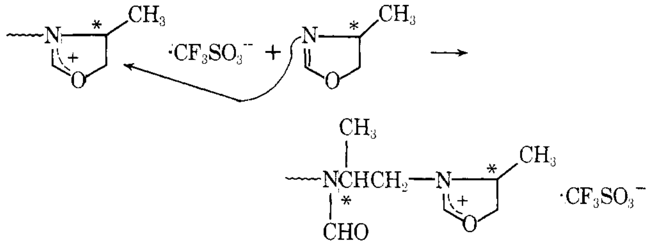
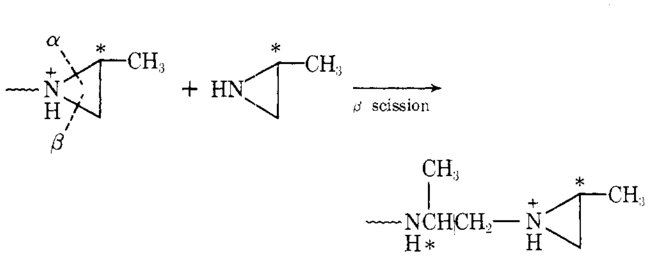
To a solution of 0.54 g of **1** in 6.2 ml of 50% aqueous methanol was added 0.44 g of NaOH. The homogeneous solution was kept at 100°. The reaction proceeded very slowly; *e.g.*, the extent of the reaction (followed by nmr) was 80% conversion after 68 hr and 95% after 160 hr. After a reaction time of 330 hr, the mixture was cooled to room temperature. The solvent was evaporated at reduced pressure. The residue was then extracted three times with cold chloroform and filtered and chloroform was evaporated. A waxy polymer was obtained in 84% yield. The nmr spectrum of the polymer (Figure 1b) supported the structure of poly(propylenimine) (**2**). A signal at δ 3.0–2.2 is ascribed to methylene (2 H) and methine (1 H) protons of **2**. A doublet centered at δ 1.1 is due to methyl protons (3 H) of **2**. It should be noted that the signal centered at δ 8.0 due to NCHO was completely absent, indicating that the alkaline hydrolysis had proceeded quantitatively.

Poly(propylenimine) (**2**) is also very hygroscopic. The ir spectrum of **2** showed strong absorption bands at 3400 and 1630 cm^{-1} due to H_2O. Therefore, the band of ν_{N-H} of **2** overlapped at a region of 3400 cm^{-1}. The optical activity was measured after the net content of polymer **2** in solution was determined also by nmr similarly to the measurement of **1** with C_6H_6 as internal standard. The specific rotation of **2** was found to be $[\alpha]^{26}\text{D}$ +105° (CH_3OH).

The present study provides a new route to optically active poly(propylenimine). It was established by nmr[4] that the polymerization proceeds *via* an S$_N$2 reaction between oxazolinium trifluoromethanesulfonate and monomer, in which the attack at the asymmetric carbon atom is never involved in the propagation. In the cationic polymerization of propylenimine, on the other hand, the possibility of the inversion or racemization at the chiral carbon atom in propagation (α scission) cannot be ruled out, although Price, *et al.*,[1] claimed that β scission took place exclusively.





As an additional consideration for the structure of Price's poly(propylenimine), considerable branching must be unavoidable in the cationic ring-opening polymerization of the aziridine ring.[5]

The obtained value of $[\alpha]\text{D}$ +105° in our present study is close to the highest values of the polymers prepared by the polymerization of L-propylenimine.[1] The molecular weight of the sample polymer of the present study is low. Therefore, higher values of specific rotation will be obtained when the molecular weight of **2** is increased. Preparation of higher molecular weight polymers of **2** as well as kinetic studies are now being undertaken.

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Received June 22, 1974

Direct Measurement of Polymer Dimensions in Concentrated Solutions by Small-Angle X-Ray Scattering

During the last 20 years the concentration dependence of polymer chain dimensions has been predicted by several authors theoretically[1-5] and by computer simulation.[6] To our knowledge, however, no experimental evaluation has been published, though molecular dimensions in bulk polymers have been estimated by a few authors.[7-9] Here we would like to report a new method for the direct measurement of polymer dimensions in concentrated solution and in bulk, as well as some preliminary results.

In X-ray scattering, polymers with heavy atom labels at both ends (end-tagged polymer)[7,10] have usually been employed for this purpose. In this case, however, the difference between the scattered intensity of tagged polymer and that of untagged polymer is rather small, because the number of heavy atoms is not sufficiently large. The higher the molecular weight, the smaller the difference, so that the application of this method may be limited to polymers of relatively low molecular weight, as has been pointed out by Ballard, *et al.*[9]

It is true that neutron scattering is a powerful technique, but it does not lie ready to everyone's hands. So we intend to improve the tagged polymer method in the X-ray scattering using random copolymers of styrene and *p*-iodostyrene synthesized by iodination of polystyrene.[11] These copolymers are assumed to be "randomly tagged polymers," which have heavy atom labels (iodine) along the molecular chains. Using this copolymer, we can expect stronger scattered intensity than that for end-tagged polymer, but the iodine atoms attached to the chain may give rise to conformational changes in the chain, the effect of which must be eliminated by an appropriate method.

As a sample, monodisperse polystyrene (batch no. 4b, Pressure Chemicals Ltd.), whose nominal molecular weight was 110,000 and $M_W/M_N < 1.06$, was used. The iodine content of copolymer was determined by argentometry.[12] As solvent, spectral grade toluene, which is a good solvent for polystyrene, was used without further purification.

Random copolymers of styrene and *p*-iodostyrene with various compositions were synthesized by iodination of polystyrene. Solutions of polystyrene and of a mixture of polystyrene and a small amount of tagged polystyrene (copolymer), both of which had the same total concentration, were studied by small-angle X-ray scattering with a Kratky camera.[13] The fluctuation of the intensity of the primary beam of the Kratky camera was smaller than 0.2% during the measurement. The temperature of the sample was maintained at 25 ± 0.1°.

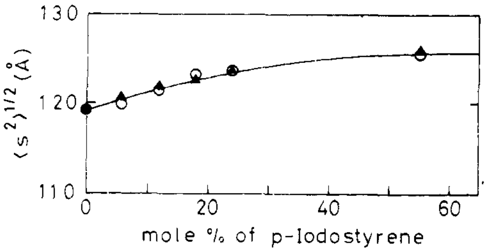

Figure 1. Plot of radius of gyration *vs.* composition of tagged polystyrene (copolymer). Open circles: radius of gyration of the groups of iodine atoms in tagged polystyrene. Triangles: radius of gyration of tagged polystyrene. Filled circle: radius of gyration of polystyrene. All measurements were made in dilute solution (0.5 g/dl). Concentration of tagged polystyrene is represented by weight (grams) of polystyrene without iodine per deciliter of solution.

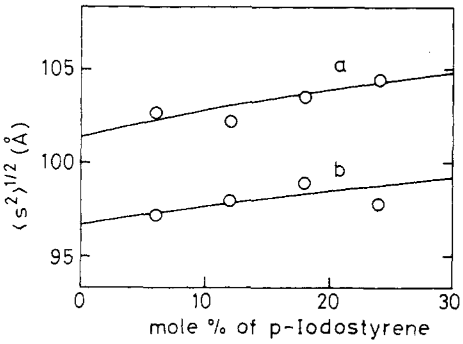

Figure 2. Plot of radius of gyration *vs.* composition of tagged polystyrene (copolymer). Curve a: polystyrene 2.575 g/dl; tagged polystyrene 0.5 g/dl. Curve b: polystyrene 5.614 g/dl; tagged polystyrene 0.5 g/dl. Concentration of tagged polystyrene is represented by weight (grams) of polystyrene without iodine per deciliter of solution.

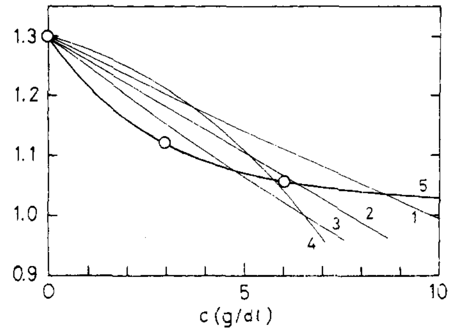

Figure 3. Dependence of α on concentration. Curves 1–4 are theoretical: (1) Yamakawa,[2] (2) Grimley,[3] (3) Fixman,[1] (4) Simha, *et al.*[5] Curve 5 represents the data in this work.

Throughout this experiment the concentration of tagged polystyrene in solution was kept constant at 0.5 g/dl, which is represented by the weight (grams) of polystyrene without iodine per deciliter of solution. The correction for absorption was carried out by a conventional method.[14]

The difference between the scattered intensities of solutions of a mixture of polystyrene and tagged polystyrene and of polystyrene alone is considered to originate from the iodine atoms. As the iodine atoms are distributed randomly in the tagged polystyrene, the molecular dimension of the tagged polystyrene can be assumed to be that of the groups of iodine atoms in the molecule. If the concentration of groups of iodine atoms is so dilute as to be independent of one another, we can obtain the radius of gyration of the tagged polystyrene at that concentration from the plot of the logarithm of the excess scattering intensity against the square of the scattering angle, the Guinier plot, after the correction for collimation error.[15] Indeed it is necessary to extrapolate the value obtained at 0.5 g/dl to that at zero concentration to get the exact value of the radius of gyration of tagged polystyrene, but we regarded the radius of gyration at 0.5 g/dl as the molecular dimension of tagged polystyrene within an error of several per cent, because the molecular weight of the polystyrene used is relatively low, so that the concentration of 0.5 g/dl may be considered sufficiently dilute to assure independence of intermolecular effects for this polymer.[16,17]

At one concentration a series of solutions of the mixture of tagged polystyrene of various iodine compositions and polystyrene was studied, and the molecular dimensions of the tagged polystyrene were estimated. These values were plotted against the compositions of tagged polystyrene and extrapolated to zero concentration of p-iodostyrene in the tagged polystyrene. Thus we can eliminate the conformational change owing to the substituent iodine.

In order to verify this technique, we applied it to dilute solutions of 0.5 g/dl concentration in which the dimensions of polystyrene and tagged polystyrene can be obtained directly by the Guinier plot. The scattered intensity of the solution of tagged polystyrene with various iodine contents and that of the solution of polystyrene, both of which have the same concentration of 0.5 g/dl, were determined. From the Guinier plot of the excess scattering intensity, the radius of gyration of the groups of iodine atoms in the tagged polystyrene was estimated. These values are shown by open circles in Figure 1. In addition, the scattered intensity of the solvent was measured. The difference between the scattered intensity of the solution of the tagged polystyrene (0.5 g/dl) and that of the solvent was calculated. From the Guinier plot of this excess intensity, the radius of gyration of the tagged polystyrene was estimated. These values are shown by triangles in Figure 1. As shown in Figure 1, the radius of gyration of the groups of iodine atoms in tagged polystyrene and that of tagged polystyrene agreed well with each other. This provides evidence that the dimension of the groups of iodine atoms in tagged polystyrene can represent that of tagged polystyrene.

Moreover, as shown in Figure 1, the extrapolation of the observed radius of gyration to zero iodine content agreed with the radius of gyration, 119 Å (filled circle), obtained from the Guinier plot of the scattered intensity of untagged polystyrene at 0.5 g/dl; the latter value agreed well with the radii of gyration of polystyrene in toluene, 119[18] and 120 Å,[19] obtained from the literature. Thus it was demonstrated that the value found by extrapolation of the observed radius of gyration to zero iodine content can be regarded as the dimension of the untagged polystyrene.

In Figure 2 the radius of gyration was plotted against the composition of tagged polystyrene at two concentrations. For polystyrene $\langle S_0{}^2\rangle/M = 7.6 \times 10^{-18}$, from which the unperturbed radius of gyration $\langle S_0{}^2\rangle^{1/2}$ of the sample is estimated to be 91.4 Å.[18] From this value the expansion factor α $(=\langle S^2\rangle^{1/2}/\langle S_0{}^2\rangle^{1/2})$ was calculated, in which $\langle S^2\rangle^{1/2}$ is the radius of gyration obtained by extrapolation in Figure 2. The value of α, 1.30, at infinite dilution was calculated from the radius of gyration of untagged polystyrene obtained at 0.5 g/dl.

In Figure 3 α is plotted against the concentration. Also included in the figure are curves predicted from some theoretical equations.[1-3,5] In the treatment of Fixman,[1] Yamakawa,[2] and Simha, *et al.*,[5] the only empirical parameter needed is α at infinite dilution, to which we assign the measured value of 1.30, provided that $\langle S_0{}^2\rangle^{1/2}$ and molecular weight are known. Grimley's treatment,[3] on the other hand, requires data on the variation of the second virial coefficient with molecular weight, for which we used the results of Berry.[18]

Our results suggest that α decreases first rapidly and then gradually as concentration increases. Such behavior has been predicted by some authors.[1-3,5,6] However, further measurements are required for more precise comparison with these predictions.

Experiments are under way to determine the dimensions over a wider concentration range, including the bulk state, and to study the effects of solvent and molecular weight of polymer.

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Kinetic Studies on the Conformational Transition of the Copolymer of Styrene and Maleic Acid in Aqueous Salt Solution

The pH-induced conformational transition of the hydrophobic poly(carboxylic acids) in aqueous salt solutions has been studied by many authors,[1-5] and the transition has been found to take place from a compact form in the noncharged state to an expanded coil form in the fully charged state. Such polyacids may be useful to study the intramolecular hydrophobic interaction, which may contribute to the structural stability of the globular proteins. Recently, two research groups[6,7] found a similar pH-induced conformational transition of an alternating copolymer of styrene and maleic acid (St–MA). The thermodynamic analysis of the transition in aqueous NaCl solution was investigated with data for fractionated samples from pH titration, viscosity, and dilatometric measurements.[6] The compact form at small degrees of dissociation of the primary carboxyl group seems to be stabilized by the hydrophobic interaction between phenyl residues buried in the compact polymer, and the coil form appears to have exposed phenyl residues. Therefore ultraviolet absorption of the phenyl group may reflect the conformational transition.

Kinetic studies of the transition by means of measurements of change in ultraviolet absorption of the phenyl group are reported here. Although there have been many equilibrium studies of the conformational transition of the hydrophobic poly(carboxylic acids), no kinetic studies have been found.

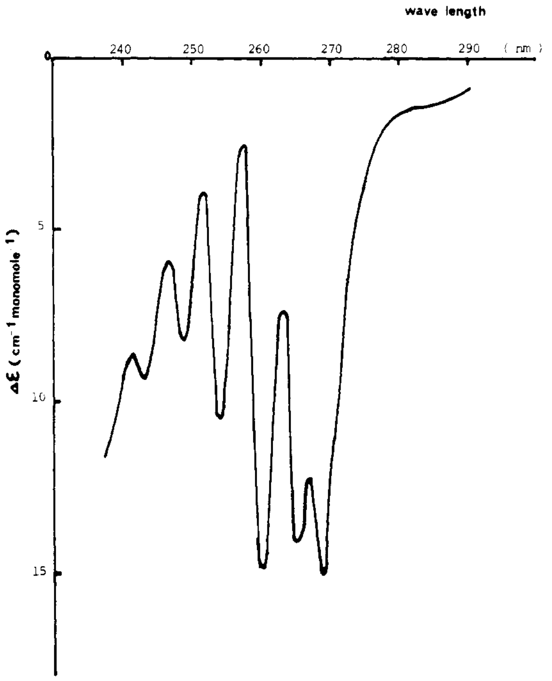

Figure 1. Difference spectrum of St–MA with $\alpha = 0.18$ in aqueous NaCl solution (polymer concentration = 0.0123 monomol/l. $I = 0.0091$, mol wt = 580,000).

St–MA was obtained and fractionated by the method reported previously.[6] The reagents used here and the method of preparation of the aqueous NaCl solution of St–MA were also identical.[6] Difference spectra were obtained with a Hitachi Perkin-Elmer spectrophotometer 139 or EPU-2A having a sample and reference temperature control at 25.0 ± 0.25°. As a reference the aqueous NaCl solution of St–MA completely in the coil form with the degree of dissociation of the primary carboxyl group $\alpha = 0.94$ was used. The kinetic measurements were done at 25.0 ± 0.25° with use of a rapid reaction analyzer (Union Giken, RA-1100)[8] whose dead time was less than 4 msec. The α jump of the polymer solution occurred during rapid mixing of equal volumes of polymer–NaCl and NaOH–NaCl. The change in transmittance at 269 nm of the polymer solution due to the α jump at constant NaCl concentration was recorded by use of a digital memory (Union Giken, RA-108S) and a pen recorder. The α value of the solution before mixing α_0 was determined by pH measurements with a Radiometer pH meter M-4 calibrated by use of the standard buffers, and its change $\Delta\alpha$ due to mixing was calculated from the quantities of NaOH introduced.

In Figure 1, an example of the difference spectra of the aqueous NaCl solution of St–MA is shown. The spectrum has some peaks at 269 nm and so on, and such a red-shift spectrum may be characteristic of the phenyl group buried in the hydrophobic domain.[9] The difference between the molar extinction coefficients of the sample and the reference at 269 nm, $\Delta\epsilon_{269}$, decreases in a sigmoidal fashion with increasing α in the case of low ionic strength I as shown in Figure 2. In the case of $I = 0.27$, molecular aggregation seems to affect the change in $\Delta\epsilon_{269}$ in the region of small α.

$\Delta\epsilon_{269}$ may be taken to be composed of two terms: perturbation of the phenyl group produced by change in the charge on the nearby carboxyl group in the same molecule, $\Delta\epsilon_{269}{}^{\mathrm{e}}$, and that by change of environment near the phenyl group, $\Delta\epsilon_{269}{}^{\mathrm{t}}$. The former should be proportional to this