Temperature Coefficient of Unperturbed Polymer Chain Dimensions from Thermoelastic and Solution Properties. I. Poly(ethylene oxide)

F. de Candia,[1a] V. Vittoria,*[1a] U. Bianchi,[1b] and E. Patrone[1b]

Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del C.N.R., 80072 Naples, Italy, and Istituto di Chimica Industriale dell'Università di Genova, 16100 Genoa, Italy. Received January 14, 1972

ABSTRACT: The temperature dependence of unperturbed chain dimensions has been investigated for poly(ethylene oxide) (PEO). The analysis was carried out following two different methods. The first regards the determination of the energetic component in the total elastic force for a stretched PEO network in swelling equilibrium. The temperature coefficient, on the other hand, is given directly by $[\eta]$ *vs.* T plots obtained with low molecular weight PEO fractions. The experimental thermoelasticity data give for $d \ln \langle r_0^2\rangle/dT$ -0.14 to -0.28×10^{-3} °K^{-1}, depending on different extrapolation methods, while solution data give -0.85 to -1.13×10^{-3} °K^{-1}, depending on different solvents. These values disagree with the results of a previous conformational analysis of the PEO chain. The reasons for these different results are discussed in terms of solvent effects on conformational properties and intermolecular contributions to the energetic component in swollen and unswollen networks. It is concluded that, at least for PEO, experimental data for CDT cannot be safely interpreted as a measure of the temperature effect on unperturbed single chain dimensions, but rather reflect a more involved situation, much of it still unknown.

It is well known that the temperature coefficient of the unperturbed chain dimensions (CDT) of polymers may be related to short-range interactions between adjacent chain groups. Two main experimental methods are available in order to evaluate the CDT of macromolecules. The first regards the direct determination of the energetic contribution to the total retroactive elastic force of a stretched rubberlike network.[2] By light scattering or viscosity data, on the other hand, the values of the unperturbed mean dimensions $\langle \overline{r_0}^2\rangle$ can be obtained as a function of temperature, according to different theories.[3-6] Although a comparison of the values given by the two different methods for the same polymer chain is of theoretical interest, only a few experimental data of this kind are available. In particular, for poly(ethylene oxide) (PEO), only bulk thermoelastic investigations are reported.[7] Since PEO is a polar, semicrystalline polymer, one can expect some special problems to arise on studying bulk or solution properties; it is therefore particularly useful to extend experimental knowledge of this polymeric system and to test the validity of the results obtained by different methods. Swollen PEO networks were used in our thermoelasticity determinations in order to minimize eventual intermolecular effects on the energetic component of the total elastic force. On the other hand, it must be underlined that solvent effects may play an important role in the determination of the value of CDT from solution methods. It follows that thermoelastic measurements on swollen systems may be better correlated with solution data than those obtained with bulk polymers, particularly if comparable polymer–solvent interactions are introduced.

Materials and Methods

PEO (Fluka) with a molecular weight of 15,000 was vulcanized following the method previously described,[7] without inclusion of any plasticizer. Since the cross-linking agent (a commercial triisocyanate) is trifunctional and reacts with the terminal OH groups of the polymer, the resulting network should be characterized by an M_c equal to or less than the initial molecular weight, depending on the amount of chain entanglement. The thermoelastic measurements were performed according to the usual method,[2b] using a standard apparatus.[8]

Low molecular weight PEO fractions were obtained from a commercial sample (Carbowax 1000, Union Carbide) by a fractional dissolution procedure using benzene–*n*-heptane as the solvent–nonsolvent system. Further refractionation was obtained by suspending every fraction in its own extraction solvent mixture, and by stirring for 1 day, in order to remove lower molecular weight contaminants. Reagent grade, twice-distilled solvents (Fluka) were used. Dioxane was purified by prolonged refluxing on Na pellets prior to distillation. A Bischoff suspended-level viscometer, having a negligible kinetic energy correction, was used for viscosity determinations. The temperature was kept constant within 0.01°. The M_n values of the fractions were evaluated by using an $[\eta]$–M_n relationship determined in our laboratory.[9]

Experimental Results

(A) CDT from Thermoelasticity in an Open System. The theory for the rubber elasticity gives for the stress f the following expression[2,10]

$$f = nkT\frac{\langle r_i^2\rangle}{\langle r_0^2\rangle}(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the force on the unit of cross-sectional area, n is the number of the effective elastic chains in the volume unit, k is the Boltzmann constant, $\langle r_i^2\rangle$ and $\langle r_0^2\rangle$ are the end-to-end mean-square chain lengths for a network chain and a free chain, respectively, and α is the strain ratio. Assuming that $\langle r_i^2\rangle \propto V^{2/3}$, the derivative of the eq 1 at constant length and volume gives

$$\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{V,L} = -\frac{d \ln \langle r_0^2\rangle}{dT} \qquad (2a)$$

---

(1) (a) Laboratorio di Richerche su Tecnologia dei Polimeri e Reologia del C.N.R.; (b) Istituto di Chimica Industriale dell'Università di Genovà.

(2) (a) L. R. G. Treolar, "The Physics of Rubber Elasticity," Oxford University Press, London, 1958; (b) P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polym. Sci.*, **45**, 235 (1960).

(3) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).

(4) P. J. Flory and T. G. Fox, Jr., *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

(5) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **No. 1**, 137 (1963).

(6) U. Bianchi, E. Patrone, and M. Dalpiaz, *Makromol. Chem.*, **84**, 230 (1965).

(7) J. E. Mark and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1415 (1965).

(8) J. F. M. Oth and P. J. Flory, *ibid.*, **80**, 1297 (1958).

(9) C. Rossi and C. Cuniberti, *J. Polym. Sci., Part B*, **2**, 681 (1964).

(10) P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).

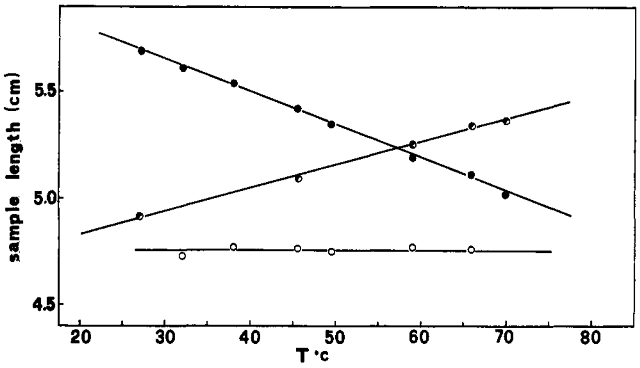

Figure 1. The sample length is reported *vs.* the temperature for three PEO networks in swelling equilibrium: (●) water, (◐) toluene, (○) acetone.

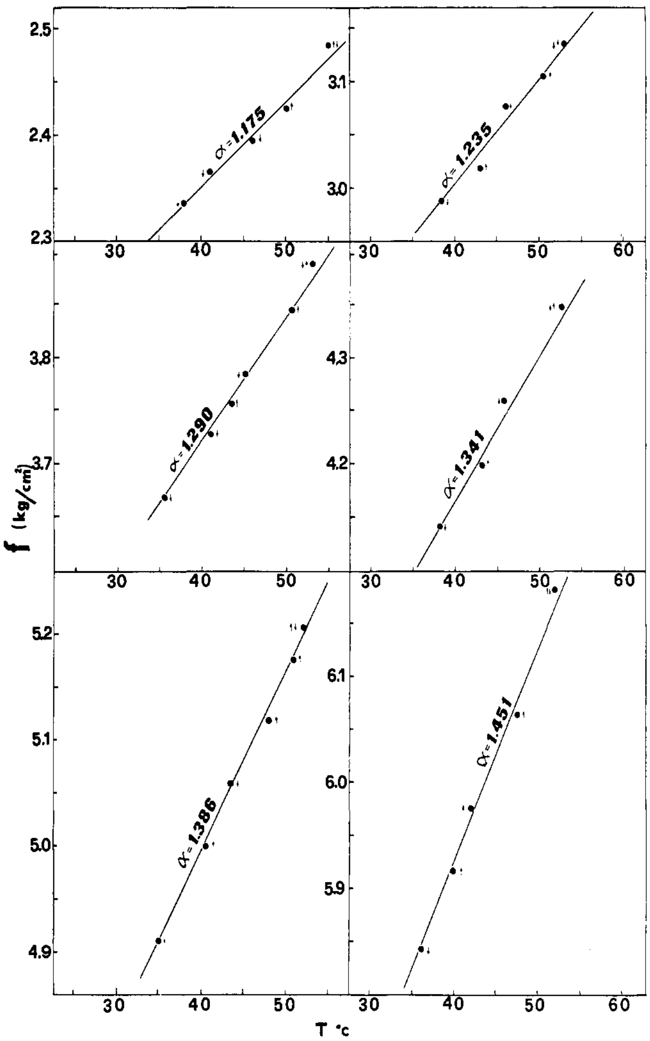

Figure 2. Stress–temperature plots obtained with a PEO network in swelling equilibrium with acetone. The α value is calculated at 40°.

TABLE I
EXPERIMENTAL DATA OBTAINED FROM THERMOELASTIC MEASUREMENTS[a]

α	f (T = 313°K), kg/cm²	$\partial f/\partial T$, kg/cm² × 10³	f_e/f	$\overline{f_e/f}$ (T = 313°K)
1.175	2.350	8.1	−0.08	
1.235	3.004	9.9	−0.03	
1.290	3.722	11.8	0.01	
1.341	4.165	13.7	−0.03	
1.386	5.038	17.1	−0.06	
1.451	5.925	20.6	−0.08	
				−0.045 ±0.02

[a] Acetone solvent.

and from the theory[2]

$$\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{V,L} = -\frac{f_e}{fT} \tag{2b}$$

f_e being the energetic contribution to the total stress f. From eq 2b, valid for any bulk system at constant volume, a theory extended to elastic networks in swelling equilibrium has been developed.[11,12] According to this theory, the following expression for the f_e/f ratio can be given

$$f_e/f = -T\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{P,L} - \frac{5\beta_s T}{(\alpha^{5/2} - 1)} \tag{3}$$

where P is the pressure and β_s is defined as $(1/V_s)\ (\partial V_s/\partial T)_P$, V_s being the swollen volume of the sample. For $\beta_s = 0$

$$\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{P,L} = \left[\frac{\partial \ln (f/T)}{\partial T}\right]_{V,L} \tag{4}$$

From the relation 4 it follows that the condition $\beta_s = 0$ allows one to obtain the f_e/f value directly from eq 2b, avoiding the use of a correction term which is affected by the experimental error in α.

In Figure 1 the length of the sample *vs.* temperature in three different solvents is reported. Results clearly indicate that for the system PEO–acetone the term β_s is nearly zero. Therefore, the thermoelastic behavior of PEO in equilibrium swelling in acetone was investigated. The swelling under equilibrium conditions gave v_r = 0.355 at 50°, v_r being the rubber volume fraction in the swollen sample. Stress–strain isotherms carried out at 50°, reported in terms of the Mooney–Rivlin equation,[2] give $2C_1$ = 3.7 kg/cm² and $2C_2$ = 0.0 in the strain range α = 1.0–1.35. Under these conditions,[13,14] we can use the $2C_1$ term in order to calculate the molecular weight M_c of rubber chains in the network. The experimental value was M_c = 7000.

In Figure 2 typical stress–temperature plots at a different strain ratio are reported. In Table I we report the experimental values obtained for the ratio f_e/f, giving to β_s the value zero. The mean value of f_e/f in Table I gives, for CDT, -0.14×10^{-3} ($\pm 0.06 \times 10^{-3}$).

Following the other analytical approach, in Figure 3 the function $6\{1 - [(T/f)(\partial f/\partial T)_{P,L}\}(\alpha^{5/2} - 1)$ *vs.* $6(\alpha^{5/2} - 1)$ is reported. With the assumption that f_e/f does not depend on α, the slope of the plot in Figure 3 gives a mean value for f_e/f, and extrapolation to α = 1 gives the β_s value. Results give $f_e/f = -0.09$ and, for CDT, -0.28×10^{-3} °K⁻¹.

(B) The CDT of PEO from Viscosity Determinations. The Bianchi–Patrone–Dalpiaz[6] method was used to obtain CDT values of PEO in solution. It has been shown that for every polymer–solvent system, a range of molecular weight may be

---

(11) J. Bashaw and K. J. Smith, Jr., *J. Polym. Sci., Part A-2*, **6**, 1041 (1968).

(12) J. Bashaw and K. J. Smith, Jr., *ibid.*, **6**, 1051 (1968).

(13) F. de Candia and A. Ciferri, *Makromol. Chem.*, **134**, 335 (1970).

(14) F. de Candia and L. Amelino, *J. Polym. Sci., Part A-2*, in press.

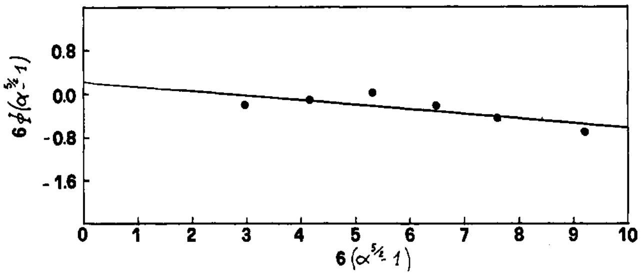

Figure 3. The data of Figure 2 are reported in terms of $6\Phi(\alpha^{5/2} - 1)$ *vs.* $6(\alpha^{5/2} - 1)$, where $\Phi = 1 - (T/f)(\partial f/\partial T)_{P,L}$. The slope gives $f_e/f = -0.09$ and the intercept gives $\beta_s = 1.53 \times 10^{-4}$.

found, in which the a exponent of the Mark–Houwink equation

$$[\eta] = KM^a$$

will assume the value of 0.5. In this range of molecular weight, Flory's expansion coefficient is equal to unity at each temperature.[15,16] This allows us to drop the $b(\mathrm{d}\ln a/\mathrm{d}T)$ term from the relation

$$\frac{\mathrm{d}\ln[\eta]}{\mathrm{d}T} = \frac{3}{2}\frac{\mathrm{d}\ln\langle\overline{r_0^2}\rangle}{\mathrm{d}T} + b\frac{\mathrm{d}\ln a}{\mathrm{d}T}$$

so that the dependence of $[\eta]$ on T will immediately give, for sufficiently low molecular weight fractions, the value of CDT. Experimental $[\eta]/T$ values in acetone and dioxane, for PEO fractions having an M_n ranging from 4×10^2 to 4×10^3 are reported in Figures 4 and 5. The values of $\mathrm{d}\ln[\eta]/\mathrm{d}T$ and of $\mathrm{d}\ln\langle\overline{r_0^2}\rangle/\mathrm{d}T$ are listed in Table IIa and IIb; in both solvents a negative value of CDT is obtained, $\mathrm{d}\ln\langle\overline{r_0^2}\rangle/\mathrm{d}T \times 10^3$ being equal to -0.85 ± 0.07 in dioxane and to -1.13 ± 0.15 in acetone. The difference between the CDT values in the two solvents is not too large, but greater than the experimental error.

Discussion

The purpose of this work was to compare values of the temperature coefficient of unperturbed dimensions derived from two different methods. Both thermoelastic and viscosity measurements indicate a tendency of PEO chains to contract on heating, even if the values of this temperature coefficient differ according to the method used: -0.14 to -0.28×10^{-3} °K^{-1} from thermoelasticity and -0.85 to -1.13×10^{-3} °K^{-1} from viscosity. These negative values are at variance with the only previous estimate of this quantity appearing in the literature.[7] A positive value of 0.5×10^{-3} °K^{-1} was obtained by thermoelastic analysis performed on plasticized bulk networks.

The disagreement between the several thermoelastic values and the difference between the CDT values derived from $[\eta]/T$ measurements in two different solvents call for great caution in interpreting these results. A first possible source of error in the interpretation of the viscosity data lies in the assumption that the expansion factor is rigorously equal to unity. A small deviation from unity could have a rather large effect on the CDT value. Moreover, the Bashaw–Smith theory gives rise to a good approximation only at very large swelling degrees, possibly larger than our $v_r = 0.355$. However, more than effects depending on different theoretical approaches, there is a difficulty in measuring the temperature effect on single chain.

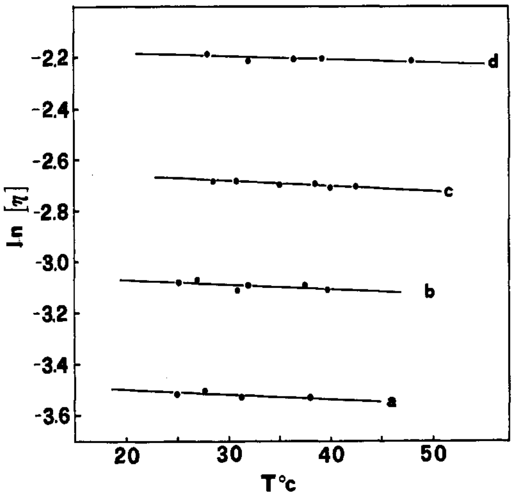

Figure 4. Ln $[\eta]$ is reported *vs.* T for different PEO fractions: (a) M_n = 400, (b) M_n = 1000, (c) M_n = 2000, (d) M_n = 4000; solvent, acetone.

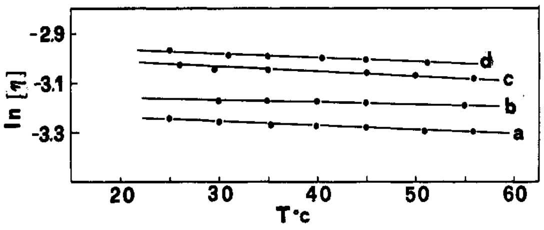

Figure 5. Ln $[\eta]$ is reported *vs.* T for different PEO fractions: (a) M_n = 430, (b) M_n = 590, (c) M_n = 1000, (d) M_n = 1100; solvent, dioxane.

TABLE II
EXPERIMENTAL DATA OBTAINED FROM VISCOMETRIC MEASUREMENTS

M_n	$\mathrm{d}\ln[\eta]/\mathrm{d}T$	$\mathrm{d}\ln\langle\overline{r_0^2}\rangle/\mathrm{d}T$	$\mathrm{d}\ln\langle\overline{r_0^2}\rangle/\mathrm{d}T$
	(a) Solvent acetone		
400	-1.80×10^{-3}	-1.20×10^{-3}	
1000	-1.75×10^{-3}	-1.17×10^{-3}	
2000	-2.00×10^{-3}	-1.33×10^{-3}	
4000	-1.25×10^{-3}	-0.83×10^{-3}	
			-1.13×10^{-3} ± 0.15
	(b) Solvent dioxane		
430	-1.24×10^{-3}	-0.83×10^{-3}	
590	-1.20×10^{-3}	-0.80×10^{-3}	
1000	-1.50×10^{-3}	-1.00×10^{-3}	
1100	-1.20×10^{-3}	-0.80×10^{-3}	
			-0.85×10^{-3} ± 0.07

Two points, in fact, deserve particular attention: solvent effects on conformational properties of a chain and intermolecular contributions to the energy component f_e in swollen or unswollen networks. The possibility of a solvent to interfering with the properties of a dissolved polymer has been widely demonstrated;[17,18,19] it is therefore not surprising

---

[15] P. J. Flory, *Makromol. Chem.*, **98**, 128 (1966).

[16] E. Patrone and U. Bianchi, *ibid.*, **94**, 52 (1966).

[17] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[18] U. Bianchi, *J. Polym. Sci., Part A*, **2**, 3083 (1964).

[19] M. Kurata and W. H. Stockmayer, *Advan. Polym. Sci.*, **3**, 196 (1963).

that our results indicate two different CDT values for the same chain into two solvents. One would, however, expect the CDT values derived from thermoelasticity in acetone-swollen PEO and the ones from $[\eta]/T$ in acetone to agree within experimental error. The fact that they do not agree must be discussed in terms of the possibility of having intermolecular contributions to f_e even in a thermoelastic analysis performed at a constant volume. This possibility has been already explored by several workers[20,21] and, when present, would introduce an intermolecular contribution even in a quantity like the CDT, which should be strictly intramolecular in character.

For PEO chains, in particular, an intermolecular interaction energy varying with v_r at a constant volume seems to be very possible, owing to the tendency of PEO to aggregate in several solvents even at a very high degree of dilution.[22,23] The relatively high concentration of the networks studied (v_r = 0.8 used by Mark and Flory and v_r = 0.3 used by us) is certainly a factor favoring the formation of supermolecular structures, whose stretching behavior is not presently known. Intermolecular contributions of this nature can be reasonably assumed to play an important role. If this is the case, experimental values of CDT would give only an "apparent" measure of the temperature effect on single-chain dimensions. These, on the other hand, represent the only rather simplified situation with which present theory can deal. Conformational analysis of a polymer chain, based on an experimentally measured CDT value, through any of the presently known techniques, should therefore be regarded as a preliminary attempt only, necessarily to be discussed in the light of a much wider experimental basis.

Acknowledgments. The assistance of Mr. L. Amelino, Mr. V. Capodanno, and Mr. G. Romano with the many measurements involved in this investigation is deeply appreciated.

---

[20] V. A. Kargin, Z. Ya. Berestneva, and V. G. Kalashnikova, *Usp. Khim.*, **36**, 203 (1967).

[21] K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

[22] C. Cuniberti, manuscript in preparation.

[23] H. G. Elias, *Makromol. Chem.*, **99**, 291 (1966).

Elasticity Theory. I. Distribution Functions for Perfect Phantom Networks

B. E. Eichinger

Department of Chemistry, University of Washington, Seattle, Washington 98195.

Received April 3, 1972

ABSTRACT: Distribution functions for chains, cross-links, and whole networks are obtained for networks composed of chains of a single length which are connected to one another by tetrafunctional cross-linkages, such that there are no free chain ends. The chains do not interact with one another except through the cross-links. Results are largely formal, save for the explicit demonstration that the formation of a perfect network results in chain shrinkage by a factor of 2 for perfect networks, as was shown by James. Graph theory is exploited to formulate the partition function for the perfect network, and by its means we show that the connectivity of the tetrafunctional network composed of μ chains can be defined in all details by specification of a $(\mu - 1)$-dimensional vector whose elements are the lengths of fundamental circuits. The calculation of the characteristic function for the radius of gyration of the network is carried to the penultimate stage; a later paper will deal with its evaluation. Two methods are used to solve the problem; the first considers the network as it exists, while in the second the formation of the network is stressed.

The influence of topological connectivity on the properties of macroscopic networks is considered in this paper. We do not purport to solve the problem of rubber elasticity; rather we consider a model for an elastic network which can be treated in some detail. With the aid of graph theory, it is possible to formulate the configuration integral for perfect phantom[1] networks in a particularly simple way.[2] The connectivity of graphs corresponding to networks can be expressed in terms of various matrices, and properties of these matrices give one some insight into the manner in which the connectivity influences properties.

We consider the main results of this paper to be (1) proof that chains in perfect phantom networks of any connectivity are contracted by a factor of 2,[2] on the average, from their unconstrained dimensions; (2) for networks composed of ν chains and $\mu = \nu/2$ cross-links, the network is completely defined by a $(\mu - 1)$-dimension vector; and (3) a formal result is obtained for the distribution function of the radius of gyration of a network, in which $\mu - 1$ normal modes of network oscillation are encountered.

The calculations follow closely the method used by Berlin and Kac[3] in their treatment of ferromagnetism, and by Fixman[4] in his calculation of the distribution function for a single chain. Dyson[5] has treated the similar problem of oscillations in a one-dimensional system of springs and masses. In several recent papers Edwards and Freed[6] have developed a powerful theory for elasticity which stresses the importance of topological constraints. Our treatment of the connectivity of the network (without entanglements) is compatible with that of Edwards and Freed. Simplicity in our approach is, however, accompanied by a concomitant preaverage over

---

[1] P. J. Flory, unpublished notes.

[2] H. M. James, *J. Chem. Phys.*, **15**, 651 (1947).

[3] T. H. Berlin and M. Kac, *Phys. Rev.*, **86**, 821 (1952).

[4] M. Fixman, *J. Chem. Phys.*, **36**, 306 (1962).

[5] F. J. Dyson, *Phys. Rev.*, **92**, 1331 (1953).

[6] S. F. Edwards, *Proc. Phys. Soc.*, **91**, 513 (1967); **92**, 9 (1967); *J. Phys. A*, **1**, 15 (1968); S. F. Edwards and K. F. Freed, *ibid.*, **2**, 145 (1969); *ibid.*, *C*, **3**, 739 (1970); K. F. Freed, *J. Chem. Phys.*, **55**, 5588 (1971); S. F. Edwards in "Polymer Networks: Structural and Mechanical Properties," A. J. Chompff and S. Newman, Ed., Plenum Press, New York, N. Y., 1971, p 83.