Modified Gaussian Model for Rubber Elasticity

Jeffrey Kovac

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916.

Received September 15, 1977

ABSTRACT: The modified Gaussian model for the freely jointed chain is applied to several simple models for polymer networks. The formulation is mathematically simpler than the inverse Langevin approximation used previously and gives quantitatively similar results for linear extension experiments. Solvent swelling is also considered and corrections to the statistical theory derived.

I. Introduction

The phenomenon of rubber elasticity can be understood qualitatively and, to a large extent, quantitatively in terms of the so-called statistical theory developed by Kuhn, Flory, Wall, James and Guth, and Treloar.[1] The statistical theory assumes that the elastic resorting force of the network results from the entropy change in a set of independent, Gaussian chains which undergo affine deformation as the sample is subjected to external stress. The statistical theory is both conceptually and mathematically simple and quantitative comparisons with experiment are remarkably successful, particularly at small deformations.

Attempts at improving the statistical theory fall into two broad categories: (1) better treatment of the statistics of the individual chains,[2,3] since the Gaussian assumption is known to fail for short chains and large deformations; (2) more realistic treatment of the network including such problems as nonaffine deformation of junctions, effects of entanglements, and intermolecular obstructions, and so on.[4] The second category contains much harder problems than the first and will not be treated in this paper. The two categories are linked, however. Because of the mathematical complexity of the network problem the statistics of the individual chains in the network must have a relatively simple mathematical form. This constraint precludes the use of realistic chain models such as the rotational isomeric model. The purpose of this paper is to show that the modified Gaussian model developed by Fixman and Kovac[5] can be used to incorporate the effects of non-Gaussian chain statistics into the problem of rubber elasticity in a mathematically tractable way. Only the simplest network models are used for purposes of illustration, but it should be possible to apply the modified Gaussian model to more complicated networks.

The theory described in this paper was developed to provide a simple non-Gaussian network model to be used in understanding the first-order structure of bituminous coal.[6] Some of the formulas developed in the following sections are being applied to data on the solvent swelling and mechanical deformation of coals to provide estimates of the degree of cross-linking.[7]

In section II the modified Gaussian model will be sketched. In section III the relationship between force and extension will be derived for a freely jointed chain and related to a chain entropy. Section IV presents results for simple network models and compares them to results obtained from the statistical or Gaussian model and the inverse Langevin approximation for the freely jointed chain. Throughout this paper the statistical theory will be referred to as the Gaussian model to contrast it with the modified Gaussian theory being developed. This usage is imprecise since theories have been developed which incorporate assumptions other than those used in the statistical theory (e.g., nonaffine deformation) but still retain Gaussian statistics for the individual chains. Section V considers the swelling of non-Gaussian networks. The paper concludes with a brief discussion.

II. Modified Gaussian Model

In this section the development of the modified Gaussian model is reviewed briefly and the essential equations presented. For a detailed presentation the reader is referred to the original paper.[5]

The polymer chain is assumed to contain $N + 1$ identical backbone atoms connected by N bond vectors $\mathbf{b}_i$, $i = 1, 2, \ldots, N$. The true backbone potential V is a function of $\{b\}$ and is expressed in units such that $kT = 1$. The chain is subjected to an equilibrium force $\mathbf{f}$ acting on the end-to-end vector $\mathbf{R}$,

$$\mathbf{R} = \sum_{i=1}^{N} \mathbf{b}_i \qquad (1)$$

The exact distribution function of the set $\{b\}$ is

$$\psi_V(f) = \exp(\mathbf{R}\cdot\mathbf{f} - V)/Z_V(f) \qquad (2)$$

$$Z_V(f) = \int \exp(\mathbf{R}\cdot\mathbf{f} - V)\,\mathrm{d}\{b\} \qquad (3)$$

In the presence of $\mathbf{f}$ the mean end-to-end vector $\langle\mathbf{R}\rangle_f$ does not vanish and is calculated

$$\langle\mathbf{R}\rangle_f = \int \mathbf{R}\psi_V(f)\,\mathrm{d}\{b\} \qquad (4)$$

$$= \mathrm{d}\ln Z_V(f)/\mathrm{d}\mathbf{f} \qquad (5)$$

The idea of the modified Gaussian model is that the exact distribution function can be expanded in a series of Hermite-like polynomials orthogonal with respect to a weight function e^{-g} where

$$g = -\mathbf{R}\cdot\mathbf{f} + G(f) \qquad (6)$$

and $G(f)$ is a quadratic form in the bond vectors $\mathbf{b}_i$. The quadratic form $G(f)$ is chosen so as to make the first approximation for ψ_V, that is,

$$\psi_V \simeq \psi_G = \exp(-g)/Z_G(f) \qquad (7)$$

$$Z_G = \int \exp(-g)\,\mathrm{d}\{b\} \qquad (8)$$

as good as possible. The condition on G is that the coefficients in the Hermite expansion be made to vanish. For the first coefficient this translates into the condition

$$\langle\mathbf{b}_i\mathbf{b}_j\rangle_G = \langle\mathbf{b}_i\mathbf{b}_j\rangle_V \qquad (9)$$

where $\langle\,\rangle_G$ and $\langle\,\rangle_V$ refer to averages over the distribution functions ψ_G and ψ_V, respectively. For the freely rotating chain (fixed bond lengths, fixed bond angles) eq 9 gives the two conditions

$$\langle b_i^2\rangle_G = \langle b_i^2\rangle_V = l^2 \qquad (10)$$

$$\langle\mathbf{b}_i\cdot\mathbf{b}_{i\pm1}\rangle_G = \langle\mathbf{b}_i\cdot\mathbf{b}_{i\pm1}\rangle_V = l^2\cos\theta \qquad (11)$$

where l is the fixed bond length and θ the supplement of the bond angle. $G(f)$ is chosen to be

$$G(f) = \tfrac{1}{2}\alpha l^{-3}\sum_{i=1}^{N-1}|\mathbf{b}_i - \mathbf{b}_{i+1}|^2 + \tfrac{1}{2}\beta l^{-1}\sum_{i=1}^{N}|\mathbf{b}_i|^2 \qquad (12)$$

and the constraint eq 10 and 11 are used to determine α and

0024-9297/78/2211-0362$01.00/0

β which are taken to be functions of the external force. The probability distribution, ψ_G, retains a Gaussian form but the force constants are allowed to depend on f such that the bond length and bond angle remain constant (on the average). Physically β represents a bond stretching force constant and α represents the bond angle force constant.

The partition function Z_G can be easily evaluated from the eigenvalues of the quadratic form eq 12. The parameters α and β are evaluated from equations

$$\partial \ln Z_G/\partial\beta = -\tfrac{1}{2}Nl \tag{13}$$

$$\partial \ln Z_G/\partial\alpha = -(N-1)l^{-1}(1-\cos\theta), \tag{14}$$

and $\langle \mathbf{R}\rangle_f$ is given by

$$\langle \mathbf{R}\rangle_f = \partial \ln Z_G/\partial\mathbf{f} = Nl\mathbf{f}\beta^{-1} \tag{15}$$

In the general case of the freely rotating chain eq 13 and 14 yield a pair of coupled transcendental equations for α and β. In the special case of the freely jointed chain $\alpha = 0$ and the equation for β reduces to an algebraic equation which can be solved to give

$$\beta = \tfrac{3}{2}l^{-1}[1 + (1 + 4f^2l^2/9)^{1/2}] \tag{16}$$

This is the only case that will be considered in this paper. One can, however, solve the problem in another special case, the wormlike chain of Porod and Kratky,[8] where the coupled equations reduce to a single transcendental equation which can easily be solved numerically. Calculations for the wormlike chain are included in the original paper.[5]

III. Stress–Strain Relationship and Chain Entropy

Equations 15 and 16 can be combined to yield the equation for chain extension as a function of force

$$\langle \mathbf{R}\rangle_f = \tfrac{2}{3}Nl^2\mathbf{f}[1 + (1 + 4f^2l^2/9)^{1/2}]^{-1} \tag{17}$$

This equation gives the average value of the end-to-end vector in the presence of a constant force. Because of fluctuations the instantaneous value of $\mathbf{R}$ may differ from the average so eq 17 is a well-defined equation of state only when the fluctuations are small (as pointed out by Wang and Guth[3]). This will be strictly true only for infinite chains. We will assume that it makes sense to invert eq 17 to obtain $\mathbf{f}$ in terms of $\langle \mathbf{R}\rangle_f$ for any N. Since $\langle \mathbf{R}\rangle_f$ is along $\mathbf{f}$, eq 17 can be converted to a simpler scalar equation and inverted to obtain

$$fl = 3\overline{R}(1 - \overline{R}^2)^{-1} \tag{18}$$

where

$$f \equiv |\mathbf{f}| \text{ and } \overline{R} \equiv |\langle \vec{R}\rangle_f|/Nl \tag{19}$$

The force f can be assumed to be obtained from the chain entropy ($T\Delta S$) by differentiation

$$\mathbf{f} = -\partial T\Delta S/\partial\mathbf{R} \text{ or } f = -\partial T\Delta S/\partial R \tag{20}$$

so $T\Delta S$ can be obtained by integration of the stress–strain relationship

$$T\Delta S = -\int_0^R \mathbf{f}(R')\cdot d\mathbf{R}' + \text{constant} \tag{21}$$

Using eq 18 in eq 21 and performing the integration

$$T\Delta S = \tfrac{3}{2}N\ln(1 - \overline{R}^2) + \text{constant} \tag{22}$$

For small extensions ($\overline{R} \ll 1$) the entropy reduces to that obtained from a Gaussian distribution of the end-to-end distance.

The advantage of eq 18 and 22 over the inverse Langevin approximation for the force–extension relationship for the freely jointed chain[1] is that the functional form is simpler and can be manipulated more easily in network calculations. The numerical difference between eq 18 and the exact force–extension relationship for the freely jointed chain is small.[5] The fourth moment of the modified Gaussian distribution is also given fairly accurately.

IV. Simple Network Models

In this section the single-chain entropy eq 22 will be applied to two simple network models, the three-chain model of James and Guth[19] and the integral calculation of network entropy used by Treloar.[2] For the simple three-chain model a general expression for the network entropy can be obtained and applied to the special case of linear extension at constant volume. The integral calculation is made only for the case of linear extension of the network.

Three-Chain Model. In this model it is assumed that the random cross-linked network can be represented by three independent sets of equivalent chains directed along each of the coordinate axes. The total network entropy is then written

$$T\Delta S_{\text{net}} = T\Delta S_X + T\Delta S_Y + T\Delta S_Z \tag{23}$$

where $T\Delta S_i$ is the entropy of the equivalent chains directed along the i axis. Suppose the network contains M chains. It is then assumed that $M/3$ chains are directed along each axis. Using eq 22 for the entropy of a single chain we have

$$T\Delta S_{\text{net}} = \frac{M}{3}\left[\frac{3N}{2}(\ln(1 - \overline{X}^2) + \ln(1 - \overline{Y}^2) + \ln(1 - \overline{Z}^2))\right] \tag{24}$$

where $\overline{X}$, $\overline{Y}$, and $\overline{Z}$ are the reduced extensions of the chains along the axes defined analogously to $\overline{R}$.

In the unstrained state each of the equivalent chains is assumed to have its equilibrium end-to-end distance and the deformations are assumed to be affine. We can then write for $\overline{X}, \overline{Y}, \overline{Z}$

$$\left.\begin{aligned}\overline{X} &= \lambda_1\langle\overline{R}^2\rangle_0^{1/2}\\ \overline{Y} &= \lambda_2\langle\overline{R}^2\rangle_0^{1/2}\\ \overline{Z} &= \lambda_3\langle\overline{R}^2\rangle_0^{1/2}\end{aligned}\right\} \tag{25}$$

where $\langle\overline{R}^2\rangle_0$ is the equilibrium mean square end-to-end distance for the freely jointed chain given by

$$\langle\overline{R}^2\rangle_0 = (Nl)^{-2}\langle R^2\rangle_0 \tag{26}$$

$$\langle R^2\rangle_0 = Nl^2 \tag{27}$$

and λ_i is the fractional extension along the ith axis. Equation 25 is the affine deformation assumption used in the statistical theory. Using eq 25, 26, and 27 in eq 24 one obtains for the network entropy

$$T\Delta S_{\text{net}} = \tfrac{1}{2}NM\ln[1 - N^{-1}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + N^{-2}(\lambda_1^2\lambda_2^2 + \lambda_1^2\lambda_3^2 + \lambda_2^2\lambda_3^2) - N^{-3}(\lambda_1\lambda_2\lambda_3)] \tag{28}$$

Using eq 28 it is easy to derive stress–strain relationships for various types of experiments. As an example we will consider linear extension at constant volume. Suppose the network is stretched along the X axis by a factor λ, that is,

$$\lambda_1 = \lambda \tag{29}$$

The constant volume condition implies

$$\lambda_1\lambda_2\lambda_3 = 1 \tag{30}$$

so

$$\lambda_2 = \lambda_3 = \lambda^{-1/2} \tag{31}$$

Table I
Numerical Results for Elastic Force in Linear Extension Computed Using Various Models of a Network Where the Individual Chains are of Length $N = 25$

		f/M (in units of kT)			
		Inverse Langevin[a]		Modified Gaussian	
λ	Gaussian	Series exp	Numerical	3-chain model[b]	Integral[c]
1.0	0	0	0	0	0
1.1	0.27	0.28	0.28	0.32	0.29
1.3	0.71	0.74	0.74	0.84	0.76
1.5	1.06	1.11	1.11	1.26	1.14
2.0	1.75	1.88	1.88	2.21	1.97
2.5	2.34	2.61	2.61	3.27	2.81
3.0	2.89	3.41	3.41	4.70	4.16
3.5	3.42	4.33	4.33	6.94	5.06
4.0	3.94	5.48	5.80	11.28	7.22
4.5	4.45	6.96	8.40	24.05	10.59
5.0	4.96	8.97	∞	∞	∞

[a] Taken from Treloar ref 1 and 2. [b] Computed from eq 32. [c] Computed from eq 39.

Using eq 29 and 31 in eq 28 the force can be calculated as

$$f = -\partial T\Delta S/\partial\lambda = M[(\lambda^2 - (1/\lambda^2)) + N^{-1}(1 - \lambda^{-3})] \times [1 - N^{-1}(\lambda^2 + (2/\lambda)) + N^{-2}(2\lambda + (1/\lambda^2)) - N^{-3}]^{-1} \quad (32)$$

Expanding in powers of N^{-1} it is easy to see that eq 32 reduces to the usual Gaussian results for long chains and small extensions. Numerical results for the case $N = 25$ are collected in Table I and compared to the Gaussian approximation, results obtained by Treloar for the inverse Langevin approximation for the freely jointed chain, and results obtained in the remainder of this section.

Integral Calculation of Network Entropy. Suppose the network contains M chains with entropy given by eq 22. In the unstrained state each chain has the same vector length r_0 and the chains have random direction. If the network is extended in one dimension by a factor λ and the chains are assumed to deform affinely then the change in entropy from the unstrained to the strained state is

$$T\Delta S = T\int \Delta S(r)f(r)\,\mathrm{d}r \quad (33)$$

where $f(r)\,\mathrm{d}r$ is the number of chain vectors in the range r to $r + \mathrm{d}r$. Treloar[2] has calculated $f(r)$ for the case of linear extension at constant volume,

$$f(r) = \frac{M}{r_0(\lambda^2 - \lambda^{-1})^{1/2}}\,\frac{r}{(r^2 - r_0{}^2\lambda^{-1})^{1/2}} \quad (34)$$

For the inverse Langevin approximation for the freely jointed chain the integral eq 33 must either be done numerically or term-by-term in a series expansion in N^{-1}.[2] Using eq 22 for the free energy the integral can be done analytically to all orders in N^{-1}. The network entropy is then

$$T\Delta S = \frac{3NM}{2r_0(\lambda^2 - \lambda^{-1})^{1/2}} \times \int_{r_0\lambda^{-1/2}}^{r_0\lambda} \frac{r}{(r^2 - r_0{}^2\lambda^{-1})^{1/2}} \ln(1 - r^2(Nl)^{-2})\,\mathrm{d}r \quad (35)$$

$$= \frac{3NML}{2r_0(\lambda^2 - \lambda^{-1})^{1/2}}\Bigg\{\ln(1 - r_0{}^2\lambda^2L^{-2})r_0L^{-1}(\lambda^2 - \lambda^{-1})^{1/2} + (1 - r_0{}^2(\lambda L^2)^{-1}) \times \ln\left[\frac{1 + r_0L^{-1}(\lambda^2 - \lambda^{-1})^{1/2}(1 - r_0{}^2(\lambda L^2)^{-1})^{-1/2}}{1 - r_0L^{-1}(\lambda^2 - \lambda^{-1})^{1/2}(1 - r_0{}^2(\lambda L^2)^{-1})^{-1/2}}\right]\Bigg\} \quad (36)$$

where

$$L = Nl \quad (37)$$

Substituting

$$r_0 = N^{1/2}l \quad (38)$$

and expanding in powers of N^{-1} it is easy but a bit tedious to show that eq 37 gives the correct Gaussian free energy to lowest order in N^{-1}.

The stress–strain relationship is obtained by differentiating eq 36 with respect to λ and using eq 38. The rather complicated result is

$$\begin{aligned}\frac{f}{M} = {}& \frac{3\lambda}{1 - \lambda^2N^{-1}} - \left[\frac{3N}{4}\,\frac{(2\lambda + \lambda^{-2})(1 - (N\lambda)^{-1})}{(\lambda^2 - \lambda^{-1})} + \frac{3}{4\lambda^2}\right] \\ & \times [(1 + N^{-1/2}(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1})^{-1} \\ & + (1 - N^{-1/2}(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1})^{-1}] \\ & + \frac{3N^{1/2}(1 - (1/N\lambda))^{1/2}}{2\lambda^2(\lambda^2 - \lambda^{-1})^{1/2}}[(1 - N^{-1/2}(\lambda^2 \\ & - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1})^{-1} \\ & + (1 + N^{-1/2}(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1})^{-1}] \\ & + \left[\frac{3N^{3/2}(2\lambda + \lambda^{-2})(1 - (1/N\lambda))^{1/2}}{4(\lambda^2 - \lambda^{-1})^{1/2}} - \frac{3N^{1/2}}{4\lambda^2(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2}}\right] \times \\ & \ln\left[\frac{1 + N^{-1/2}(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1}}{1 - N^{-1/2}(\lambda^2 - \lambda^{-1})^{1/2}(1 - (1/N\lambda))^{1/2} - (N\lambda)^{-1}}\right]\end{aligned} \quad (39)$$

Numerical results for chains of length $N = 25$ obtained using eq 39 are also collected in Table I. Results obtained by Treloar using the same $f(r)$ but the inverse Langevin approximation for the single-chain entropy are also given both in the series expansion approximation and the numerical (graphical) integration of the exact distribution.

The agreement between the various results collected in Table I is rather good. At small extensions all the models agree. At high extensions the three-chain modified Gaussian model shows a much steeper rise in the f vs. λ curve than the other models. Both the modified Gaussian results show a finite extensibility of the network.

V. Solvent Swelling

As mentioned in the introduction the original motivation for this work was the investigation of non-Gaussian effects in the solvent swelling of coals. Therefore, we will develop an equation for the swelling of the three-chain model introduced in the previous section. The derivation follows that given by Treloar.[1]

The free energy of dilution of a polymer system can be described by the Flory–Huggins equation

$$\Delta G_1 = RT\{\ln(1 - \upsilon_2) + \upsilon_2 + \chi\upsilon_2{}^2\} \quad (40)$$

where N is the chain length, υ_2 is the volume fraction of polymer, and χ is the Flory solubility parameter. For isotropic swelling

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda \quad (41)$$

and the free energy of the elastic network is

$$\Delta G_e = -T\Delta S = -{}^3\!/_2\rho RTNM_c{}^{-1}\ln\left[1 - \frac{3}{N}\lambda^2 + \frac{3}{N^2}\lambda^4 - \frac{1}{N^6}\lambda^6\right] \quad (42)$$

where we have explicitly included the factor of kT and written

$$M/N_a = \rho/M_c \quad (43)$$

where ρ is the density, M_c is the chain molecular weight, and N_a is Avagadro's number. The free energy of dilution of the network is given

$$\Delta G_{1e} = \partial \Delta G_e / \partial n_1 \qquad (44)$$

where n_1 is the mole fraction of solvent and can be calculated with aid of the substitution

$$v_2^{-1} = 1 + n_1 V_1 \qquad (45)$$

where V_1 is the molar volume of the solvent.

$$\frac{\partial \Delta G_e}{\partial n_1} = \rho R T V_1 v_2^{1/3} M_c^{-1} \left[1 - \frac{2}{N} v_2^{-2/3} + \frac{1}{N^2} v_2^{2/3} \right] \times \left[1 - \frac{3}{N} v_2^{-2/3} + \frac{3}{N^2} v_2^{-4/3} - \frac{1}{N^3} v_2^{-2} \right]^{-1} \qquad (46)$$

The total free energy of the system is the sum of eq 46 and 40. At equilibrium $\Delta G = 0$, this condition yields the following equation relating v_2, M_c, and N

$$\ln (1 - v_2) + v_2 + \chi v_2^2 + \rho V_1 v_2^{1/3} M_c^{-1} \left[1 + \frac{2}{N} v_2^{-2/3} + \frac{1}{N^2} v_2^{2/3} \right] \times \left[1 - \frac{3}{N} v_2^{-2/3} + \frac{3}{N^2} v_2^{-4/3} - \frac{1}{N^3} v_2^{-2} \right]^{-1} = 0 \qquad (47)$$

The deviations from the Gaussian theory can best be seen by expanding in powers of N^{-1}. This task is straightforward yielding

$$\ln (1 - v_2) + v_2 + \chi v_2^2 + \rho V_1 v_2^{1/3} M_c^{-1} + N^{-1} \rho V_1 v_2^{-1/3} M_c^{-1} + O(N^{-2}) = 0 \qquad (48)$$

The term proportional to N^{-1} is the first correction to the statistical theory. Further corrections can easily be obtained but are probably unjustified since the Flory–Huggins equation describing the polymer–solvent interactions only contains terms to order N^{-1}. Equation 48 is currently being used to interpret data on coal swelling.[7]

VI. Discussion

The purpose of this paper has been to show that the modified Gaussian model can be used to incorporate non-Gaussian effects into the theory of rubber elasticity in a mathematically tractable way. The modified Gaussian treatment of the freely jointed chain gives a simpler functional form for the chain entropy than the conventional treatment. This allows the calculation of the network entropy analytically to all orders in N^{-1} as in eq 33. The calculations in this paper have followed the approach of the simple statistical theory in which the contributions of individual independent chains are summed. It should be possible to apply the ideas sketched in section II to an entire network. This should avoid the problem of fluctuations and allow a more accurate treatment of the network.

The modified Gaussian model of the wormlike chain has not been considered in this paper because the equation determining the parameter β is trancendental and hence not analytically invertible. This problem might be avoided in an application of the modified technique to the entire network. These problems are being investigated.

Acknowledgments. I should like to thank Professor John W. Larsen for asking the questions that led to this work. Support of the Faculty Research Fellowship Fund of the University of Tennessee is gratefully acknowledged.

References and Notes

(1) For a lucid exposition and review of the statistical theory, see L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd ed, Clarendon Press, Oxford, 1975.

(2) L. R. G. Treloar, *Trans. Faraday Soc.*, **50**, 881 (1954).

(3) M. C. Wang and E. Guth, *J. Chem. Phys.*, **20**, 1144 (1952).

(4) For example, see E. A. DiMarzio, *J. Chem. Phys.*, **36**, 1563 (1962); J. L. Jackson, M. C. Shen, and D. A. McQuarrie, *ibid.*, **44**, 2388 (1966); K. F. Freed, *ibid.*, **55**, 5588 (1971); P. J. Flory, *ibid.*, **66**, 5720 (1977), and many others.

(5) M. Fixman and J. Kovac, *J. Chem. Phys.*, **58**, 1564 (1973).

(6) J. W. Larsen and J. Kovac, "The Polymer Structure of Bututminous Coals", submitted to Fuel, London.

(7) J. W. Larsen and J. Kovac, work in progress.

(8) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949); see also H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.

(9) H. M. James and E. Guth, *J. Chem. Phys.*, **10**, 455 (1943).

The Intramolecular Scattering Function of Model Branched Polymers

P. M. Toporowski and J. Roovers*

National Research Council of Canada, Division of Chemistry,
Ottawa, Ontario K1A 0R9, Canada. *Received September 30, 1977*

ABSTRACT: A light-scattering study of the intramolecular scattering function of a regular star-branched and a comb polymer is described. Angular and wavelength dependence of scattering was used to cover a wide range of μ values. The random-coil model for these branched polymers satisfactorily describes the observed scattering functions.

When light is scattered from one macromolecule in dilute solution, different parts of the light beam may have traveled slightly different distances when they hit the light detector. As a result destructive interference can occur, and the intensity of the scattered light will vary depending on the size of the scattering molecule and the magnitude of the scattering vector $|\mathbf{h}|$.

$$|\mathbf{h}| = \frac{4\pi}{\lambda'} \sin \frac{\theta}{2} \qquad (1)$$

where λ' is the wavelength in the medium and θ the scattering angle.

At zero scattering angle there is no interference. The variation of the ratio of the scattered light intensity, I, to the extrapolated zero angle scattered light intensity, $I_{\theta=0}$, is called the intramolecular particle scattering function, $P(\mu)$, where $\mu = h^2 \langle S^2 \rangle_z$ and $\langle S^2 \rangle_z$ is the z-average mean-square radius of gyration.

$$P(\mu) = (I / I_{\theta=0})_{c=0} \qquad (2)$$

0024-9297/78/2211-0365$01.00/0