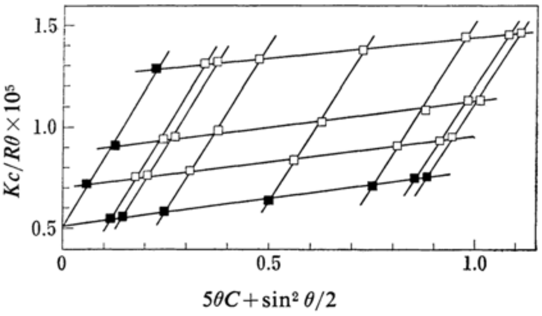

Fig. 4. Zimm plot for fraction 4 of F-2.

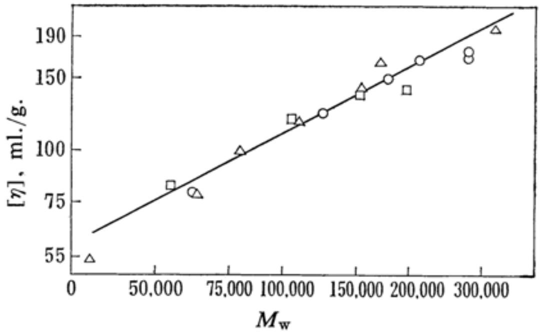

Fig. 5. Relation between limiting viscosity number and M_w.

△ Fraction of SO968; ○ XF-13; □ F-2

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[3] S. Krimm, *Chem. & Ind.*, **1959**, 433.

[4] T. Shimanouchi et al., *High Polymers* (*Kobunshi*), **8**, 202 (1959); *J. Chem. Phys.*, **30**, 1365 (1959).

[5] M. Asahina et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1011 (1960); *Chem. High Polym.* (*Kobunshi Kagaku*), **17**, 612 (1960).

[6] M. Asahina et al., ibid., **17**, 441, 612 (1960).

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[10] H. Staudinger, *Makromol. Chem.*, **9**, 35 (1952).

[11] R. M. Fuoss, *J. Phys. Chem.*, **47**, 59 (1943).

the given polymer solvent system. This equation holds not only for a polymer of uniform molecular weight but also for a polymer with a molecular weight distribution, although with the latter polymer M must be replaced by some average molecular weight. For both the monodisperse and polydisperse samples of the same polymer species in the same solvent, the parameter α remains the same although the values of K are different. If α is given and the form of molecular weight distribution is specified, it is possible to examine by calculation the variation of K with the ratio of M_w/M_n. The results of this calculation[12] with logarithmic[13] and exponential[14] distribution functions show that when M_n is substituted for M in Eq. 1, K varies appreciably with the ratio M_w/M_n, but when $[\eta]$ is plotted against M_w, K is almost independent of M_w/M_n. This affords the advantage of using M_w over M_n when we wish to establish a relation between the limiting viscosity number and the molecular weight for a given polymeric substance.

The straight line in Fig. 5, determined by the least square procedure, yields

$$[\eta]=2.19\times10^{-1}M_w^{0.54}$$

or

$$[\eta]=2.05\times P_w^{0.54}$$

where P_w denotes the weight-average degree of polymerization. The value 0.54 obtained for the exponent to M_w suggests that the molecules of polyvinyl chloride in tetrahydrofuran assume a random coil form. Ciampa[15], who obtained the value of unity for this exponent, suggested a worm-like form for the molecule of this polymer in cyclohexanone. The lack of non-Newtonian behavior of the solution of F-5-M illustrated in Fig. 6 appears to lend some support to the pertinence of our value for the exponent in the viscosity vs. molecular weight relation.

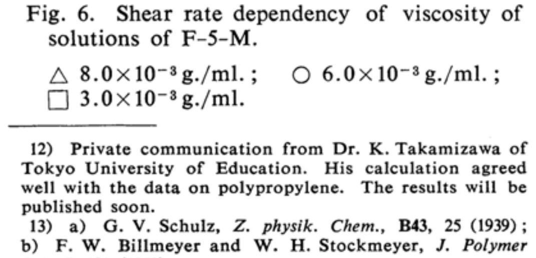

Fig. 6. Shear rate dependency of viscosity of solutions of F-5-M.

△ 8.0×10^{-3} g./ml.; ○ 6.0×10^{-3} g./ml.; □ 3.0×10^{-3} g./ml.

Weight-average Root Mean Square End-to-end Distance, $\langle r^2\rangle_w^{1/2}$ and Light-scattering Second Virial Coefficient, A_2.—The values of $\langle r^2\rangle_w^{1/2}$ and A_2 for fractions of samples SO968, XF-13 and F-2 determined from light-scattering data are listed in Tables II, III and IV. In converting the directly-obtained $\langle r^2\rangle_z^{1/2}$, the z-average root mean square end-to-end distance, to $\langle r^2\rangle_w^{1/2}$ following relations were assumed between the average molecular weights and the average dimensions of the solute molecule:

$$M_n/l+1=M_w/l+2=M_z/l+3 \qquad (2)$$

$$M_n/\langle r^2\rangle_n^{1/2}=M_w/\langle r^2\rangle_w^{1/2}=M_z/\langle r^2\rangle_z^{1/2} \qquad (3)$$

which are valid for the exponential molecular weight distribution[13]. Figure 7 plots A_2 against M_w on a log-log graph paper. The straight line, which was drawn to fit the data for sample SO968, has a slope of −0.21, comparable to the reported values on polyvinyl acetate[16-18] in butanone and polystyrene[19] in toluene at 30°C. The A_2 values for XF-13 and F-2 are generally smaller than those for SO968 when a comparison is made with the same values of M_w. This fact suggests that the thermodynamic interaction between solute and solvent molecules becomes weaker as the polymerization temperature is lowered. In other words, tetrahyhrofuran acts as a poorer solvent for a polyvinyl chloride sample which has been polymerized at a lower temperature. It is interesting that this difference is in line with the differences in solution properties observed in the study described in Part I of this series.

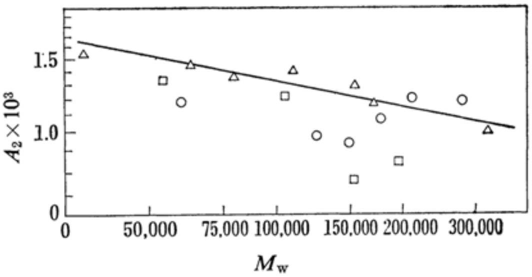

Fig. 7. Relation between A_2 and M_w.

△ Fractions of SO968; ○ XF-13; □ F-2
Full line is for SO968.

Figure 8 shows a log-log plot for $\langle r^2\rangle_w^{1/2}$ against P_w, together with that for polystyrene in butanone at 25 and 20°C reported by Outer,

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[12] Private communication from Dr. K. Takamizawa of Tokyo University of Education. His calculation agreed well with the data on polypropylene. The results will be published soon.

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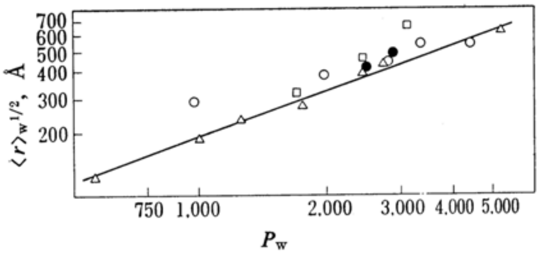

Fig. 8. Relation between dimension of molecules and P_w.

△ Fractions of SO968 ; ○ XF-13 ; □ F-2 ; ● Polystyrene reported by Zimm20).
Full line is for SO968.

Carr and Zimm20). From the straight line drawn, which fits best for SO968, one finds that the weight-average root mean square end-to-end distance of SO968 increases in proportion to the 0.73 power of the weight-average degree of polymerization. One also finds that the average dimension of polyvinyl chloride in tetrahydrofuran increases as the polymerization temperature is lowered. Finally, it is of interest to note that polyvinyl chloride in this solvent has a dimension similar to that of polystyrene in butanone when the degree of polymerization of both polymers are comparable.

Doty et al.21) pointed out that the polyvinyl chloride molecule has a tendency to become partially syndiotactic, that its chain flexibility is relatively low, and, moreover, that the syndiotactic portions interact with each other through their dipoles, thus limiting its possible configurations in solution. This affords a reasonable explanation for the finding that the molecular dimension of this polymer in solution increases as the polymerization temperature is lowered, since a sample prepared at a lower temperature should be richer in syndiotactic portion. The fact that the relation between the limiting viscosity number and the molecular weight is practically independent of polymerization temperature may be accounted for by the fact that the effect caused by the increase in molecular dimension is cancelled out by the accompanying increase in the permeability of the solute to solvent molecules.

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

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