June, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(6), 1363—1367 (1974)

Anomalous Light Scattering by Poly(2-vinylpyridine) in Methanol

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(Received October 15, 1973)

The light scattering of a poly(2-vinylpyridine) solution was measured under various conditions. In solvents such as methanol, ethanol, 2-propanol, 2-butanone, and pyridine, anomalous Zimm plots with an upward inflection at lower angles were observed. This anomaly was especially striking in methanol, in which the dissymmetry coefficient was frequently less than unity. Systematic investigations carried out with methanol as a solvent revealed that; (1) the anomaly does not depend appreciably on the concentration or tacticity of the polymer, the temperature, or the wavelength of the incident light; (2) the anomaly diminishes with an increase in the molecular weight of the polymer; (3) the anomaly disappears upon the addition of dry ammonia of 10^{-2} mol/l or more in methanol, and (4) similar perturbed Zimm plots are realized by the addition of a trace amount of hydrochloric acid or sulfuric acid in a methanol solution of a higher-molecular-weight fraction which showed a normal Zimm plot in pure methanol. The anomaly can not be explained in terms of the effects of the optical anisotropy of the polymer segment, but the external interference arising from the non-random arrangement of the polymer in solution may contribute to it.

Recently several reports on the anomalous light-scattering behavior of solutions of vinylpyridine polymers have been published. Miura *et al.*[1] reported an anomaly with poly(2-methyl-5-vinylpyridine) in methanol; Cashin,[2] with poly(2-vinylpyridine) in nitromethane, and Fuoss *et al.*[3] suggested the existence of some trouble in the measurement of the light scattering of poly(4-vinylpyridine) in absolute ethanol. In the course of studies of the poly(2-vinylpyridine) solution one of the present authors[4] showed in brief the existence of the anomaly in several solvents. More recently, Seely[5] reported on the anomaly with poly(4-vinylpyridine) in nitromethane. However, no reasonable explanation of the origin of the anomaly of the light scattering of the poly(vinylpyridine) solution has yet been given. On the other hand, the similar anomaly of the light-scattering behavior of several other polymers has been clarified by some theoretical considerations.[6-10] In this paper we will present the results of our experimental investigation of the light-scattering behavior of the poly(2-vinylpyridine) solution, especially when the measurement is carried out in methanol. The results will be discussed in terms of the theories proposed for the other polymers.

Experimental

Atactic Poly(2-vinylpyridine). The polymerization, fractionation, and characterization of atactic poly(2-vinylpyridine), our sample number A-2 ($M_w=3.4\times10^4$), E-2 (1.20×10^5), G-2 (2.19×10^5) and I-2 (3.11×10^5), were described in a previous paper.[4] Three other higher-molecular-weight fractions, P-4 (1.1×10^6), P-3 (1.6×10^6), and P-2 (4.0×10^6), were obtained by redox polymerization using potassium persulfate and sodium bisulfite in an acidic aqueous solution of the monomer[11] and by subsequent fractionation.[12] The $2U_0$ sample (3.30×10^5) was obtained by thermal polymerization in an ampoule without any initiator or diluents, and was then purified by repeated precipitation.

Isotactic Poly(2-vinylpyridine). The polymerization and purification of isotactic poly(2-vinylpyridine) were carried out in the same way as in a previous paper.[13] The polymres were fractionated by the precipitation method, using the benzene-ligroin system. The tacticity was checked by the methods of X-ray diffraction, IR spectrum, melting point, and insolubility in hot acetone.[13] The fourth fraction, S4F-4 (3.25×10^5), was mainly used in this study.

Solvent. All the solvents used in this study were dried by the standard methods[14] and were fractionally distilled before use. The middle fractions of each solvent were retained for use in the experiment described below.

Light-scattering and Viscosity. All the apparatus and procedure for the measurements of the light scattering and viscosity were approximately the same as those previously described by one of the present authors.[4] Measurements were made of the intensity of scattered light in eleven different directions, ranging from 30° to 150° with unpolarized or polarized blue light (436 mμ) or green light (546 mμ) of Hg. The correction for the backward reflection was applied throughout the measurements.[15] The solutions were ordinarily optically purified by filtering the solution by means of double membranes of "mittel" or "fein" supplied by the Sartorius Co., Göttingen, West Germany.

Results and Discussion

The fundamental equation of the light scattering of the polymer solution is expressed,[16] as is well known, by:

$$Kc/R(\theta) = 1/[M_wP(\theta)] + 2A_2c$$
$$= 1/M_w + (16\pi^2/3\lambda^2M_w)\langle s^2\rangle\sin^2(\theta/2) + 2A_2c$$

where K is the optical constant; c the concentration expressed by g/ml; $R(\theta)$, the reduced intensity of scattering at the angle θ; M_w, the molecular weight of the polymer; $P(\theta)$, the factor arising from the internal interference of scattered light in the polymer molecule; A_2, the second virial coefficient; λ, the wavelength of the incident light, and $\langle s^2\rangle$, the mean square of the radius of gyration of the polymer chain.

For random coils of linear polymers, straight lines are obtained to a good approximation if $Kc/R(\theta)$ is plotted against $\sin^2(\theta/2)$; therefore, in the so-called Zimm plots (plots of $Kc/\mathrm{R}(\theta)$ *vs.* $\sin^2(\theta/2)+kc$, where k is the arbitrary constant) the initial slope of the extrapolated straight line at $c=0$ corresponds to the radius

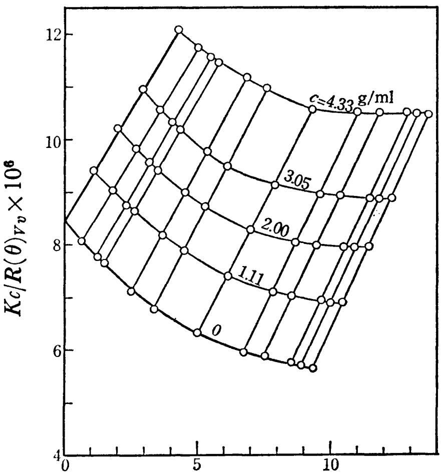

Fig. 1. Zimm plot for an isotactic poly(2-vinylpyridine) fraction, S4F-4 ($M_w=3.25\times 10^5$), in methanol at 25 °C. Concentration is expressed in g/ml. The wavelength of vertically polarized incident light was 436 mμ. $R(\theta)_{Vv}$ was corrected for depolarization.

of gyration, $\langle s^2\rangle$, of the polymer chain in a solution.

Now, as a typical example, the anomalous light-scattering behavior of the isotactic poly(2-vinylpyridine) fraction, S4F-4, in methanol at 25 °C is shown in Fig. 1; it was obtained by the use of the vertically-polarized light of 436 mμ as the incident light. The angular distribution of the reciprocal light-scattering intensity shows the inflection, especially at lower angles at all concentrations. As is illustrated by Fig. 1, the values of the dissymmetry coefficient in methanol are often less than unity and the values of $\langle s^2\rangle$ become negative. Similar anomalous Zimm plots for atactic poly(2-vinylpyridine), G-2, in methanol have been shown in Fig. 3 in a previous paper.[4] The evidence of the anomaly was confirmed by repeated experiments, although the reproducibility of the degree of inflection could not be exactly determined.

The anomalous angular distribution of scattered light was likewise observed for the G-2 sample in ethanol, 2-propanol, 2-butanone, and pyridine. Similarly, it was observed with poly(4-vinylpyridine) in methanol and with poly(2-methyl-5-vinylpyridine) in nitroethane. The detailed investigation of the anomaly with the last polymer will be reported later in this Bulletin.

Additional systematic experiments carried out with a solution of G-2 in methanol revealed that the anomaly was independent of; (1) polymer concentrations ranging from 1.87×10^{-3} to 1.41×10^{-2} g/ml at 25 °C; (2) temperatures ranging from 15 to 45 °C, (3) the wavelengths of the incident light, and (4) the tacticity of the polymer. It was found, however, as is shown in Fig. 2, that the anomaly depends on the molecular weight of the polymer and that the lower the molecular weight, the larger the degree of inflection of the curves; moreover, the anomaly disappears for solutions of polymers with molecular weights higher than about 10^6. In addition, it was found that the degree of inflection is related to the successive amount of dry ammonia absorbed in methanol and that the anomaly disappears for solutions with concentrations of ammonia higher than 10^{-2} mol/l, as is shown in Fig. 3.

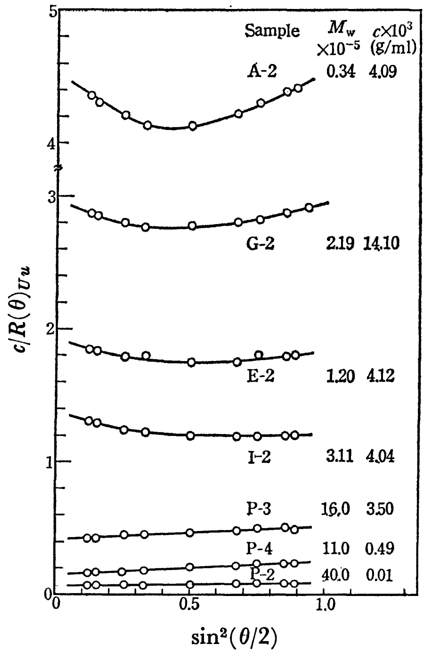

Fig. 2. Effects of molecular weight of atactic poly-(2-vinylpyridine) on the degree of inflection in the plots of $c/R(\theta)_{Uu}$ *vs.* $\sin^2(\theta/2)$ for methanol solution at 25 °C.

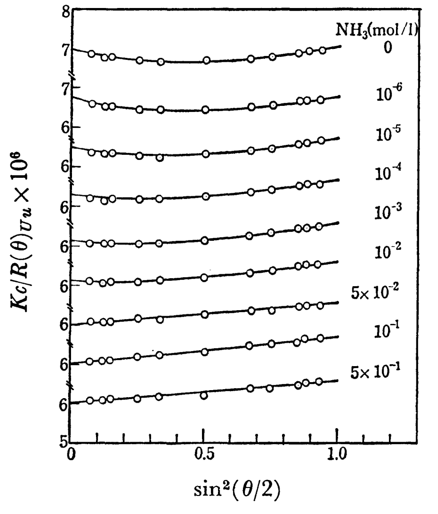

Fig. 3. Effects of the concentration of added dry ammonia in methanol at 25 °C in the plots of $Kc/R(\theta)_{Uu}$ *vs.* $\sin^2(\theta/2)$ for atactic poly-(2-vinylpyridine), G-2 ($M_w=2.19\times 10^5$).

Several causes may be supposed for the anomaly described above. First of all, we might point out the mechanics of the instrumentation or the procedure for the measurement of the light scattering. However, the angular distribution of each component of scattered light, *Uu*, *Vv*, *Hv*, *Vh*, and *Hh*, showed a normal behavior for all solvents, where *Vv* and *Hv* represent the vertical and holizontal components of the scattered light for the vertically-polarized incident light, where *Vh* and *Hh* have a corresponding significance for horizontally-polarized light, and where *Uu* represents all the components of scattered light when unpolarized incident light is used.

In addition, the Zimm plots of the light scattering of the standard polystyrene, MS-I,[17)] in benzene was a normal one, from which no inflection of lines for $Kc/R(\theta)$ *vs.* $\sin^2(\theta/2)$ is observed; the molecular weight as estimated from the plots is 2.20×10^5, which is in accord with the average value of 2.53×10^5 reported in the literature.[17)] Furthermore, the results of our measurements of the absolute scattering intensity of a polystyrene solution of the identical sample showed no particular defect in our apparatus or procedure.[18)]

Concerning the optical purification of the solution, similar results were obtained even if the solution of the G-2 sample in methanol was ultra-centrifugated at 2×10^4 *G* for 2 hr. The effect of fluorescence from the polymer was checked and found to have no considerable effect in methanol.

Recently theoretical investigations of similar anomalies in light scattering have been reported for other polymer-solvent systems as well. According to those results, the anomaly can be explained in some cases by the effects of the optical anisotropy of segments,[7)–9)] while in the other cases it can be explained by the effects of intermolecular interference arising from a non-random arrangement of the solute molecules in solution.[6),10)] Some qualitative examinations of our results with regard to these theories were carried out as follows.

The Effect of the Optical Anisotropy of the Polymer. Uchiyama and Kurata[7),8)] have shown that the unusual Zimm plots obtained by Ehrlich and Doty[19)] for aqueous solutions close to the isoionic point of a copolymer consisting of approximately equal amounts of methacrylic acid and 2-dimethylaminoethylmethacrylate, and also obtained by Uchiyama and Kurata themselves for the monochlorobenzene solution of isotactic polystyrene can be explained by the effects of the large optical anisotropy of the polymer. In such cases they proposed primarily to use polarized incident light and to correct the effects of anisotropy by subtracting four-thirds of the amount of the *Vh* or *Hv* component of the scattered light from that of the *Vv* component at each scattering angle. Schurz *et al.*[20)] found that the anomaly they observed with solutions of vinyon N (copolymer of 40% acrylonitrile and 60% vinylchloride) in dimethylformamide disappeared when they used verticallypolarized light.

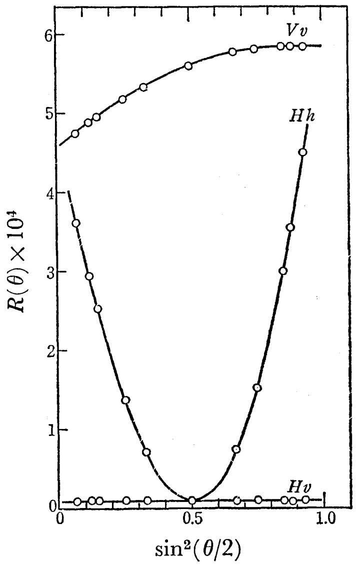

Fig. 4. The angular variation of each component of the scattered intensity of a fraction of isotactic poly(2-vinylpyridine), S4F-4, in methanol at 25 °C. $\lambda=436$ mμ and $c=2.00\times10^{-3}$ g/m*l*.

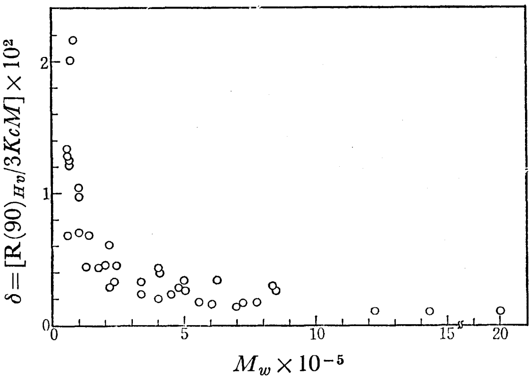

Fig. 5. Dependence of the values of optical anisotropy parameter, $\delta=R(90)_{Hv}/3K_cM$, of isotactic poly(2-vinylpyridine) in methanol at 25 °C on molecular weight of the polymers.

The results of the measurements of all the components of scattered light with vertically-polarized incident light are given in Fig. 4 for the fraction of isotactic poly(2-vinylpyridine) S4F-4 in methanol. As is illustrated by the figure, the intensity of the *Hv* component and, consequently, the effects of depolarization for this polymer in methanol are, in general, comparatively small, and the anomaly can not be corrected by subtracting $(4/3)R_{Hv}$ from R_{Vv}. This situation was further confirmed by additional experiments carried out with a series of fractions whose molecular weights covered a wide range. In Fig. 5 the values of the optical anisotropy parameter, δ, defined[7)] by:

$$\delta = R_{Hv}/3KcM$$

for a series of isotactic poly(2-vinylpyridine) in methanol are plotted as a function of the molecular weight of the polymers. The amounts of depolarization are not very large, and the values of δ are, in general, in the order of 10^{-3} except for very-low-molecular-weight fractions.

Secondly, when the measurements were carried out with unpolarized incident light in methanol, the values of the dissymmetry coefficient were often smaller than unity; consequently, the application of the data to the equations proposed by Uchiyama and Kurata for the correction of the effect of optical anisotropy was impossible. Even in the solvents other than methanol, where the application of the data to the equations is possible, the effects of the correction were not appreciable. In conclusion, the anomaly in Zimm plots can not be explained by the effect of the optical anisotropy of polymer segments.

The Effect of Order in Solution. It was first reported by Doty and Steiner[6)] in the case of bovine serum albumin, and later by Oth and Doty[21)] in the case of polyelectrolytes in the absence of added electrolytes, that unusual light scattering was caused by the external interference arising from non-random rearrangements of the polymer, the so-called "order" in solution. More recently, Burchard[10] has explained an anomalous light-sattering behavior like ours for poly(vinylcarbanilate) in diethyl ketone in terms of the influence of order arising from a certain strong solvation due to hydrogen bonding in solution.

According to Burchard, the ordering rearrangements of polymer coils in solution are perhaps caused by the effects of; (1) electrostatic repulsion force, (2) the formation of an intramolecular-bond-forming wire netting, and (3) a certain strong solvation.

First, we tried to check for the possible ionization of our polymer at nitrogen atoms in solution. Figures 6-1—6-4 demonstrate several Zimm plots observed for a fraction of atactic poly(2-vinylpyridine), P-2, in methanol, to which were added increasing amounts of hydrochloric acid. The light-scattering behavior for this fraction in pure methanol is normal, as is shown in Fig. 6-1. A similar perturbation as observed for lower-molecular-weight fractions in pure methanol appeared when the fraction was partially ionized by the addition of hydrochloric acid to methanol until the concentration reaches 10^{-8}—10^{-6} mol/l; the degree of anomaly increased with the concentration of hydrochloric acid, as is shown in Figs. 6-2 and 6-3. The pattern of the Zimm diagram at the concentration of 10^{-4} mol/l shows some similarities to the one reported for a polyampholite based on methacrylate by Ehrlich and Doty.[19]

The results of viscometric measurements for the same fraction in the solvents used above are shown in Fig. 7. The curves for these systems are typical for polyelectrolytes in a medium with a low ionic strength.

Similar results of light-scattering measurements were obtained when a trace amount of sulfuric acid was added to methanol used as a solvent until the con-

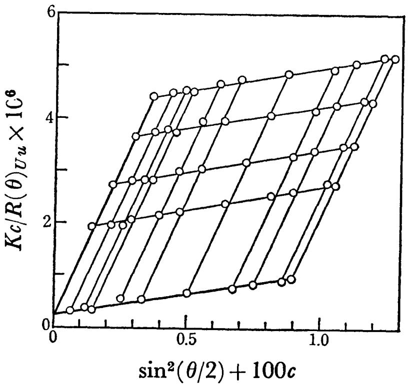

Fig. 6-1. Effects of the concentration, c, of added hydrogen chloride in methanol at 25 °C on the inflection in Zimm plots for atactic poly-(2-vinylpyridine), P-2 ($M_w=4.0\times10^6$). $\lambda=436$ mμ, unpolarized light. $c=0$ mol/l.

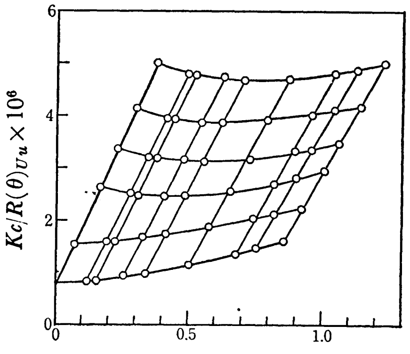

Fig. 6-2. $c=10^{-8}$ mol/l.

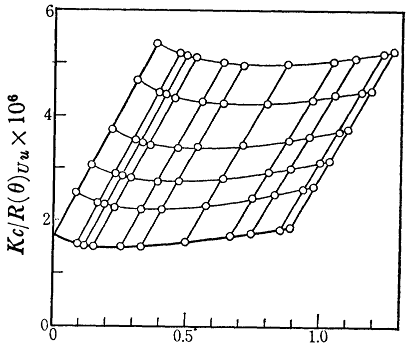

Fig. 6-3. $c=10^{-6}$ mol/l.

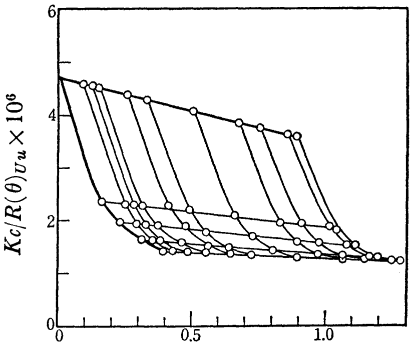

Fig. 6-4. $c=10^{-4}$ mol/l.

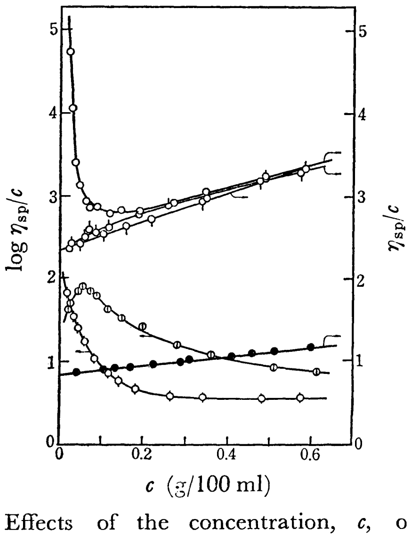

Fig. 7. Effects of the concentration, c, of added hydrogen chloride in methanol at 25 °C on the reduced viscosity number for fractions of atactic poly-(2-vinylpyridine) P-2 [○ ($c=0$ mol/l), ○ (10^{-8}), ○ (10^{-6}), ○ (10^{-4}), ⦶ (10^{-3})] and G-2 [● (0)].

centration reaches 10^{-8}—10^{-4} mol/l. From these results, it may be concluded that the anomaly in these cases depends on the effects of electrostatic interaction between ionized groups of the polymer.

We then considered whether the anomaly was affected by the same origin in the case of lower-molecular-weight-fractions. We have repeatedly measured the reduced viscosity numbers of many fractions of poly(2-vinylpyridine) in pure methanol and have always obtained normal viscosity curves typical of non-electrolytic polymers, as is shown in Fig. 7 for the G-2 fraction as an example.

On the other hand, the results of light scattering and viscosity in pure methanol for the $2U_0$ sample, which had been prepared with particular care taken to diminish any possibility of contamination by electrolytes, were the same as those of other fractions. Judging from these results, the explanation of the anomaly in terms of ionization in methanol may not be possible.

Secondly, the occurrence of strong solvation by means of hydrogen bonding between poly(vinylpyridine) homologues and alcohols has been ascertained by the large value of the Flory constant,22,23) defined by:

$$K = 6^{3/2}\Phi_0(\langle s^2\rangle_0/M)^{3/2}$$

where Φ_0 is the universal constant and $\langle s^2\rangle_0$ the unperturbed radius of the gyration of the polymer chain, and by the large negative values of the parameters of excess enthalpy and entropy for dilution, as evaluated by measurements of the temperature coefficient of the intrinsic viscosity and the osmotic second virial coefficient.24) The results of the direct calorimetric determination of the heat of solution equally support the possibility of hydrogen-bonding formation in these systems.25)

Judging from these facts, it may be supposed that the anomalous light-scattering behavior with poly(2-vinylpyridine) in methanol was caused by strong fixation due to hydrogen bonds between the nitrogen atoms in the pyridine residue and the -OH groups of the methanol, as in the case of poly(vinylcarbanilate) in diethyl ketone.10) Such a coil may have a weakly elastic repulsive potential and might resist the overlapping of the segment clouds.

The molecular-weight dependence of the degree of inflection of the light-scattering curves shown in Fig. 2 may be explained by the masking of the external interference by the internal one for larger particules, as was pointed out by Doty and Steiner.6)

It may be supposed that the influence of added ammonia on the anomalous light scattering for methanol solutions is due to the diminution of solvation rather than some possible dissociation of the polymer. This may be supposed on the basis of the facts that the values of the intrinsic viscosity number and those of the Flory constant decrease considerably with an increase in the amount of added ammonia in methanol and ethanol, as has previously been shown by one of the present authours.22)

In conclusion, it seems probable that anomalous behavior of light scattering such as is reported here is caused by the effect of order in solution, arising from a strong solvation.

References

1) M. Miura, Y. Kubota, and T. Masuzukawa, This Bulletin, **38**, 316 (1965).
2) W. M. Cashin, *J. Colloid Sci.*, **6**, 271 (1951).
3) J. B. Berkowits, M. Yamin, and R. M. Fuoss, *J. Polym. Sci.*, **28**, 69 (1958).
4) S. Arichi, This Bulletin, **39**, 439 (1966).
5) G. R. Seely, *Macromolecules*, **2**, 302 (1969).
6) P. Doty and F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).
7) H. Uchiyama and M. Kurata, *Bull. Inst. Chem. Research, Kyoto Univ.*, **42**, 128 (1964).
8) H. Uchiyama, *J. Phys. Chem.*, **69**, 4138 (1965).
9) M. Nakagaki, This Bulletin, **34**, 834 (1961).
10) W. Burchard, *Polymer*, **9**, 29 (1968).
11) J. M. Pritchard, M. H. Opheim, and P. H. Moyer, *Ind. Eng. Chem.*, **47**, 863 (1955).
12) S. Arichi, S. Mitsuta, N. Sakamoto, and H. Murata, This Bulletin, **39**, 428 (1966).
13) S. Arichi, *ibid.*, **21**, 244 (1967).
14) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, Vol. II Organic Solvents," Third Edition, Edited by A. Weissberger, Wiley-Interscience (1970).
15) J. P. Kratohvil, *J. Colloid Interface Sci.*, **21**, 498 (1966).
16) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).
17) The Committee on Molecular Weight and Molecular Weight Distribution of the Society of Polymer Science, Japan, *Report. Prog. Polymer Phys., Japan*, **4**, 141 (1961).
18) The Committee on Molecular Weight and Molecular Weight Distribution of the Society of Polymer Science, Japan, *Rept, Prog. Polymer Phys., Japan*, **14**, Appendix 1 (1971).
19) G. Ehrlich and P. Doty, *J. Amer. Chem. Soc.*, **76**, 3764 (1954).
20) J. Schurz, G. Warnecke, and Th. Steiner, *Monatsh. Chem.*, **91**, 561 (1960).
21) A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).
22) S. Arichi, This Bulletin, **41**, 548 (1968).
23) A. Dondos, *Makromol. Chem.*, **135**, 181 (1970).
24) S. Arichi, Y. Tanimoto, and H. Murata, This Bulletin, **41**, 1296 (1968).
25) Unpublished Data.