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References and Notes

(1) T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1956).
(2) R. B. Beevers and E. F. T. White, *Trans. Faraday Soc.*, **56**, 1529 (1960).
(3) R. B. Beevers, *Trans. Faraday Soc.*, **58**, 1465 (1962).
(4) N. W. Johnston, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **10**, 608 (1969); **13**, 1029 (1972); **14**, 46, 634 (1973); *J. Macromol. Sci., Chem.*, **7**, 531 (1973); *Macromolecules*, **6**, 453 (1973).
(5) S. Yabumoto, K. Ishii, M. Kawamori, K. Arita, and H. Yano, *J. Polym. Sci., Part A-1*, **7**, 1933 (1969).
(6) J. Furakawa and A. Nishioka, *J. Polym. Sci., Part B*, **9**, 199 (1971).
(7) M. Hirooka and T. Kato, *J. Polym. Sci., Part B*, **12**, 31 (1974).
(8) D. R. Herschbach, *Proc. Int. Symp. Mol. Struct. Spectrosc.*, **1962**, 1 (1963).
(9) D. A. Brant and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 2791 (1965).
(10) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.*, **23**, 47 (1967).
(11) V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, "Dipole Moments in Organic Chemistry," Plenum Press, New York, N. Y., 1970, Chapter III.
(12) O. G. Lewis, "Physical Constants of Linear Homopolymers," Springer-Verlag, New York, N. Y., 1968.
(13) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3**, 294 (1970).
(14) A. E. Tonelli, *Macromolecules*, **6**, 682 (1973).
(15) z_{dyad} is the configurational partition function of the chain segment encompassing two asymmetric centers (see Figure 1a). Interactions between the atoms of this segment and neighboring segments have been ignored.
(16) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1963.
(17) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, Chapter III.
(18) None of these observations are qualitatively affected by ignoring the electrostatic interactions. The nonbonded steric, or van der Waals, interactions dominate the conformational energy estimates.
(19) It is clearly not necessary to postulate[4] the existence of interactions, such as are possible between the π-electron clouds of the phenyl ring and nitrile group, any more exotic in nature than those of the ordinary van der Waals type in order to achieve this qualitative understanding.
(20) F. E. Karasz and W. J. MacKnight, *Macromolecules*, **1**, 537 (1968).
(21) It must be stressed that the proposed correlation between the equilibrium chain flexibility and the T_{gp}'s of copolymers is applicable to the sequence distribution-dependent deviations from the simple bulk additive behavior predicted by the Fox relation, and should not be construed as a means for predicting the absolute value of the glass transition temperature.

Calculation of Neutron Diffraction Pattern by Polymer Chains in the Bulk State

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ABSTRACT: The incompressibility of the bulk polymer is assumed in order to calculate the neutron diffraction pattern from labeled polymer chains in a matrix of unlabeled chains. The scattering law obtained is the Fourier transform of the pair correlation function of atoms along the labeled polymer chain. When the scattering vector $\mathbf{q}$ is small relative to the inverse monomer dimensions we find that the chain has a Gaussian configuration in the bulk polymer. In the range of higher values of q the diffraction pattern is associated with the short-range interactions (corresponding to the transfer matrix) which characterize the polymer studied. The neutron diffraction pattern is obtained from a computer experiment using hydrogenous n-alkanes in a matrix of deuterated n-alkanes in a q range between 10^{-2} and 2.5 Å^{-1}. The results are discussed in order to obtain experimental evidence about the transfer matrix.

In the discussion of the pair correlation function $p(r)$ of atoms along the chain,[1] three ranges of magnitude of r are usually considered. For large distance $r \sim R$ where $R^2 = \langle R^2 \rangle$ is the mean-squared end-to-end distance, the analysis of $p(r)$ is carried out in terms of the moments of r. In the intermediate range $l < r < R$, where l^2 is the mean-squared length of a statistical element, $p(r)$ has the characteristic dependence $r^{-\alpha}$, $1 \leq \alpha \leq 2$. In the short correlation distance range $r \leq l$, one expects to find patterns associated with the short-range interactions. There is, however, no analytical form for $p(r)$ in this range.

The ranges of r are naturally transposed into ranges of the momentum transfer q, since the Fourier transform of $p(r)$ is the scattering law $S(q)$ for a single chain.

The study of the first two ranges has shown a close relationship between $p(r)$ and the chain environment. This is particularly clear in the case of the molecular mass dependence of the second moment and in the case of the exponant α. Similarly, one may expect that the diffraction patterns for $q \geq l^{-1}$ will reflect chain environment, although perhaps for different reasons. The main interest in the study of this range is, however, the detailed nature of the conformation. The analysis should give evidence of conformational differences among chemically different polymers. It should also reveal local modifications due to environment, such as the partial alignment predicted in the amorphous state.

Conformation is an expression of enthalpy and conformational entropy. The latter is calculated from internal rotation potential barriers and nearest neighbor interactions. The result of the calculation is expressed in the form of a "transfer" matrix.[2] Values of the matrix elements are determined by calorimetric measurements. They are consistent with the value of l measured by scattering experiment at $q \leq l^{-1}$. The study of the range $q \geq l^{-1}$ will bring, however, a closed relationship between the observed conformation and the transfer matrix.

There are yet few experimental results in this momentum transfer range. If one considers chains dispersed in a solvent, the contrast between solvent and solute will be too small to be observed, as q increases away from the $q^{-\alpha}$ singularity. The diffraction pattern will mostly reflect the solvent liquid state. Scattering by bulk material yields the polymer diffraction patterns. However, the pair correlation along the chain and the pair correlation between chains are not easily discernible from the intensity momentum transfer dependence.

The possibility of labeling chains by deuteration[3] and the use of high flux neutron sources has suggested experiments which give complementary information with respect to the unlabeled bulk material. These experiments have proven to be very successful in the first two momentum ranges[4] ($q \leq l^{-1}$). We investigate here the condition for the observation of diffraction patterns of labeled chains in the range $q \geq l^{-1}$. A model of chain interaction which is an expression for the incompressibility hypothesis will be used. The theoretical cross section has already[1,3] been discussed in terms of incompressibility and will be derived here in section one. Next, a computer simulated calculation will give patterns for n-alkanes. We discuss experimental conditions giving the closed relation between the transfer matrix and chain configuration.

I. Calculation of the Scattering Intensity

(A) Scattering Cross Section of a Labeled Chain in the Bulk. (a) Contrast Factor. We call $\rho_{l\alpha}(\mathbf{r})$ the density of the lth atom in the αth chain at the point $\mathbf{r}$ of a bulk polymer consisting of N_{P} chains each containing N' atoms. In terms of the linear response function theory,[5] the scattering cross section $S(\mathbf{q})$ can be written

$$S(q) = k_{\beta}T \sum_{\substack{l,\alpha \\ k,\beta}} \mathcal{a}_{l\alpha}\chi_{\substack{l\alpha \\ k\beta}}(q)\mathcal{a}_{k\beta} \tag{1}$$

where k_{B} is the Boltzmann constant, T the temperature, and $\mathcal{a}_{l\alpha}$ the scattering amplitude of the (l,α) atom. $\chi_{k\beta^{l\alpha}}(\mathbf{q})$ is the Fourier transform of the response function which is proportional to the fluctuation density correlations of the atoms (l,α) and (k,β)

$$k_{\beta}T\chi_{\substack{l\alpha \\ k\beta}}(\mathbf{r} - \mathbf{r}') = \langle \rho_{l\alpha}(\mathbf{r})\rho_{k\beta}(\mathbf{r}')\rangle - \langle \rho_{l\alpha}\rangle\langle \rho_{k\beta}\rangle \tag{2}$$

or in the Fourier space

$$k_{B}T\chi_{\substack{l\alpha \\ k\beta}}(\mathbf{q}) = \langle e^{i\mathbf{q}\mathbf{r}_{l\alpha}}e^{-i\mathbf{q}\mathbf{r}_{k\beta}}\rangle$$

In the bulk polymer we consider that only the chain $\alpha = 1$ has one or more labeled atoms and we define

$$\begin{aligned} \mathcal{a}_{l\alpha} &= A_{l} \text{ for } \alpha = 1 \\ \mathcal{a}_{l\alpha} &= B_{l\alpha} \text{ for } \alpha > 1 \end{aligned} \tag{3}$$

The separation of the labeled chain response from the others in the sums of eq 1 leads to

$$S(\mathbf{q}) = \sum_{k,l} A_{k}\chi_{\substack{k1 \\ l1}}(\mathbf{q})A_{l} + \sum_{\substack{k,\alpha>1 \\ l,\beta>1}} B_{k\alpha}\chi_{\substack{k\alpha \\ l\beta}}(\mathbf{q})B_{l\beta} + 2\sum_{\substack{k,1 \\ l,\beta>1}} A_{k}\chi_{\substack{k1 \\ l\beta}}(\mathbf{q})B_{l\beta} \tag{4}$$

For experimental reasons it is interesting to introduce the scattering cross section $S^{B}(\mathbf{q})$ of the sample without labeled polymers

$$S^{B}(\mathbf{q}) = \sum_{\substack{k\alpha \\ l\beta}} B_{k\alpha}\chi_{k\alpha}(\mathbf{q})B_{l\beta} \equiv \sum_{\substack{k1 \\ l1}} B_{k1}\chi_{\substack{k1 \\ l1}}(\mathbf{q})B_{l} + \sum_{\substack{k,\alpha>1 \\ l,\beta>1}} B_{k\alpha}\chi_{\substack{k\alpha \\ l\beta}}(\mathbf{q})B_{l\beta} + 2\sum_{\substack{k,1 \\ l,\beta>1}} B_{k1}\chi_{\substack{k1 \\ l\beta}}(\mathbf{q})B_{l\beta} \tag{5}$$

Using relation 5 in eq 4 and adding to it the term

$$2\sum_{k,l} (A_{k} - B_{k})\chi_{kl}(\mathbf{q})B_{l} - 2\sum_{k,l} (A_{k} - B_{k})\chi_{kl}(\mathbf{q})B_{l} \equiv 0 \tag{6}$$

which introduces the correlations between the labeled chain and that which it replaces. This is, of course, zero in $S(\mathbf{q})$. We obtain

$$S(\mathbf{q}) = S_{11}(\mathbf{q}) + S_{12}(\mathbf{q}) + S^{B}(\mathbf{q})$$

with

$$S_{11}(\mathbf{q}) = \sum_{l,k} C_{k}\chi_{kl}(\mathbf{q})C_{l} \tag{7}$$

$$S_{12}(\mathbf{q}) = \sum_{\substack{k,1 \\ l,\beta}} C_{k}\chi_{\substack{k,1 \\ l,\beta}}(q)B_{l\beta}$$

where C_{k} is given by

$$C_{k} = A_{k} - B_{k} \tag{8}$$

If, from the N' atoms of the chain $\alpha = 1$, only the N first are labeled, then

$$\begin{aligned} C_{k} &= 0 \text{ for } N < k \leq N' \\ C_{k} &\neq 0 \text{ for } 1 \leq k \leq N \end{aligned} \tag{9}$$

Equation 7 is a general relationship. It can be used, for instance, in the case of a liquid which contains a labeled molecule. The term $S_{11}(\mathbf{q})$ in (7) gives the response function of only the labeled atoms with a weight given by the contrast factor C_{k}^{2}. The second term $S_{12}(\mathbf{q})$ is an interference term between the labeled atoms and all the atoms of the sample.

(b) Determination of the Response Function. Recently de Gennes[5] has given a determination of the scattering cross section of a bulk polymer in which each chain has labeled ends. We follow the same development assuming the incompressibility of the bulk; *i.e.*, we consider as in the Flory-Huggins theory[6] that each atom of the polymeric bulk is on a site of a lattice and a site $\mathbf{r}$ is always occupied by only one atom. Then at $\mathbf{r}$ the atomic density is constant and we can write this condition

$$\sum_{l=1}^{N'} \sum_{\alpha=1}^{N_{\mathrm{P}}} \rho_{l\alpha}(\mathbf{r}) = \text{const} \tag{10}$$

or

$$\sum_{l\alpha} \langle \delta\rho_{l\alpha}(\mathbf{r})\rangle = 0 \tag{11}$$

The theory gives[7] the density fluctuations resulting from small externally applied potential in terms of the linear response functions. In the Fourier space

$$\langle \delta\rho_{l\alpha}(\mathbf{q})\rangle = \sum_{k,\beta} \chi_{\substack{l\alpha \\ k\beta}}(\mathbf{q})U_{k\beta}{}^{\mathrm{ex}}(\mathbf{q}) \tag{12}$$

the response function $\chi_{k\beta^{l\alpha}}(\mathbf{q})$ may be deduced from $\chi_{k\beta^{l\alpha}}{}^{0}(\mathbf{q})$, the response function of an "ideal polymer." We define this ideal polymer as an isolated chain with only nearest neighbor sequential interactions.

$$\chi_{\substack{l\alpha \\ k\beta}}{}^{0}(\mathbf{q}) = \chi_{lk}{}^{0}(\mathbf{q})\delta(\alpha - \beta) \tag{13}$$

where δ is a Dirac function. We assume, in a random phase approximation, that the interactions between an atom on a given chain and the atoms both of all the other chains and far away on the same chain (excluded volume effect) can be reduced to a mean internal potential $U(\mathbf{q})$. Therefore we write the double equality

$$\langle \delta\rho_{l\alpha}(\mathbf{q})\rangle = \sum_{k,\beta} \chi_{\substack{l\alpha \\ k\beta}}{}^{0}(\mathbf{q})[U_{k\beta}{}^{\mathrm{ex}}(\mathbf{q}) + U(\mathbf{q})] = \sum_{k\beta} \chi_{\substack{l\alpha \\ k\beta}}(\mathbf{q})U_{k\beta}{}^{\mathrm{ex}}(\mathbf{q}) \tag{14}$$

Now we have an expression for the internal potential

$$U(q) = -\sum_{\substack{l,\alpha\\k,\beta}} \chi_{\substack{l\alpha\\k\beta}}{}^{0}(\mathbf{q})U_{k\beta}{}^{\mathrm{ex}}(\mathbf{q}) \Big/ \sum_{\substack{m\gamma\\n\delta}} \chi_{\substack{m\gamma\\n\delta}}{}^{0}(\mathbf{q}) \qquad (15)$$

Then the insertion of (15) in the first equation (eq 14) using the assumption in (2) leads, by identifying with zero the coefficient of $U_{k\beta}{}^{l\alpha}(\mathbf{q})$, to an expression of the atomic response function

$$\chi_{\substack{l\alpha\\k\beta}}(\mathbf{q}) = \chi_{\substack{l\alpha\\k\beta}}{}^{0}(\mathbf{q}) - D^{-1}(\mathbf{q})\sum_{n\delta}\sum_{m\gamma} \chi_{\substack{l\alpha\\n\delta}}{}^{0}(\mathbf{q})\chi_{\substack{m\gamma\\k\beta}}{}^{0}(\mathbf{q}) \qquad (16)$$

with

$$D(\mathbf{q}) = \sum_{\substack{m\gamma\\n\delta}} \chi_{\substack{m\gamma\\n\delta}}{}^{0}(\mathbf{q}) \qquad (17)$$

Using (13) we find

$$\chi_{\substack{l\alpha\\k\beta}}(\mathbf{q}) = \chi_{lk}{}^{0}(\mathbf{q})\delta(\alpha - \beta) - D^{-1}(\mathbf{q})\sum_{n}^{N'}\sum_{m}^{N'} \chi_{ln}{}^{0}(\mathbf{q})\chi_{km}{}^{0}(\mathbf{q}) \qquad (18)$$

and

$$D(q) = N_{\mathrm{p}}\sum_{m}^{N'}\sum_{n}^{N'} \chi_{mn}{}^{0}(q) \qquad (19)$$

We now have the general response function in terms of the response of an isolated chain without interactions. The results can be used in all scattering techniques. In the following we give an application to the neutron scattering from a polymeric bulk containing deuterated polymers. This labeling method is very good, because the chemical properties of the labeled chains remain unaltered in an isotropic substitution.

(c) Application to Neutron Scattering. Here we consider only polymers made with $N' - N$ carbon and N hydrogen. The labeling consists in replacing the hydrogen atoms by deuterium atoms. In neutron scattering the coherent lengths of these atoms[8] are

$$a_{\mathrm{C}} = +0.663 \times 10^{-12} \text{ cm}$$
$$a_{\mathrm{H}} = -0.372 \times 10^{-12} \text{ cm}$$
$$a_{\mathrm{D}} = +0.670 \times 10^{-12} \text{ cm}$$

so the change of an atom H by atom D is very important in this technique.

It is convenient to write the scattering $S_0(\mathbf{q})$ of an "ideal polymer" (see eq 13), which has all its atoms with the same coherent length (here $a_{\mathrm{C}} = a_{\mathrm{H}} = 1$), in the form

$$S_0(\mathbf{q}) = k_{\mathrm{B}}T\sum_{kl}\chi_{kl}{}^{0}(\mathbf{q}) = S^{\mathrm{HH}}(\mathbf{q}) + 2S^{\mathrm{HC}}(\mathbf{q}) + S^{\mathrm{CC}}(\mathbf{q}) \qquad (20)$$

$S^{\mathrm{HH}}(\mathbf{q})$ and $S^{\mathrm{CC}}(\mathbf{q})$ are the scattering cross sections of chains with $a_{\mathrm{C}} = 0$ and $a_{\mathrm{H}} = 1$ and with $a_{\mathrm{C}} = 1$ and $a_{\mathrm{H}} = 0$, respectively. $S^{\mathrm{HC}}(\mathbf{q})$ is the interference term which can have a negative value.

Using now the coherent lengths, we apply the relations in (7) and (17) to the calculation of $S(\mathbf{q})$ of a deuterated polymer in a nondeuterated matrix (see Appendix I) and we find

$$S_{11}(\mathbf{q}) = (a_{\mathrm{D}} - a_{\mathrm{H}})^2\left\{S^{\mathrm{HH}}(\mathbf{q}) - \frac{1}{N_{\mathrm{p}}S_0(\mathbf{q})}(S^{\mathrm{HH}}(\mathbf{q}) + S^{\mathrm{HC}}(\mathbf{q}))^2\right\} \qquad (21)$$

$$S_{12}(\mathbf{q}) = 2(a_{\mathrm{D}} - a_{\mathrm{H}})(a_{\mathrm{H}} - a_{\mathrm{D}})f(\mathbf{q}) \qquad (22)$$

$$S^{B}(\mathbf{q}) = N_{\mathrm{p}}(a_{\mathrm{H}} - a_{\mathrm{C}})^2 f(\mathbf{q}) \qquad (23)$$

where

$$f(\mathbf{q}) = \frac{1}{S_0(\mathbf{q})}[S^{\mathrm{HH}}(\mathbf{q})S^{\mathrm{CC}}(\mathbf{q}) - (S^{\mathrm{HC}}(\mathbf{q}))^2] = S^{\mathrm{HH}}(\mathbf{q}) - \frac{1}{S_0(\mathbf{q})}[S^{\mathrm{HH}}(\mathbf{q}) + S^{\mathrm{HC}}(\mathbf{q})]^2 \qquad (24)$$

Then the total scattering cross section can be written

$$S(\mathbf{q}) = (a_{\mathrm{D}} - a_{\mathrm{H}})^2\left(1 - \frac{1}{N_{\mathrm{p}}}\right)S^{\mathrm{HH}}(\mathbf{q}) + \frac{1}{N_{\mathrm{p}}}[(a_{\mathrm{D}} - a_{\mathrm{H}}) + N_{\mathrm{p}}(a_{\mathrm{H}} - a_{\mathrm{C}})]^2 f(\mathbf{q}) \qquad (25)$$

If the bulk contains N_{L} labeled chains *without* interaction between themselves the total scattering cross section becomes

$$S(\mathbf{q}) = cN_{\mathrm{p}}\{(a_{\mathrm{D}} - a_{\mathrm{H}})^2(1 - c)S^{\mathrm{HH}}(\mathbf{q}) + c[a_{\mathrm{D}} - a_{\mathrm{H}} + c^{-1}(a_{\mathrm{H}} - a_{\mathrm{C}})]^2 f(\mathbf{q})\} \qquad (26)$$

where c is the labeled chain concentration

$$c = N_{\mathrm{L}}/N_{\mathrm{p}} \qquad (27)$$

Experimentally it is often convenient to subtract the scattered intensity of the matrix from that of the matrix containing deuterated chains. The intensity so obtained is proportional to $S^{\mathrm{M}}(\mathbf{q})$.

$$S^{\mathrm{M}}(\mathbf{q}) = S(\mathbf{q}) - S^{B}(\mathbf{q}) = cN_{\mathrm{p}}\{(a_{\mathrm{D}} - a_{\mathrm{H}})^2(1 - c)S^{\mathrm{HH}}(\mathbf{q}) + c(a_{\mathrm{D}} - a_{\mathrm{H}})[a_{\mathrm{D}} - a_{\mathrm{H}} + 2c^{-1}(a_{\mathrm{H}} - a_{\mathrm{C}})f(\mathbf{q})]\} \qquad (28)$$

(d) Discussion. The intensity scattered by a single chain in the bulk material is written in eq 25 as the sum of two contributions. We discuss the significance and the weight of these two terms.

(1) The following relations

$$S^{\mathrm{HH}}(0) = N^2$$
$$S^{\mathrm{CC}}(0) = (N' - N)^2 \qquad (29)$$
$$S^{\mathrm{CH}}(0) = (N' - N)N$$

and eq 24 imply that $f(q) = 0$ at $q = 0$. In fact $f(q)$ will be different from zero only if the monomer form factor is different from unity, *i.e.*, in a momentum transfer range where q is larger than the monomer inverse dimensions. We also notice from eq 24 that $f(q)$ is strictly zero at all q in the case of an ideal chain in which the monomer is reduced to a material point. Thus $f(q)$ is a function associated with the monomer structure of the chain.

(2) In the small angle scattering range $q < l^{-1}$, the scattered intensity in (25) is practically identical with the scattering law of an ideal chain. Thus the calculation indicates that, in the bulk state, the chain has the ideal random conformation[9]

$$S^{\mathrm{HH}}(\mathbf{q}) = \frac{2N^2}{X^2}(e^{-x} - 1 + X) \qquad X = q^2\langle R^2\rangle/6 \qquad (30)$$

This result confirms the predictions derived by Flory[6] from thermodynamic arguments by which the excluded volume effects are found to be insignificant because of the low entropy of mixing chains. Scattering experiments from hydrogenous PMMA in a deuterated PMMA matrix[10] and from deuterated polystyrene in a hydrogenous polystyrene matrix[4] and *vice versa*[11] show indeed no deviations from the ideal random coil, in the range $ql < 1$. The real problem of the polymer chain in the bulk state is thus the evaluation of deviations from the ideal random coil in the higher momentum transfer range.

(3) Equation 25 has two terms independent of N_p, the total number of chains. The first term $S^{HH}(q)$ is proportional to the square of the contrast factor $(a_D - a_H)$. The second term $f(q)$ is a linear function of the contrast factor. Variation of the contrast factor was recognized by Kirste and Stuhrmann[12] as a powerful tool to separate the "structural" factor $f(q)$ from the "shape" factor $S^{HH}(q)$ in polymer solutions. In the particular case of the experiment with bulk material the contrast factor can take two and only two values, namely $a_D - a_H$ and zero.

$$S(q) = (a_D - a_H)^2 S^{HH}(q) + 2(a_D - a_H)(a_C - a_H)f(q) + F(N_p) \tag{31}$$

(4) The commutation of a_H and a_D leaves $S(q)$ unchanged only in the range of small angle scattering. In the larger momentum range $q > l^{-1}$, the factor $f(q)$ is weighted by $(a_H - a_C)$ in the case of an hydrogenous matrix and by $(a_D - a_C)$ in the case of a deuterated matrix. We notice that a_D is practically equal to a_C.

(5) If the sample contains no labeled chains ($a_H = a_D$), eq 25 reduces to (23). Then in the small momentum transfer range, the scattering law is zero.

$$S^B(q) = 0 \qquad ql < 1 \tag{32}$$

In a chain where the monomer is a single atom, the scattering law is zero at any value of q.

If the sample consists of only one chain ($N_p = 1$) the scattered intensity is proportional to the structure factor

$$S(q) = (a_D - a_C)^2 f(q) \tag{33}$$

(6) The incompressibility hypothesis yields a structure factor $f(q)$ which is nonzero for $ql > 1$. This result raises the following problem. To what extent is the formulation of the incompressibility hypothesis (eq 11) valid for distances below the interatomic distance?

(B) Method of Calculation. It was shown in the preceding section that the scattering cross section $S(\mathbf{q})$ may be obtained using only the response $S_0(\mathbf{q})$ of an isolated chain. Calculation of $S_0(\mathbf{q})$ itself requires the different configuration of the polyethylene chain and their probabilities as may be seen in Flory.[2] The molecular geometry is characterized by the bond lengths and angles and by the bond rotation angles. The bond lengths C–C and C–H are 1.53 and 1.09 Å, respectively, the angles C–C–C 112° and H–C–H 109°.[2] The C–C bond angle φ has three preferred values, trans ($\varphi = 0$), gauche$^+$ ($\varphi = +120°$), and gauche$^-$ ($\varphi = -120°$), corresponding to the three minima in the configurational energy. A configuration may be represented by the ensemble $\{\varphi\} = \{\varphi_2, \ldots, \varphi_i, \ldots, \varphi_{n-1}\}$ of bond rotation angles where φ_i is the rotation angle of the ith bond with respect to the $(i-1)$th bond and n is the number of carbon atoms.

If α is the state of the $(i-1)$th bond and β that of the ith bond, $E_{\alpha\beta;i}$ represents the contribution to the total energy associated with the ith bond. For each energy $E_{\alpha\beta;i}$ there is an associated statistical weight $U_{\alpha\beta;i}$ defined by

$$U_{\alpha\beta;i} = \exp(-E_{\alpha\beta;i}/RT) \tag{34}$$

These statistical weights may be written in the form of a transfer matrix

$$[U_{\alpha\beta}] = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\varphi & \sigma\omega \\ 1 & \sigma\omega & \sigma\varphi \end{bmatrix} \tag{35}$$

which includes first- and second-order interactions and where

$$\sigma = \exp(-E_\sigma/RT)$$
$$\varphi = \exp(-E_\varphi/RT)$$
$$\omega = \exp(-E_\omega/RT)$$

for polyethylene[13] $E_\sigma = 500$ cal mol^{-1}, $E_\varphi = 0$, and $E_\omega = 2200$ cal mol^{-1}, and the statistical weight of a chain composed of n bonds is

$$\Omega\{\varphi\} = \prod_{i=2}^{n-1} U_{\alpha\beta;i}$$

The probability $P\{\varphi\}$ that a given molecule will be found in the configuration $\{\varphi\}$ is the configurational partition function

$$P\{\varphi\} = Z^{-1} \prod_{i=2}^{n-1} U_{\alpha\beta;i} \tag{36}$$

where

$$Z = \sum_{\{\varphi\}} \Omega\{\varphi\}$$

For each configuration the chain is represented by a succession of CH_2 groups with CH_3 end groups and each atom in a group is considered separately. The determination of the position of each atom in each configuration $\{\varphi\}$ allows $S_0(\mathbf{q})$ to be calculated from eq 20 and 2

$$S_0(\mathbf{q}) = \sum_{\{\varphi\}} P\{\varphi\} \left\langle \sum_{i=1}^{N'} \sum_{j=1}^{N'} e^{i\mathbf{q}\mathbf{r}_{ij}\{\varphi\}} \right\rangle \tag{37}$$

where $\mathbf{r}_{ij}\{\varphi\} = \mathbf{r}_i\{\varphi\} - \mathbf{r}_j\{\varphi\}$ is the vector between atoms i and j of an isolated chain in the configuration $\{\varphi\}$, $\langle \ldots \rangle$ represents the average of all possible orientations of a chain configuration with respect to $\mathbf{q}$, $\sum_{\{\varphi\}}$ is a sum over all configurations each with probability $P\{\varphi\}$ given by eq 36.

We examine two cases.

(a) An isotropic case where all orientations of a configuration relative to the vector $\mathbf{q}$ are equally probable. Making the orientational average (37) becomes

$$S_0(\mathbf{q}) = \sum_{\{\varphi\}} P\{\varphi\} \sum_{i=1}^{N'} \sum_{j=1}^{N'} \frac{\sin |\mathbf{q}| |\mathbf{r}_{ij}\{\varphi\}|}{|\mathbf{q}| |\mathbf{r}_{ij}\{\varphi\}|} \tag{38}$$

(b) An anisotropic case, where for each configuration a direction defined by the first two chain segments is fixed relative to the vector $\mathbf{q}$. We chose two particular orientations which we defined in Figure 1.

(1) $q^{\parallel}$. The $\mathbf{q}$ vector is parallel to the axis a joining the first and third carbon atoms. The orientational average in (37) must take account of all the positions into which the chain may rotate about the axis. The orientational average disappears and (37) becomes

$$S_0(\mathbf{q}) = \sum_{\{\varphi\}} P\{\varphi\} \sum_{i=1}^{N'} \sum_{j=1}^{N'} \cos \mathbf{q}\mathbf{r}_{ij}\{\varphi\} \tag{39a}$$

(2) $q^{\perp}$. The $\mathbf{q}$ vector is perpendicular to the defined abscissa axis. In this case it is necessary to average over all the

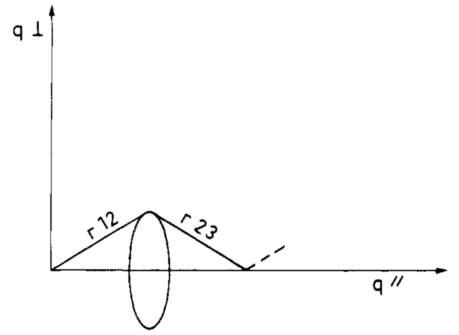

Figure 1. Representation of the first two segments r_{12} and r_{23} of the polymer chain. In the anisotropic scattering experiment the momentum transfer is successively taken as $q^{\parallel}$ and $q^{\perp}$.

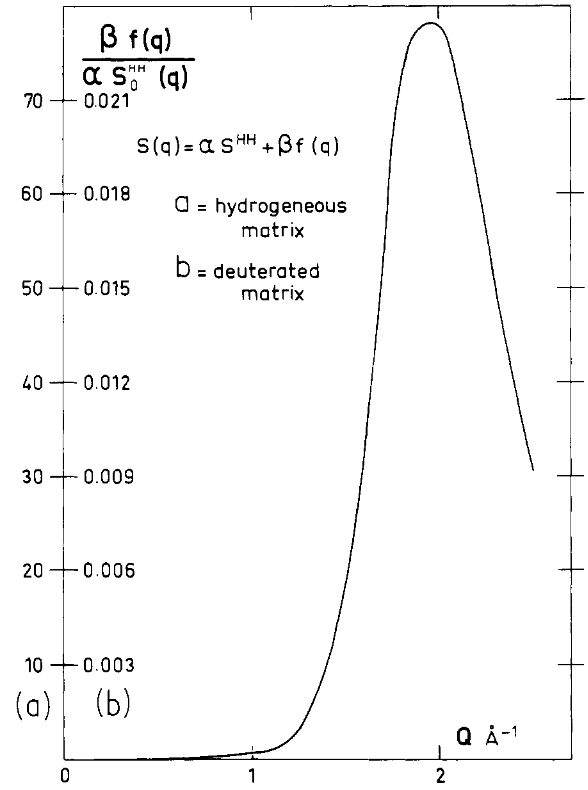

Figure 2. Representation of the normalized structure function $\mathfrak{F}(q) = f(q)/S^{HH}(q)$. The numerical calculations indicate that $\mathfrak{F}(q)$ is not sensitive whereas $f(q)$ is sensitive to the chain conformation. The weight β/α measures the degree of disymmetry between the labeled chain in the bulk state and its dual experiment. The first scale refers to deuterated chains in the hydrogenous matrix. The second refers to the reverse situation.

different projections of r_{ij} on $\mathbf{q}$. If we define $r_{ij}{}^{\perp}$ as the projection of r_{ij} in the plane perpendicular to the axis a, the orientational average in eq 37 becomes

$$S_0(\mathbf{q}) = \sum_{\{\varphi\}} P\{\varphi\} \sum_{i=1}^{N'} \sum_{j=1}^{N'} J_0(\mathbf{q} \cdot \mathbf{r}_{ij}{}^{\perp}\{\varphi\}) \qquad (39b)$$

where J_0 is a Bessel function. Equations 38 and 39 may be separated in the same way as eq 20 into three terms $S^{HH}(q)$, $S^{HC}(q)$, and $S^{CC}(q)$.

II. Numerical Results

For numerical application it is convenient to reduce the general problem to a particular experiment using the following simplification. In order to test the transfer matrix which represents the short-range interactions, it is sufficient to apply the computer simulation to the case of short chains. Thus we have used n-alkanes where $n \leq 16$.

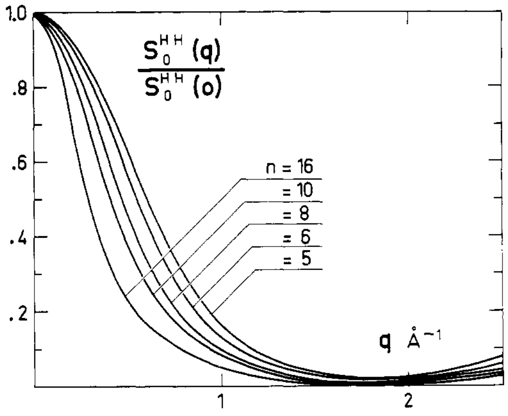

Figure 3. Scattering law $S^{HH}(q)$ in the isotropic scattering experiment by n-alkanes, for n = 5, 6, 8, 10, 12, and 16.

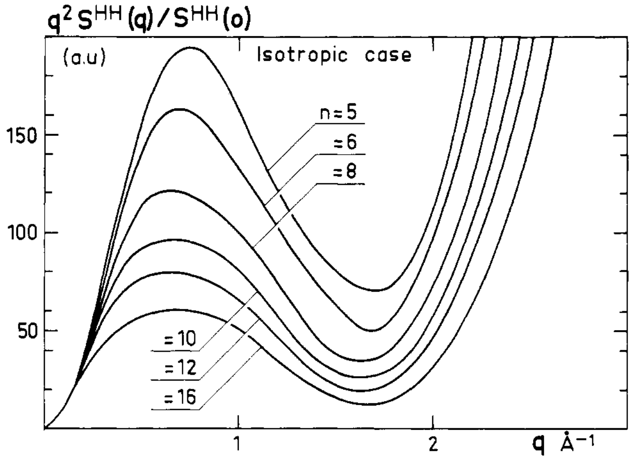

Figure 4. Representation of the function $q^2S^{HH}(q)$ corresponding to the situation in Figure 2.

For such chains, the repeat unit is made of two different atomic species. Thus the structure function $f(q)$ will appear in the scattered intensity $S(q)$. The weight of this function depends on the method of labeling. We consider the case where the labeled chains are hydrogenous and the matrix deuterated. This commutes a_D and a_H in eq 21, 22, and 23. Then eq 22 and 23 contain the multiplicative term $a_D - a_C = 7 \times 10^{-15}$ cm; the corresponding term appearing in eq 21 has the much larger value 10^{-12} cm, thus heavily weighting the term $S_{11}(q)$ in the calculation of $S(q)$. This effect is shown in Figure 2. The scattered intensity (eq 25) is rewritten as

$$S(q) = \alpha S^{HH}(q) + \beta f(q) \qquad (40)$$

In going from one labeling method to its opposite, the ratio β/α is modified. Two ordinate scales are drawn in Figure 2 showing the strong discrepencies of the ratios. Thus $f(q)$ could be determined from successive measurements with both labeling methods. At the present state of our investigation, it is not clear what information is contained in the structure function $f(q)$. However, the following points may be noticed: as expected, $f(q)$ is neglectible in the range $q < 1$Å^{-1}; above this threshold the shape of the normalized function $f(q)/S^{HH}(q)$ is insensitive to conformation; the structure function $f(q)$ is very sensitive to the conformation. The numerical calculation indicates that it rises much more sharply in the case of a random conformation than in the rod conformation.

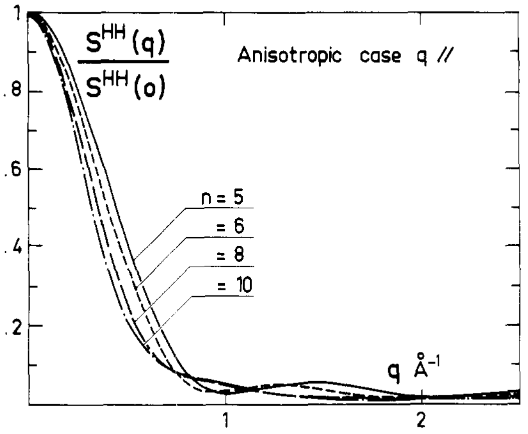

Figure 5. Scattering law $S^{HH}(q)$ in the anisotropic scattering experiment by n-alkanes for $q = q^{\parallel}$ (see Figure 1).

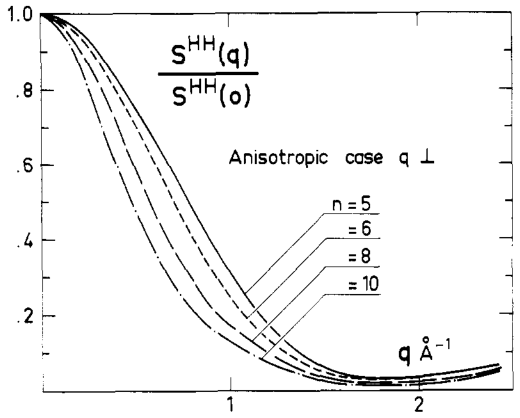

Figure 6. Scattering law $S^{HH}(q)$ in the anisotropic scattering experiment by n-alkanes for $q = q^{\perp}$ (see Figure 1).

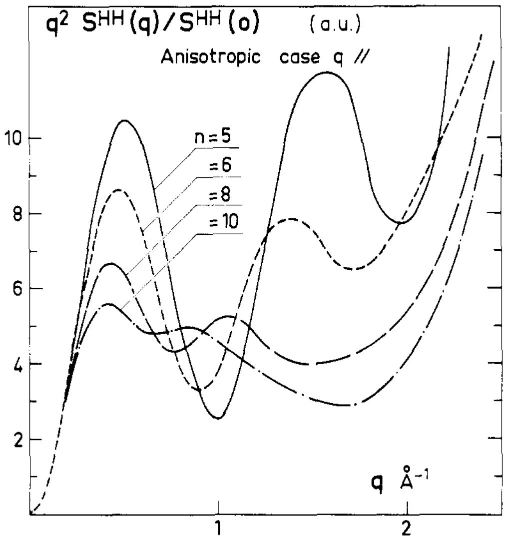

Figure 7. Representation of the functions $q^2S^{HH}(q)$ corresponding to the situation described in Figure 5.

The case of the hydrogenous n-alkanes in a deuterated n-alkane matrix is of special interest since we can neglect the contribution of $f(q)$. The scattered intensity is reduced to

$$S(q) = cN_p(a_D - a_C)^2S^{HH}(q) \qquad (41)$$

A fortran program has been written to calculate all the configurations $\{\varphi\}$ and their probabilities $P\{\varphi\}$ for each chain. For each configuration the positions of all the atoms were determined and applying eq 37 and 38 $S(q)$ was calculated. In fact it is not necessary, for reasons of symmetry, to make these calculations for every configuration and we reduced the calculation time by considering in the ensemble $\{\varphi\}$ classes of equivalence, comprising 1, 2, or 4 configurations which conserve the value of $S(q)$. The results are divided into isotropic and anisotropic experiments.

Figure 3 shows $S^{HH}(q)$ plotted against q for n-alkane chains where n has the values 5, 6, 8, 10, and 16 and S^{HH} has been evaluated isotropically. The narrowing of the law q region with increasing molecular weight is clearly seen. The numerical data obtained for $S^{HH}(q)$ using the 3 × 3 transfer matrix $[U_{\alpha\beta}]$ have been compared with these obtained using the more precise 5 × 5 matrix given by Flory.[2] No real difference between the two sets of data has been seen in this range of q values. This result is consistent with another computer experiment[2] in which only the long-range interactions have been observed. In Figure 4 the same calculated $S^{HH}(q)$ functions are plotted as $q^2S(q)$ against q. It is interesting to note the minima which occur between 1 and 2 Å^{-1} but have not before been predicted theoretically.

Figures 5 and 6 show $S^{HH}(q)$ for the anisotropic case (a) q parallel and (b) q perpendicular. In each case n = 5, 6, 8, and 10. The difference between the two q directions is marked particularly in the low q region. Differences in the higher q region are more clearly visible in Figures 7 and 8 where we show $q^2S(q)$. For $q^{\perp}$ in the region 1–3 Å^{-1}, the curves are very similar to the isotropic case, but for $q^{\parallel}$ there are peaks which change position as the chain length increases.

In order to watch the effect of the transfer matrix on the calculated $S(q)$ we chose two extreme examples. First, the three orientational probabilities of each segment relative to the preceding one are given equal weight, so that each element in the matrix is unity. This gives equal probability to every chain conformation, the so called Gaussian chain. In this case, three directional correlations are quickly lost as the chain molecular weight increases, and $S(q^{\parallel})$ takes the same form as for the isotropic scattering. The other example we chose allows only trans configurations: the transfer matrix is diagonal and unity.

In the isotropic scattering experiment, the differences introduced in $S(q)$ by varying the transfer matrix are small. The change in probability of the various chain conformations manifests itself mainly as a different mean value of R^2 and hence in a different form of the low q region. In Table I we list half-widths of this region and it is clear that these differences cannot be easily measured in an experimental situation. In the anisotropic scattering experiment the effects of varying the transfer matrix are clearly visible. The effects are summarized in Table II where we have listed the ratio of the momentum transfer half-width of $S(q)$, for $q^{\perp}$ and $q^{\parallel}$, for each of the three transfer matrices. The "Gaussian" chain should tend toward a symmetrical distribution in space for chains sufficiently long and in fact the tendency of $q_{1/2}{}^{\perp}q_{1/2}{}^{\parallel}$ toward unity may be seen even for these rather short chains. On the other hand a "trans" chain becomes more and more asymmetrical as it increases in length and $q_{1/2}{}^{\perp}q_{1/2}{}^{\parallel}$ is a steadily increasing function of N. It is easy to see that initially the "real chain" lies between these extremes but quickly tends toward the Gaussian as the chains become longer. In the higher q region peaks appear for $q^{\parallel}$ which must be associated with correlations between atoms. For the "trans" chain the correlation

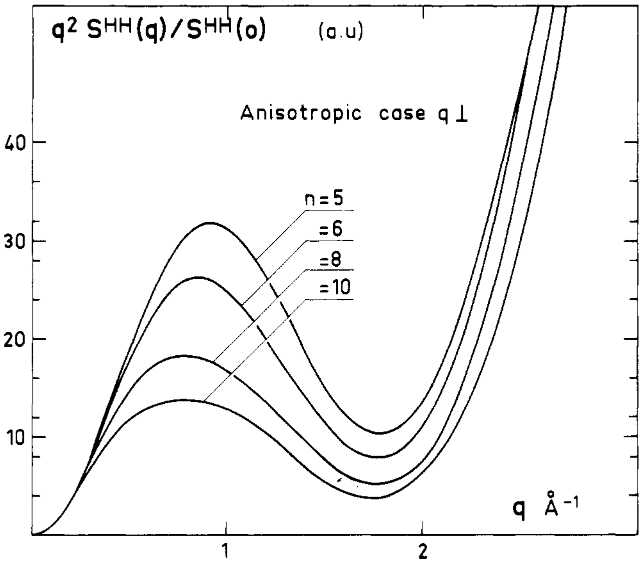

Figure 8. Representation of the functions $q^2S^{HH}(q)$ corresponding to the situation in Figure 6.

Table I
Half-Width $q_{1/2}$ of the Isotropic Scattering Law $S(q)$ for Different Chain Lengths[a]

N	Trans	Gaussian	Real
5	0.585	0.615	0.605
6			0.550
8	0.435	0.520	0.465
10	0.365	0.470	0.405
16	0.250		0.295

[a] N is the number of monomers. The column "Trans" gives the half-width for a chain of which monomers are in a "trans" configuration with respect to their predecessors. The column "Gaussian" corresponds to a transfer matrix with identical weight for each element. The matrix elements of the real chain are taken from ref 2.

direction remains well defined as the chain lengthens and the peaks in $S(q)$ become more and more frequent.

III. Conclusion

The incompressibility hypothesis applied to the bulk polymer material with labeled polymer chains leads to the scattering law equation (eq 25). This law shows that in the amorphous bulk state, the environment does not exert any long-range constraint on the polymer chain, which behaves as if it were a random coil. The scattering law (eq 25) is applied to *liquid n*-alkanes. It indicates two types of experiments.

(1) The measurement of the scattered intensity by labeled chains in an anisotropic situation, such as in a flow, yields information on the transfer matrix or inversely on the degree of anisotropy.

(2) The determination of the structure function $f(q)$ can be made by comparing the scattered intensities from both the labeling methods. In our opinion, this measurement will provide new information about small range effects in polymer conformation.

The numerical simulation did not show the Kratky–Porod effect[14,15] as the momentum transfer increases beyond l^{-1}. It is perhaps relevant to note that in a neutron scattering experiment, the nuclei (which scatter the neutron radiation) are far from being continuously distributed along the chain.[16]

Acknowledgments. We wish to thank Dr. Jannink for suggesting this study and for his guidance in the formulation of our results.

Appendix I

In this appendix we detail the calculations of the terms $S_{11}(q)$ and $S_{12}(q)$ and $S^{B}(q)$. The labeled chain contains $l = 1, \ldots, N$ atoms of deuterium and $l = N+1, \ldots, N'$ carbon atoms.

In this case relation 9 becomes

$$\begin{aligned} c_k &= a_D - a_H \text{ for } 1 \le k \le N \\ c_k &= 0 \qquad\quad \text{for } k > N \end{aligned} \tag{A-1}$$

and $S_{11}(\mathbf{q})$ is

$$S_{11}(\mathbf{q}) = (a_D - a_H)^2 \sum_{l=1}^{N} \sum_{k=1}^{N} \chi_{kl}(\mathbf{q}) \tag{A-2}$$

in this expression the indexes k and l correspond only to the deuterium atoms of labeled polymer. Using (17) we obtain

$$S_{11}(\mathbf{q}) = (a_D - a_H)^2 \left\{ \sum_{l}^{N} \sum_{k}^{N} \chi_{kl}{}^{0}(\mathbf{q}) - D^{-1}(\mathbf{q}) \sum_{k}^{N} \sum_{l}^{N} \sum_{n}^{N'} \chi_{ln}{}^{0}(\mathbf{q}) \sum_{m}^{N'} \chi_{km}{}^{0}(\mathbf{q}) \right\} \tag{A-3}$$

It is convenient to take the following notations of which the physical meaning is given in the text

$$S_0(\mathbf{q}) = \sum_{l=1}^{N'} \sum_{k=1}^{N'} \chi_{kl}{}^{0}(\mathbf{q}) \tag{A-4}$$

$$S^{HH}(\mathbf{q}) = \sum_{l=1}^{N} \sum_{k=1}^{N} \chi_{kl}{}^{0}(\mathbf{q}) \tag{A-5}$$

$$S^{HC}(\mathbf{q}) = \sum_{l=1}^{N} \sum_{k=N+1}^{N'} \chi_{kl}{}^{0}(\mathbf{q}) = S^{CH}(\mathbf{q}) \tag{A-6}$$

$$S^{CC}(\mathbf{q}) = \sum_{l=N+1}^{N'} \sum_{k=N+1}^{N'} \chi_{kl}{}^{0}(\mathbf{q}) \tag{A-7}$$

then (A-3) can be written

$$S_{11}(\mathbf{q}) = (a_D - a_H)^2 \left\{ S^{HH}(\mathbf{q}) - \frac{1}{N_p S_0(\mathbf{q})} (S^{HH}(\mathbf{q}) + S^{HC}(\mathbf{q}))^2 \right\} \tag{A-8}$$

the term $S_{12}(\mathbf{q})$ takes into account the interactions between the deuterated chains and the others

$$S_{12}(\mathbf{q}) = 2(a_D - a_H) \left\{ \sum_{k=1}^{N} \sum_{l=1}^{N'} \sum_{\beta}^{N_p} B_{l\beta} \chi_{kl}{}^{0}(\mathbf{q}) \delta(1 - \beta) - \frac{N_p}{N_p S_0(\mathbf{q})} \left(\sum_{k=1}^{N} \sum_{m=1}^{N'} \chi_{mk}{}^{0}(\mathbf{q}) \right) \left(\sum_{l=1}^{N'} \sum_{m=1}^{N'} B_l \chi_{lm}{}^{0}(\mathbf{q}) \right) \right\} \tag{A-9}$$

These terms are given by

$$\sum_{k=1}^{N} \sum_{l=1}^{N'} B_l \chi_{kl}{}^{0}(\mathbf{q}) = a_H S^{HH}(\mathbf{q}) + a_C S^{HC}(\mathbf{q}) \tag{A-10}$$

$$\sum_{k=1}^{N} \sum_{m=1}^{N'} \chi_{mk}{}^{0}(\mathbf{q}) = S^{HH}(\mathbf{q}) + S^{HC}(\mathbf{q}) \tag{A-11}$$

$$\sum_{l=1}^{N'} \sum_{n=1}^{N'} B_l \chi_{ln}{}^{0}(\mathbf{q}) = a_H S^{HH}(\mathbf{q}) + a_C S^{CC}(\mathbf{q}) + (a_H + a_C) S^{HC}(\mathbf{q}) \tag{A-12}$$

Table II
Ratio of Perpendicular to Parallel Half-Widths $q_{1/2}{}^{\perp}/q_{1/2}{}^{\parallel}$ in the Isotropic Scattering Experiment as a Function of Chain Length

N	Trans	Gaussian	Real
5	2.42	1.36	1.73
6	2.74	1.32	1.75
8	3.24	1.20	1.68
10	3.80	1.16	1.50

[a] N is the number of monomers. The column "Trans" gives the ratio $q_{1/2}{}^{\perp}/q_{1/2}{}^{\parallel}$ for a chain of which monomers are in a trans configuration with respect to their predecessors. The column "Gaussian" refers to a transfer matrix with identical elements. The matrix elements of the real chain are taken from ref 2.

and $S_{12}(\mathbf{q})$ becomes

$$S_{12}(\mathbf{q}) = 2(a_D - a_H)(a_H - a_C)f(\mathbf{q}) \quad \text{(A-13)}$$

where using (20), $f(\mathbf{q})$ is

$$f(\mathbf{q}) = S^{HH}(\mathbf{q}) - \frac{[S^{HH}(\mathbf{q}) + S^{HC}(\mathbf{q})]^2}{S_0(\mathbf{q})} = [S^{HH}(\mathbf{q})S^{CC}(\mathbf{q}) - (S^{HC}(\mathbf{q}))^2]\frac{1}{S_0(\mathbf{q})} \quad \text{(A-14)}$$

$S^B(\mathbf{q})$ is obtained in the same way

$$S^B(\mathbf{q}) = N_p(a_H - a_C)^2 f(\mathbf{q}) \quad \text{(A-15)}$$

References and Notes

(1) P. G. de Gennes, *Rep. Progr. Phys.*, **32**, 186 (1969).
(2) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.
(3) J. P. Cotton, B. Farnoux, G. Jannink, J. Mons, and C. Picot, *C. R. Acad. Sci., Ser. C*, **275**, 175 (1972).
(4) H. Benoit, J. P. Cotton, D. Decker, B. Farnoux, J. S. Higgins, G. Jannink, R. Ober, and C. Picot, *Nature (London)*, **245**, 13 (1973).
(5) P. G. de Gennes, *J. Phys. (Paris)*, **31**, 235 (1970).
(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1967.
(7) J. P. Cotton, B. Farnoux, G. Jannink, C. Picot, and G. C. Summerfield, *J. Polym. Sci., Part C*, **42**, 807 (1973).
(8) Tables of MIT, 1971, collected by C. G. Shull.
(9) P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).
(10) R. G. Kirste, W. A. Kruse, and J. Schelten, *Makromol. Chem.*, **162**, 299 (1972).
(11) D. G. Ballard, J. Schelten, and G. D. Wignall, 3rd International Conference on X-Ray and Neutron Small Angle Scattering, Grenoble, 1973.
(12) H. B. Stuhrmann and R. G. Kirste, *Z. Phys. Chem. (Frankfurt am Main)*, **46**, 247 (1965).
(13) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).
(14) G. Porod, *J. Polym. Sci.*, **10**, 157 (1953).
(15) J. des Cloizeaux, *Macromolecules*, **6**, 403 (1973).
(16) G. Jannink and G. C. Summerfield, "Neutron Inclastic Scattering," I A E A, Vienna, 1972.

Light Scattering from Polymers in Mixed Solvents, Polystyrenes

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ABSTRACT: Light-scattering and viscosity measurements were carried out on anionically prepared polystyrene samples in benzene–cyclohexane mixtures (good or medium solvents) of three different compositions at 30° and in a benzene (64%)–isopropy alcohol (36%) mixture (poor or theta solvent) at temperatures ranging from 23 to 40°. For refractive index increment and scattering-intensity measurements, the test solutions were diluted conventionally, and also under the osmotic condition, following the procedure of Casassa and Eisenberg. This dialysis method gave fairly accurate values of the polymer molecular weight. The relationship, $A_2M_2 = A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$, derived previously in the distribution-function theory was found to hold in benzene–cyclohexane mixtures with the small preferential adsorption coefficient λ, but not in a benzene–isopropyl alcohol mixture with large λ, where M_2 is the polymer molecular weight, A_2 is its second virial coefficient, and $M_{2,\mathrm{ap}}$ and $A_{2,\mathrm{ap}}$ are the respective apparent quantities. In this connection, a thermodynamic discussion of the difference between A_2M_2 and $A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$ is given. For the present Θ-solvent system, A_2 vanished at 25.5° (Θ), while $A_{2,\mathrm{ap}}$ vanished at 25.0° (Θ_{ap}). The ratio $[\eta]_\theta/M_2{}^{1/2}$ first increased with increasing M_2 and then leveled off for $M_2 \gtrsim 7 \times 10^5$ for which λ was nearly independent of M_2, where $[\eta]_\theta$ is the intrinsic viscosity at the Θ temperature. The solvent effect on $[\eta]_\theta/M_2{}^{1/2}$ and $\langle S^2\rangle_0/M_2$ was also observed, where $\langle S^2\rangle_0$ is the unperturbed mean-square radius of the polymer. The two-parameter theory of the excluded-volume effect was found to work well in the range of M_2 for which $[\eta]_\theta/M_2{}^{1/2}$ was independent of M_2. This also implies that the method proposed previously for the determination of $\langle S^2\rangle$ is valid.

There have been a number of theoretical and experimental investigations of light scattering from solutions of polymers in mixed solvents, following the pioneering contributions of Ewart *et al.*,[1] Kirkwood and Goldberg,[2] and Stockmayer.[3] Three important aspects may be deduced from these investigations: (1) thermodynamic study of preferential adsorption or interactions between polymer and solvent molecules;[1,4-10] (2) establishment of the light-scattering method of determining molecular weights, second virial coefficients, and mean-square radii of polymers in mixed solvents;[11-16] and (3) study of the validity of the two-parameter scheme in polymer–mixed-solvent systems.[17,18] The present paper is mainly concerned with the second and third topics.

In a previous paper on the distribution-function theory of light scattering in multicomponent systems,[16] it has been shown that the true second virial coefficient and mean-square radius may be determined in mixed solvents by the conventional method of Debye[19] and Zimm[20] under the condition

$$0.8 < M_{2,\mathrm{ap}}{}^{(Y)}/M_2 < 1.2 \quad (1)$$

where M_2 is the molecular weight of the polymer and $M_{2,\mathrm{ap}}{}^{(Y)}$ is its apparent molecular weight defined by Yamakawa.[16] We must note that eq 1 has been derived as a sufficient condition but not as a necessary condition. In fact, this condition is very severe, as will be seen, and the light-scattering procedure we proposed[16] is expected to be