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ANOMALOUS LIGHT SCATTERING OF POLY(2-METHYL-5-VINYLPYRIDINE) IN NITROETHANE

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The peculiar anomalous light scatterings have been repeatedly observed for poly(2-methyl-5-vinylpyridine) in nitroethane, which were suppressed by the addition of tetramethylammonium iodide. Such behaviors were found due to the intermolecular interference caused by some ionization of the polymer in the solution.

Earlier, Seely has disclosed the anomalous light scattering by poly(4-vinylpyridine)(P4VP) in nitromethane which was a type that a greater amount of light was scattered backward than forward, but the causes bringing about such a trouble have yet remained unknown.1) Such anomalies on vinylpyridine polymers have also been observed in certain solvents by several other investigators.2),3),4),5) The fluorescence6) and the optical anisotropy of segments7) in solution are blamed for that, but these solutions were not in the case. One of the authors, et al. recently reported on the light scattering for poly(2-vinylpyridine)(P2VP) in methanol that its anomaly might be brought about by the interparticle interference effect due to the strong polymer-solvent interaction.3) On the other hand, decisive data about the influence of the ionization of particles in salt-free media on the light scattering have scarcely been published till now, which was usually noticed as a most probable idea for the origines of their abnormality specially in the case of these polymers.

In this investigation, several anomalous light scatterings of poly(2-methyl-5-vinylpyridine)(PMVP) in nitroethane will be observed to obtain some informations concerned with those.

The PMVP sample was prepared at 60°C for 13 hr. under a nitrogen atomosphere by the bulk polymerization in sealed glass ampoules which contained 2-methyl-5-vinylpyridine monomer and dibenzoylperoxide(0.4%) as an initiator. After purification of reactants, the whole polymer was fractionated to five fractions (denoted A-1, A-2, ---) with the column elution method.8) The second fraction, A-2, from the lowest molecular weight one was used almost in the main for the following measurements, whose weight-average molecular weight(M_w) determined in benzene was 5.85×10^5. As a solvent, nitroethane of guaranteed reagent grade (Nakarai Chemicals Ltd.) was dried for a few days with anhydrous sodium sulfate, and then distilled prior to use with a 100-cm rectifying column under reduced pressure.

All the light scatterings were measured in the range 35° to 145° of scattered angles(θ) at 25°C by the vertically polarized incedent light of 436 nm with a Brice-type light cattering photometer PG-21 (Shimadzu Seisakusho Ltd.). All solvents and solutions were optically clarified by filtering through double sheets of Millipore filters "Solvinert-UH, and UG" (Millipore Co.). The refractive index increment was also measured at 25°C by 436 nm light with a Brice-type Shimadzu differential refractometer DR-3, under which condition its specific refractive index increment of the fraction in nitroethane was 0.181. Viscosity measurements were performed at 35°C with Ubbelohde-type capillary viscometers.

First, from preliminally measurements of the angular dependence of scattered light for various solutions, it was found that the reciprocal reduced scattering intensities$(R_\theta)^{-1}$ only for nitromethane and nitroethane solutions were considerably curved with a downward convex curvature against $\sin^2(\theta/2)$, but that they were not so, that is to say normal, in the other solvents such as chloroform, pyridine, dimethylformamide and benzene, except both solvents methanol and ethanol where such a curvature as those in nitroalkanes, but a very slight one, was observed.

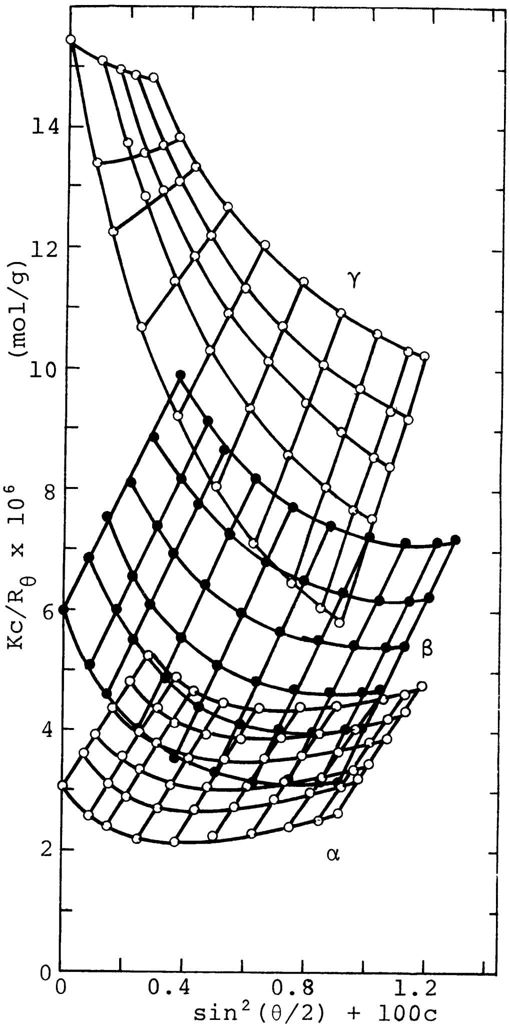

Fig.1 Three examples (α, β and γ) of the anomalous Zimm plots obtained for the same PMVP-nitroethane system at 25°C with 436 nm(Vv).

Fig. 1 shows three typical examples (indicated respectively α, β and γ) of the extraordinary Zimm plots obtained at every measurement for several times on the PMVP-nitroethane system under the same condition. Each was made on solutions ranging in concentrations from about 7×10^{-4} to 3×10^{-3} g/ml. Thus these observations are laborious and delicate in the reproducibility of the magnitude of anomaly as usually known. Here the plot denoted β wasn't for the fraction A-2, but was for another fraction of the PMVP, I-2-b, ($M_w = 6.1 \times 10^5$) previously presented by Prof. Miura of Hiroshima University,9) whose molecular weight is close to that of the fraction A-2, and then the differences between these two samples may be neglisible in such behaviors. In Fig. 2, viscosity data for the same system observed above at 35°C were graphed according to the Huggins plot, where notation α, β and γ respectively correspond to those in Fig. 1. Judging from the facts in Fig. 2, it is likely that the considerable differences among the degrees of distortion of curves in Fig. 1 may arise from a very small amount of impurities such as water inevitably contained in each nitroethane used, though each was naturally purified with care before use. It may be presumable from reports of Chasin for the P2VP in nitromethane10) and Arichi for the same polymer in nitroethane11) that

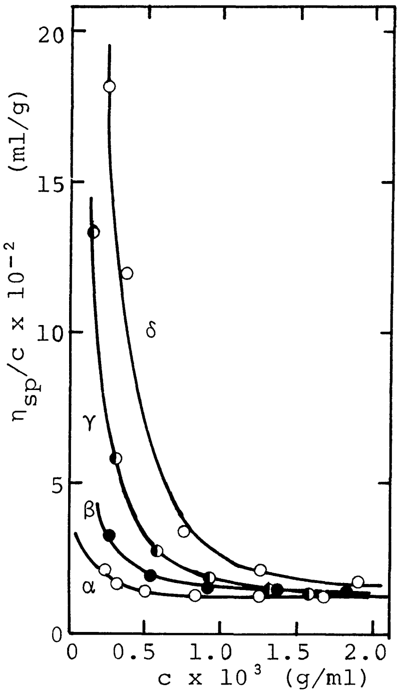

Fig.2 Viscosities for the same systems in Fig.1 at 35°C, where the indicated letters correspond to those except δ, which is a plot from Fig.3.

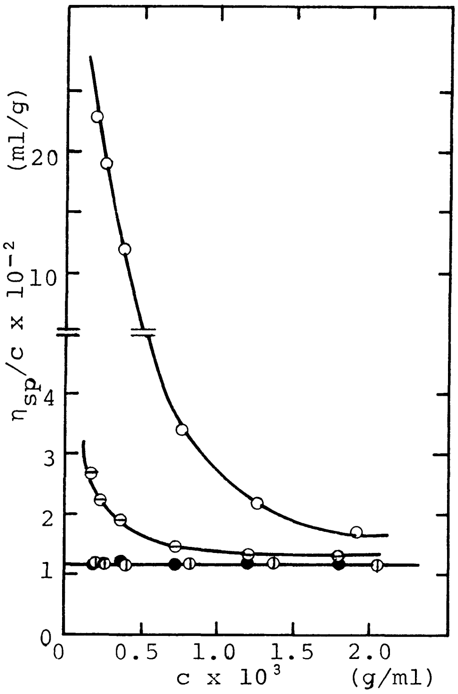

Fig.3 Effect of tetramethylammonium iodide on the viscosity of the PMVP in nitroethane at 35°C, each concentration of the salt is respectively; (○) 0.0 M, (⊖) 10^{-5} M, (●) 2x10^{-4}M, (⦶) 10^{-3}M.

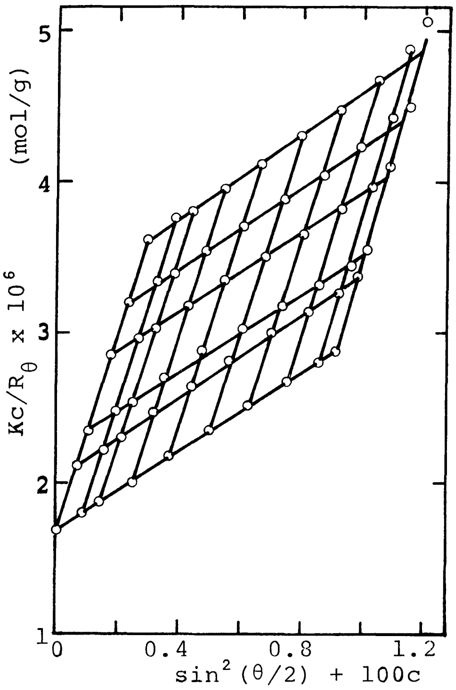

Fig.4 Normal Zimm plot for the fraction A-2 in nitroethane + tetramethylammonium iodide (2.2 x10^{-3}M) at 25°C with 436 nm(Vv).

thus the PMVP polymer viscometrically behaves in nitroethane like a polyelectrolyte. Where, it should be noticed that such a behavior in this investigation was appeared solely at much more diluted concentrations, compared with theirs. Hence it's very slight. On the other hand, Seely has noted that a nitromethane solution of the P4VP didn't take any polyelectrolytic behavior in viscometry, but that it behaved anomalous in the light scattering as shown in Fig. 1.1)

Anyhow, it may be naturally supposed from our results shown in Figs. 1 and 2 that the anomaly in the light scattering as well as in the viscosity would be able to be eliminated by the extreme repurification of nitroethane, but to our disappointment it was not accomplished in either case. Phenomenologically it is at least plausible that these anomalies may be ascribed to some ionization of the polymer. After various trials from this point of view, an addition of tetramethylammonium iodide salt was found effective to suppress it. In Fig. 3, viscosity curves of the fraction A-2 obtained at 35°C in nitroethane are shown, which contained respectively several amounts of its salt. For comparison, a curve measured in salt-free nitroethane at that time is also illustrated as δ in Fig. 2, which was most remarkable in polyelectrolytic behaviors. As indicated in the Figure, an addition more than 2 x 10^{-4}mol/l of the salt is necessary to recover the linearity in the Huggins plot like a nonelectrolyte polymer. Moreover, it was also found that the coexistence over ca. 1 x 10^{-3} mol/l of the salt needed at least to suppress the light scattering abnormality, though the data were not given here. On the basis of these facts, the light scattering of the PMVP was measured at 25°C with 436 nm(Vv) in nitroethane containing 2.2 x 10^{-3}mol/l of tetramethylammonium iodide. A normal Zimm plot obtained for the fraction A-2 was shown in Fig. 4, from which the values of its M_w, A_2 and $\langle s^2\rangle_z^{1/2}$ were estimated as 5.92 x 10^5, 3.20 x 10^{-4}ml·mol/g^2 and 377 A, respectively. The M_w likewise obtained for the fraction I-2-b was 6.29 x 10^5, and both values well coincide with each one formerly determined in benzene.

According to these results, it will be concluded that the anomalous light scattering in this investigation might be due to the intermolecular interference effect which becomes effective as the long-range electrostatic interaction brought about by some ionization of vinylpyridine polymers would cause a considerable ordering of the particles in the solution. And now, one of the mechanisms by means of which the PMVP is made to ionize may be supposed, for instance, as follows; it's well known that nitroalkanes possessing a hydrogen atom on the α-carbon may exist in two tautomeric forms,[12] nitro and aci, both of which exhibit acidic properties when traces of water were unfavorably contained in it, and successively the basic pyridines of side chains of the polymer should react with those to ionize.

For another support to our explanation that the origins of the anomaly are related to the above effect, the Guinier plots were made in Fig. 5, where P*(θ) at the ordinate is the apparent particle scattering factor including the interparticle scattering, and P(θ) is the normal particle scattering factor. These values at the extrapolated zero concentration were deduced from Fig. 1 for P*(θ) and from Fig. 4 for P(θ), respectively. As found in the Figure, satisfactory curves were obtained according to the theoretical formula. The root mean square distances between the centers of two polymer coils, $\langle r^2\rangle^{1/2}$ were calculated from each initial slope of plots to be 1690 A for α, 1030 A for β and 947 A for γ, respectively.

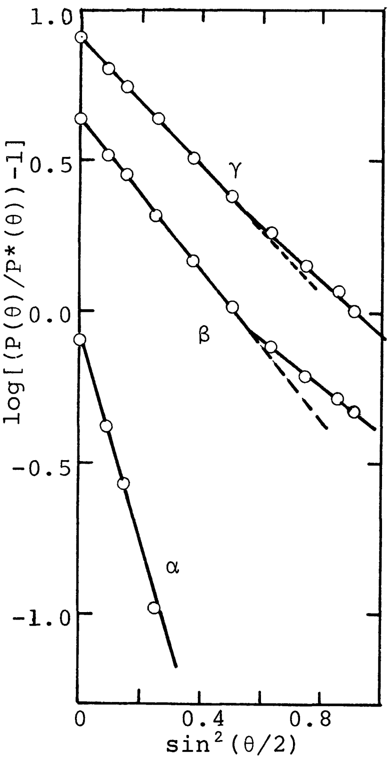

Fig.5 Guinier plots for each nitroethane solution of the PMVP at c→0, the indicated letters correspond to those in Figs.1 and 2.

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