# Small-Angle X-Ray Scattering Study on Conformation of Amorphous Polymer Chain in the Bulk

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ABSTRACT: The dimension and conformation of polystyrene chain in the bulk were estimated from small-angle x-ray scattering for mixtures including 0.5–1.5 mol % tagged polystyrene in polystyrene. Copolymers of styrene and *p*-iodostyrene with various compositions were used as the tagged polystyrene. The dimensions and conformation of polystyrene chain in the bulk were obtained from the excess scattering from the tagged polystyrene after the effects of iodine and the concentration of the tagged polystyrene were eliminated. The radius of gyration of the polystyrene ($M = 110\,000$) in the bulk was estimated to be 91 ± 5 Å. The measured dimensions agree with the unperturbed dimensions of the polystyrene chain within experimental error. The conformation of the polystyrene chain in the bulk was found to be a Gaussian coil from the shape of the scattered intensity curves. The results do not support the individual cell structure model or the meander model proposed for the molecular conformation in the bulk.

Various concepts have been proposed concerning the conformation of amorphous polymer chain in the bulk. One of them is the random coil model which was proposed by Flory,[1] supported by Tonelli,[2] and partially supported by Hoffmann.[3] The molecules are considered to be mutually penetrable and of the same dimension as that in theta solvents, the unperturbed dimension. On the other hand, Vollmert[4] proposed the individual cell structure model for concentrated solutions, in which the molecules are arranged in close-packed structure of individual particles. Lindenmeyer[5] predicted theoretically that molecules in the amorphous bulk exist in more highly coiled conformations than the random coil form, and that the interpenetration of molecules is much more limited than for the random coils. Schoon et al.[6] proposed a pearl necklace model composed of spherical structural units. Moreover, some authors have presented more or less ordered models. For example, Kargin et al.[7] proposed a bundle model, in which aggregates of molecules exist in parallel alignment. Pechhold et al.[8] presented a meander model, in which the molecules have a defective bundle structure, folded in a meanderlike manner. Yeh[9] proposed a folded-chain fringed-micellar grain model. This model consists of two elements: the grain or the ordered domain in which the molecules are more or less parallel to one another; and the intergrain region which consists of more randomly packed molecules. Privalko et al.[10] proposed a conformation having fold structures as well as a chain dimension corresponding to the unperturbed dimension. Thus, a variety of techniques and models have been proposed; however, the problem is still in a state of uncertainty.

As is generally known, the diffraction method is one of the most useful and direct techniques for determination of the molecular conformation of a polymer. Until recently, however, this method has not been employed for bulk polymers or concentrated solutions, because in these cases molecules are packed so closely that they are indistinguishable in a diffraction experiment. In order to distinguish a single molecule in these cases, the "tagged polymer" method has been applied. Tagged polymer means the polymer carrying an atom or atoms with high scattering power. If a small fraction of the molecules in the bulk or concentrated solution is tagged, a single chain is relieved against the environment in the scattering experiment. Application of this method to small-angle x-ray scattering was first shown by Kratky et al.[11] Krigbaum et al.[12] made the first attempt to measure the molecular dimension of a polymer in the bulk by this method. They determined the mean-square end-to-end distance of a polystyrene chain using the small-angle x-ray scattering from a tagged polymer carrying silver atoms at both ends (end-tagged polymer). Molecules with heavy atoms at both ends were also used by Brady et al.[13] and Li et al.[14] for the determination of the end-to-end distance of large organic molecules. In this case, however, the difference between the scattered intensities of tagged molecule and that of untagged molecule is rather small, because only two atoms per molecule are dominant in scattering power. The contrast in scattered intensity can be increased if the fraction of tagged molecules or the number of the tags per chain is increased. In the former case, however, correlations between the heavy atoms belonging to different molecules become noticeable, and in the latter case a risk of conformational change and aggregation of tagged molecules may arise from an excess of tags. De Gennes[15] reported a theory to eliminate this intermolecular correlation assuming the random coil conformation for the case where one end or both ends of all the molecules were tagged. The higher the molecular weight, the smaller the contrast, however, so that the application of the end-tagged polymer may be limited to polymers of relatively low molecular weight, as has been pointed out by Ballard et al.[16] and Schelten et al.[17] For the purpose of increasing scattering contrast, the neutron scattering method is very favorable. The tag used in this method is not a heavy atom but an isotope with a different scattering power. The isotope is usually deuterium and substituted for all hydrogen in the molecule. Since the isotopes are considered to have almost the same properties, the number of the tags per chain can be increased without causing the risk of the conformational change and aggregation, except for very severe cases. Poly(methyl methacrylate),[17,18] polystyrene,[16,19–21] and polyethylene[22] in the bulk or melt have been studied by neutron scattering, and the chain dimensions are found to agree with the unperturbed dimensions.

On the other hand, since tags used in x-ray scattering are heavy atoms, the properties of the tags are rather different from those of the corresponding atoms in the untagged molecule. Consequently too many tags may cause conformational change and aggregation of tagged molecules. In order to overcome this anomaly, we made an attempt to attach tags at some points randomly selected along the molecular chains, which we call "randomly tagged polymer". Application of this new type of tagged polymer enables us to eliminate undesirable effects due to the tags, such as conformational change and aggregation of tagged molecules, by extrapolation of the number of tags per chain to zero. In the previous paper,[23] we have reported the experimental verification of this method and preliminary results on the dimensions of polystyrene chains in moderately concentrated solutions. The purpose of this paper is to estimate the dimensions and conformation of polystyrene chain in the bulk by this method, and compare them with the results by neutron scattering.

## Principle of Tagged Polymer Method

Randomly tagged polymers used in this work are copolymers of styrene and *p*-iodostyrene; i.e., the tags are iodine atoms. In the end-tagged polymer used by Krigbaum et al.,[12] the fraction of segments with high scattering power was only about 0.2%, while the copolymer used in this study contains at least about 10% of tagged segments (*p*-iodostyrene). In this method, therefore, sufficient contrast in scattered intensity can be obtained. In addition the end-to-end distance can be estimated in the case of end-tagged polymer, while the radius of gyration and the conformation of polymer can be determined in the case of randomly tagged polymer.

A small fraction of the tagged polystyrene is dispersed in an untagged polystyrene matrix, and the scattered intensity of the mixture is measured. The background scattering from the matrix, which was measured under the same condition, is subtracted from the scattered intensity of the mixture. The excess intensity can be considered to originate from the iodine atoms in the tagged polystyrene and is, therefore, the scattering from the groups of iodine atoms attached to the tagged polystyrene.

It is first important to examine the correlation between the scattering function of the iodine group and that of homopolymer which has the same conformation as the tagged polymer. Let us assume that the tagged molecule consists of $N$ scattering units, of which the positions along the molecule are indicated by indices $i$ and $j$ running from 1 to $N$, and that the molecule contains $n$ tagged units, the positions of which are randomly distributed, and indicated by the progression of $\mathbf{n}_m$ in the case of tagged molecule $m$. It is also assumed that all tagged polymer chains which contain $n$ tagged units have the same conformation. The scattering function $F(h)$ of a randomly oriented assembly of homopolymers which have the same conformation as the tagged polymer is written as

$$F(h) = (1/N^2)\left(N + 2\sum_i \sum_{j<i} \frac{\sin hr_{ij}}{hr_{ij}}\right) \tag{1}$$

with

$$h = 4\pi \sin \theta/\lambda$$

where $r_{ij}$ is the distance between $i$th and $j$th units, $\theta$ half of the scattering angle, and $\lambda$ the wavelength. The scattered intensity $I_m(h)$ per group of the randomly oriented assembly composed of a large number of the groups, each of which corresponds to tagged units in a tagged molecule $m$, is written as

$$I_m(h) = I_e f^2 \left(n + 2\sum_k \sum_{l<k} \frac{\sin hr_{kl}}{hr_{kl}}\right) \tag{2}$$

where $I_e$ is the scattering from a single electron, $f$ the scattering power of the tagged unit, and $k$ and $l$ are the elements of $n_m$. The summation is performed for all tagged units.

Since the positions of tagged units differ from molecule to molecule, $I_m(h)$ must be averaged over all $\mathbf{n}_m$ as shown in the following.

$$I(h) = \sum_{m=1}^{C} I_m(h)/C \tag{3}$$

$$C = \binom{N}{n} \tag{4}$$

$C$ is the number of different $n_m$. Substitution of eq 2 into eq 3 yields

$$I(h) = (I_e f^2/C)\left(\sum_{m=1}^{C} n + 2\sum_{m=1}^{C} \sum_k \sum_{l<k} \frac{\sin hr_{kl}}{hr_{kl}}\right) \tag{5}$$

*In the triple sum in eq 5, every pair of $k$ and $l$ (or $r_{kl}$) emerges with equal probability, and the frequency is*

$$\binom{N-2}{n-2} = \frac{(N-2)!}{(n-2)!(N-n)!} \tag{6}$$

Hence, eq 5 can be written as

$$I(h) = I_e f^2 \left[n + 2\binom{N-2}{n-2} \sum_i \sum_{j<i} \frac{\sin hr_{ij}}{hr_{ij}}\right] \tag{7}$$

Comparison of eq 7 with eq 1 yields

$$I(h) = I_e f^2 Nn(n-1)(N-1)^{-1}\left[F(h) + \frac{1-n/N}{n-1}\right] \tag{8}$$

Consequently, if $N$ and $n$ are sufficiently large and $n \ll N$, the scattered intensity $I(h)$ of iodine groups is practically proportional to that of homopolymer having the same conformation as the tagged polymer to which these iodine atoms are attached. Even if $N$ and $n$ are not so large, the deviation is constant all over the scattering angles, and can be eliminated easily. This fact may be rather surprising because it suggests that the scattering function of randomly tagged polymer contains all of the information that can be obtained from the scattering function of wholly tagged polymer as has been employed in neutron scattering. This is due to the superposition of the scattered intensity of groups of tagged units in a large number of tagged molecules having the same conformation.

As was shown by Berry,[31] the scattering function $P(h)$ of the particle with any shape is approximated at low angle by

$$P(h)^{-1/2} = 1 + \langle S^2\rangle h^2/6 + \ldots \tag{9}$$

where $\langle S^2\rangle^{1/2}$ is the $z$-average radius of gyration of the particle. $P(h)$ is calculated by dividing the scattered intensity by that at zero angle. The initial slope of the plot of $P^{-1/2}$ against $h^2$ (square-root plot) yields the radius of gyration. A weight average radius of gyration can be obtained by multiplying $\langle S^2\rangle^{1/2}$ by the factor $[(1+U)/(1+2U)]^{1/2}$, where $U = M_w/M_n - 1$.[24]

In order to obtain the correct value for the radius of gyration of the tagged polymer, the value obtained at finite concentration must be extrapolated to infinite dilution to eliminate the effect of interference between the tagged molecules. In addition, the radius of gyration of the tagged polymer may differ from that of untagged polymer which is to be estimated, by the effect of the iodine atoms. This effect is eliminated in the following way. The radii of gyration of tagged polymers with various iodine contents are determined by the method described above. These values are plotted against their iodine content, and extrapolated to zero iodine content. These extrapolations also enable us to eliminate the effects of weak aggregation of tagged molecules, if any. Consequently the extrapolated value can be regarded as the value for the untagged polymer. The experimental verification of the latter extrapolation was described previously.[23]

If both the concentration of tagged polymer in the matrix and the iodine content in the tagged polymer are not so high, the apparent radius of gyration of the tagged polymer may be expanded in a Taylor series around the correct value for the untagged polymer.

$$\langle S^2\rangle^{1/2}(c_t,t) = \langle S^2\rangle^{1/2}(0,0) + a_1 c_t + a_2 c_t^2 + \ldots + b_1 t + b_2 t^2 + \ldots \tag{10}$$

with

$$\langle S^2\rangle^{1/2}(0,0) = \langle S^2\rangle^{1/2}$$

where $c_t$ is the mole percent of the tagged polymer in the matrix, $t$ the mole fraction of *p*-iodostyrene in the tagged polymer, $\langle S^2\rangle^{1/2}(c_t,t)$ the apparent radius of gyration of the tagged polymer with the composition of $t$ and observed at $c_t$, and $\langle S^2\rangle^{1/2}$ the radius of gyration of untagged polymer. The

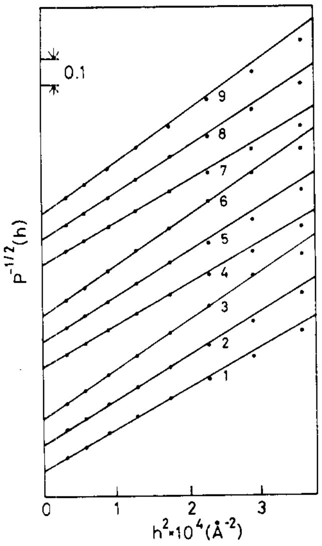

**Figure 1.** The square-root plot of the excess scattered intensity after normalization. The curves are mutually shifted along the ordinate, so that each intercept has the value of unity. Curve 1: $c_t = 0.5$, $t = 0.097$. Curve 2: $c_t = 1.0$, $t = 0.097$. Curve 3: $c_t = 1.5$, $t = 0.097$. Curve 4: $c_t = 0.5$, $t = 0.143$. Curve 5: $c_t = 1.0$, $t = 0.143$. Curve 6: $c_t = 1.5$, $t = 0.143$. Curve 7: $c_t = 0.5$, $t = 0.246$. Curve 8: $c_t = 1.0$, $t = 0.246$. Curve 9: $c_t = 1.5$, $t = 0.246$.

coefficients $a_n$ are constants referred to the intermolecular interference between the tagged molecules. The coefficients $b_n$ are also constants referred to the effects of iodine on the conformation. Consequently, the plot of $\langle S^2\rangle^{1/2}(c_t,t)$ estimated from the experiments as a function of $c_t + t$ can express the effects of the concentration and composition at the same time. Extrapolations of $\langle S^2\rangle^{1/2}(c_t,t)$ to $c_t = 0$ and $t = 0$ give the radius of gyration of the untagged polymer.

## Experimental Section

**Apparatus.** All measurements were made with a Kratky camera.[25] The x-ray source was a Phillips broadfocus tube connected with a Rigaku Denki x-ray generator operated at 45 kV and 35 mA. The detection of scattered intensity was made by a scintillation counter connected with a pulse height analyzer focussed on the Cu Kα line (1.54 Å) together with a 10 μ Ni filter to eliminate Cu Kβ. The stability of the primary beam intensity was better than 0.3% per week including the statistical error of 0.1%. The angular shift in the primary beam position was less than $5 \times 10^{-6}$ rad. The room temperature was controlled at 25 ± 0.5 °C. The temperature of the sample was kept at 25 ± 0.01 °C by circulation of water with constant temperature.

**Sample.** A narrow-distribution polystyrene (Pressure Chemical Co., batch No. 4b) with $M = 110\,000$ and $M_w/M_n < 1.06$ was used as the matrix (untagged polymer). The tagged polymers were random copolymers of styrene and *p*-iodostyrene prepared by the iodination of the polystyrene according to the procedure of Braun.[26] It was confirmed by the light scattering method that the degrees of polymerization of the tagged polymers are the same as those of the homopolymer. The mole fractions of *p*-iodostyrene in the copolymers were 0.097, 0.143, and 0.246, which were calculated from the iodine content determined by argentometry.[27]

Since the tagged polymer should be dispersed molecularly in the matrix of untagged polymer, the compatibility of the tagged and untagged polystyrene at various fractions was examined. Samples containing various fractions of tagged and untagged polymer were dissolved in ethylbenzene (bp 136 °C) and the solvent was gradually evaporated at the glass transition temperature of polystyrene (100 °C). In this way, the mobility of the molecules is increased and hence it can be determined whether the sample is compatible or not at that temperature. The tagged and untagged polystyrene were compatible only when the mole percent of tagged polystyrene does not exceed 1.5% for $t = 0.097$, 1.0% for $t = 0.143$, and 0.2% for $t = 0.246$. Consequently, the samples were prepared to avoid the phase separation by the following method. Both polystyrene and tagged polystyrene were dissolved in toluene, precipitated in methanol, and dried in a vacuum oven at 50 °C. The samples were then melted in a mold 2-mm thick within 10 min at 140 °C. All samples prepared in this way were completely transparent and isotropic, which was verified by x-ray diffraction. Thermal stability of the tagged polystyrene was confirmed by comparing the iodine content of the untreated tagged polystyrene with that of the tagged polystyrene which was heated at 170 °C for 30 min. Heated sample was dissolved in toluene, precipitated into methanol, and dried to eliminate free iodine which may evolve upon heating. No appreciable difference was detected between them. Stability of polymers toward x-ray irradiation was confirmed by reproducibility of the scattered intensity of the measured samples.

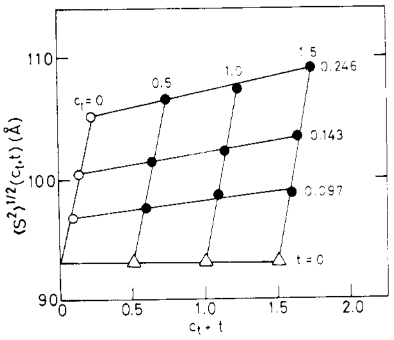

**Figure 2.** The determination of the radius of gyration of bulk polystyrene. Filled circles represent $\langle S^2\rangle^{1/2}(c_t,t)$ plotted according to eq. 10. Open circles and triangles show the extrapolations to $c_t = 0$ and $t = 0$, respectively.

**Measurements and Data Analysis.** The scattered intensity was measured by the step-scanning method by means of a fully automatic step controller. About 40 steps were scanned for each curve, and $10^4$–$10^5$ pulses were counted for each measurement, which corresponds to a statistical error of 1.0–0.3%. In order to obtain high-scattered intensity, a primary beam with a line-shaped cross section was used, which caused a collimation error. The error was corrected (desmeared) according to the method of Schmidt.[28] The absorption coefficient of the sample was determined by the conventional method.[25] The measured intensity was first corrected for the absorption and the thickness. Then the excess intensity was calculated, plotted against the scattering angle, and smoothed manually. A constant scattering background originating from the fluctuations in the electron density within the scattering particles was then eliminated according to Luzzati et al.[29] The values obtained in this way were corrected for collimation error.

## Results and Discussion

**Radius of Gyration.** Figure 1 shows the square-root plot of the excess scattered intensity after normalization, from which the apparent radius of gyration of the tagged polystyrene was determined. The values obtained are plotted according to eq 10 in Figure 2. The intercepts of two limiting curves, $\langle S^2\rangle^{1/2}(0,t)$ and $\langle S^2\rangle^{1/2}(c_t,0)$, show good agreement. From the figure the *z*-average radius of gyration of polystyrene in the bulk is estimated to be 93 ± 5 Å, and the weight average 91 ± 5 Å, with the assumption $M_w/M_n = 1.06$. As is also shown in the figure, all measured values fall between 97 and 110 Å, which are of the order of the dimensions of a single molecule. This fact suggests that the tagged polymer is dispersed molecularly in the untagged bulk phase, and that the estimate is reasonable.

For comparison, the unperturbed radius of gyration $\langle S_\theta{}^2\rangle^{1/2}$ of the polystyrene was calculated. The variation of $\langle S_\theta{}^2\rangle^{1/2}$ of polystyrene with the molecular weight was determined by various authors.[30] According to Berry,[31] $\langle S_\theta{}^2\rangle/M = 7.6 \times 10^{-18}$, and the unperturbed radius of gyration is calculated to be 91.4 Å. Consequently, the measured molecular dimensions agree well with the unperturbed dimensions.

As is shown by open triangles in Figure 2, $\langle S^2\rangle^{1/2}(c_t,0)$ is independent of the concentration of the tagged polymer within the measured concentration range. This fact suggests that no correlation exists between the tagged molecules in the matrix when the number of iodine atoms diminishes, which leads to the result that at least $a_1$ in eq 10 is equal to zero.

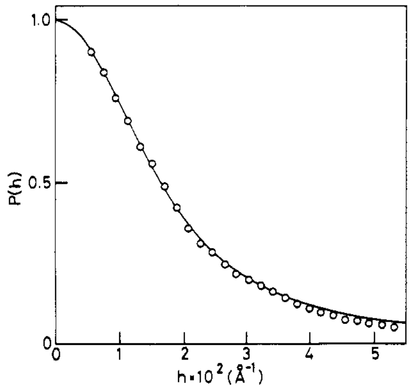

**Figure 3.** The comparison of the observed scattering function for $c_t = 0.5$ and $t = 0.097$ with the theoretical one. Open circles represent measured values after normalization and the curve represents Debye's theoretical function calculated from eq 11 with $\langle S^2\rangle^{1/2} = 97.6$ Å.

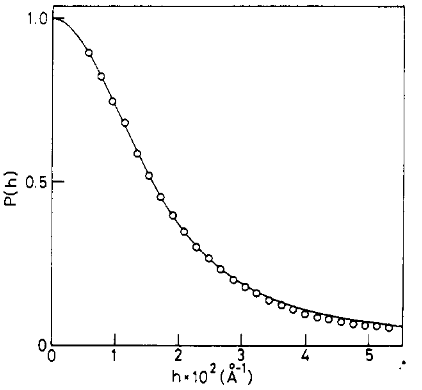

**Figure 4.** The comparison of the observed scattering function for $c_t = 0.5$ and $t = 0.143$ with the theoretical one (eq 11 with $\langle S^2\rangle^{1/2} = 101.5$ Å).

Taking into account these facts, it can be concluded that the molecular chains in the bulk are mutually penetrable and that the centers of gravity of the molecules are distributed almost randomly. These results do not support an individual cell structure model,[4] because in such a model the size of the molecule must be three or four times smaller than that observed,[32] and the penetration should be much less than that deduced from this experiment.

**Chain Conformation.** In order to estimate the conformation more minutely, the shape of the scattering curves will be discussed. Debye has shown the scattering function $P(h)$ for randomly coiled polymer in which the distribution of any two scattering elements is assumed to be Gaussian:

$$P(h) = (2/x^2)(e^{-x} + x - 1) \qquad (11)$$

with

$$x = \langle S^2\rangle h^2$$

In Figures 3–5, the examples of the scattered intensity are plotted against the angular parameter $h$ after normalization, in which open circles represent the measured values, and the curves give the Debye equation. As shown in these figures, the measured values agree well with the theoretical curve over a wide angular range, which suggests that the conformation of the tagged molecule is a random coil. It is noteworthy that no sharp conformational change of the tagged polymer occurs when iodine content varies, as is shown by the fact that the Debye equation can be fitted to all the scattering curves. From this fact, it is concluded that the most probable conformation of polystyrene chains in the bulk is also Gaussian.

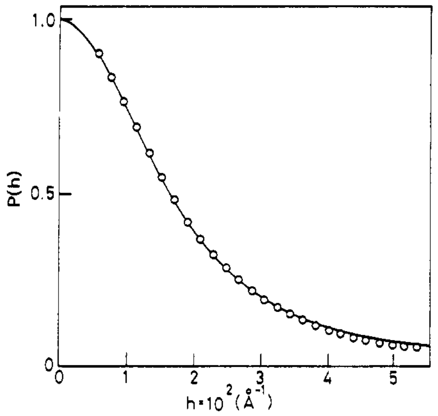

**Figure 5.** The comparison of the observed scattering function for $c_t = 0.5$ and $t = 0.246$ with the theoretical one (eq 11 with $\langle S^2\rangle^{1/2} = 106.6$ Å).

Thus the conclusion drawn from this work is that the chain conformation of bulk polystyrene is a Gaussian coil and that the chain dimensions are the same as the unperturbed dimensions. Consequently the individual cell structure model and the meander model are not supported. This conclusion is similar to that obtained by neutron scattering. However, if the size of the ordered region is very small, or the number of these regions is small, or the degree of order in this region is poor, the influence of such order upon the chain dimensions and the shape of the scattering curve may be too slight to be observed. In order to discuss the upper limit of the size or fraction of ordered region or the degree of order, it is necessary to calculate their scattering functions and compare them with the experimental curve.

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# Conformational Characteristics of Poly(vinylidene fluoride)

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ABSTRACT: Approximate conformational energy estimates have been utilized to evaluate the rotational isomeric state (RIS) model of poly(vinylidene fluoride) (PVDF). Conformational properties including the unperturbed dimensions and dipole moments and their temperature dependence and the conformational contribution to the entropy of fusion were calculated for PVDF from its RIS model. Occasional (0–20%) head to head:tail to tail (H–H:T–T) addition of monomer units in a random fashion was accounted for in the calculation of these conformational properties. In general it was found that the calculated conformational properties of PVDF were relatively insensitive to the amount of H–H:T–T addition assumed, but were instead markedly dependent upon the value of the dielectric constant ($\epsilon$) selected to mediate the electrostatic interactions encountered along a PVDF chain. For values of $\epsilon \approx 4$–6, both the unperturbed dimensions and entropy of fusion recently measured and reported by Welch and by Nakagawa and Ishida, respectively, are reproduced by the calculations. Based on a comparison of dimensions it appears that at equilibrium PVDF adopts conformations which are on the average more compact than those assumed by either poly(ethylene) or poly(tetrafluoroethylene), the two homopolymers whose repeat units in regular alternation constitute the PVDF chain.

In recent years the effort to determine and understand the physical properties of poly(vinylidene fluoride) (PVDF) has intensified. This increased activity most probably reflects an interest in the piezoelectric and pyroelectric properties[3–12] exhibited by permanently polarized electret films of PVDF. As a result, this activity has focused primarily on the study of PVDF solid state properties.

The structures of the three crystalline forms of PVDF have been studied by x-ray diffraction[13–19] and infrared[20–25] and Raman[25] spectroscopy. Effects of specimen annealing as manifested by specific volume, differential scanning calorimetry, and electron microscopy measurements[2] have yielded the equilibrium melting point, the enthalpy and entropy of fusion, and estimates of the surface free energy, enthalpy, and length of the chain folds in PVDF crystals.

The motions of PVDF chains in the solid state have also been examined. Temperature- and frequency-dependent studies of the various relaxations observed in solid PVDF samples by dielectric,[26–37] mechanical,[33] and wide line nuclear magnetic resonance[15,30,33,38,39] (NMR) spectroscopy have been reported and associated with either the amorphous or crystalline portions of this semicrystalline polymer.

In contrast to the extensive work reported on the solid state properties of PVDF and aside from the ca. 5% head to head: tail to tail (H–H:T–T) monomer addition detected[40] in PVDF by high-resolution $^{19}$F NMR spectroscopy in solution, it is only very recently that its dilute solution properties have begun to be studied. Solution viscosity and light-scattering studies by Welch[1] have led to an estimate of the unperturbed dimensions of isolated PVDF chains. It was Welch's work that prompted the present detailed study of the conformational characteristics of isolated PVDF chains described below.

Conformational energy estimates were performed on segments of PVDF chains in an attempt to determine the rotational isomeric state (RIS) model appropriate to this polymer. In addition to the predominant head to tail (H–T) arrangement of monomer units, H–H:T–T monomer addition was explicitly considered. In a departure from previous calculations,[18,41] which considered only regularily repeating structures, all rotational conformations were permitted.

Several properties characteristic of the conformational behavior of PVDF chains were calculated from its derived RIS model. The mean-square end-to-end distance and dipole moments and their temperature dependence and the conformational contribution to the entropy of fusion were calculated for isolated and unperturbed PVDF chains of high molecular weight. The calculated dimensions and entropy were compared to the appropriate experimental quantities.

## Description of Calculations

Portions of a PVDF chain whose conformations depend on one or both of two neighboring backbone bond rotation angles are illustrated in Figure 1. Segments labeled HFH and FHF are characteristic of the predominant H–T addition, while the less abundant H–H:T–T arrangements are denoted as FFH(HFF) and HHF(FHH). The conformational energies of each of these fragments were calculated as a function of the rotation angles $\Phi_1$ and $\Phi_2$ using approximate potential functions which account for the intrinsic threefold torsional potential about the C–C backbone bonds and the van der Waals and electrostatic interactions between nonbonded atoms.

A barrier of 3.0 kcal/mol was assumed[42] to separate the three rotational minima at $\Phi_1$ or $\Phi_2 = 0°$ (trans, t), $\pm 120°$ (gauche$^\pm$, g$^\pm$). Partial charges of +0.4 and −0.2 esu were assigned to the carbon and fluorine atoms of the CF$_2$ groups based on the observed C–F bond dipole moment.[18,43,44] These partial charges assigned to the carbon and fluorine atoms lie midway between the values employed by Hasegawa et al.[18] and Bates and Stockmayer.[43,44]

The value of the dielectric constant $\epsilon$ assumed to mediate the electrostatic interactions between the partially charged atoms was varied over the range $\epsilon = 2$–10, because of the un-