Short-Range Order in Deformed Polymer Networks

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ABSTRACT: Mechanism of short-range ordering in deformed polymer networks was discussed from the point of view of the lattice theory of DiMarzio. It was shown that on stretching a network, the segments tend to order along the stretching direction to decrease the mutual interference between them, i.e., the volume effects. The extent of ordering was estimated using a simple set of self-consistent models, leading to the indication that the extra amount of segment orientation would be of the same order of magnitude as the amount which the system would show in the absence of the volume effects. The effects resulted in a negative contribution to the stress–strain relation, which is much larger than DiMarzio's estimation.

When a polymer network is deformed, the orientational distribution of segments as well as the distribution of chain end-to-end vectors vary to a new equilibrium. The main subject of the classical statistical theories of rubber elasticity[2] and opticoelasticity[3] was to estimate the chain vector and segment vector distributions using idealized models in which segments were assumed to be volumeless, i.e., the effects of mutual interference between segments were neglected. They are called the gaslike theories. A liquidlike theory was proposed by DiMarzio.[4] In the theory, the total (deformation-dependent) entropy S of a network was assumed to be given by

$$S = S^* + S_{\mathrm{p}} \tag{1}$$

where S^* is the entropy derived from the gaslike theory, and S_{p} is the so-called packing entropy which arises from the competition of chains for space, i.e., the volume effects. Subsequently, DiMarzio generalized the Flory-type lattice theory[5-7] so as to describe an anisotropic system and obtained the following expression for S_{p} as a function of the fraction γ_i of links (vector lengths between connections) lying in direction i ($i = 1, 2, \ldots, Z/2$, with Z being the coordination number):[8]

$$-S_{\mathrm{p}}/k = N_0 \ln V_0 + N \ln (V/M) - (N_0 + MN) \times \sum_i \, [1 - \gamma_i V(M-1)/M] \ln [1 - \gamma_i V(M-1)/M] \tag{2}$$

where k is the Boltzman constant, N and N_0 are the numbers of chains and solvent molecules, respectively, $M - 1$ is the number of links per chain, and V and V_0 are the volume fractions of polymer and solvent, respectively, i.e., $V = MN/(N_0 + MN) = 1 - V_0$. We see that S_{p} has a minimum when the system is isotropic ($\gamma_i = 2/Z$) and increases as the system becomes more oriented, approaching virtually zero for a perfectly oriented system.[4] Thus, using the three-chain model for the estimation of the relation between γ_i and strain, DiMarzio derived a negative correction term to the stress–strain curves of the gaslike theory.

Apparently, eq 1 is equivalent to the assumption that the chain vector and segment vector distributions in the "actual" system in which the volume effects exist are the same as in the gaslike system. This is not consistent, since due to the volume effects, the internal variables may readjust themselves to minimize the free energy. Of course, the readjustment does not generally occur, since the entropy decrease due to sacrificing the configurational freedom of chains compensates the increase of the packing entropy. However, once the system becomes anisotropic due to a stretch, for example, the total entropy increases to a certain extent with the segments ordering along the stretching direction. The purpose of this work is to show this. We assume that only the chain vector distribution in the actual system remains the same as in the gaslike system, or equivalently an affine deformation is assumed. As in the DiMarzio theory, any information that we might gain is gained at no expense, since neither of the present treatments include any new assumptions or parameters other than those widely approved.

Theory

We let $\{\gamma_i^*\}$ and $\{\gamma_i\}$ express the segment vector distributions in the gaslike and "actual" systems, respectively. Here, throughout the paper an asterisk denotes the gaslike system. Now we take a pair of chains from the two systems, one from each, which have the same end-to-end vector $\mathbf{R}$. As we have already assumed that the chain vector distributions in the two systems are the same, we can take N such pairs. The chains in each pair have generally different segment vector distributions, since $\{\gamma_i\} \neq \{\gamma_i^*\}$, in general. We write the entropy of the two chains as s^* and s, respectively, and define Δs as

$$\Delta s = s - s^* \tag{3}$$

Obviously, s^* depends only on $\mathbf{R}$, while s depends on $\{\gamma_i\}$ as well as on $\mathbf{R}$. Hence, $\Delta s \leq 0$. This must be so, since on the chain in the "actual" system is imposed an extra restriction. The entropy difference between the gaslike and "actual" systems arising from this source is written as ΔS. (As will be described later, ΔS can be given as the sum of Δs over all N pairs of chains.) Then the total entropy of the "actual" system may be given, instead of eq 1, by

$$S = S^* + \Delta S(\{\gamma_i^*\}, \{\gamma_i\}) + S_{\mathrm{p}}(\{\gamma_i\}) \tag{4}$$

Here S^* and S_{p} are as in eq 1. They have been adequately treated elsewhere,[2-4] and we may cite the results directly. We note that S_{p} depends only on $\{\gamma_i\}$ (cf. eq 2), while ΔS implicitly depends also on the chain vector distribution through the dependence on $\{\gamma_i^*\}$.

The condition for equilibrium, i.e., the minimum free energy, can be formally stated as

$$\partial S/\partial\{\gamma_i\} = \partial \Delta S/\partial\{\gamma_i\} + \partial S_{\mathrm{p}}/\partial\{\gamma_i\} = 0 \tag{5}$$

from which $\{\gamma_i\}$ is determined, if the functional form of ΔS is known.

Here, the following should be noted: Since the gaslike system is also at equilibrium, the relation

$$\partial \Delta S/\partial\{\gamma_i\} = 0 \quad \text{at} \quad \{\gamma_i\} = \{\gamma_i^*\} \tag{6}$$

must hold. With eq 6 and the first equation in eq 5, we have

$$\partial S/\partial\{\gamma_i\} = \partial S_{\mathrm{p}}/\partial\{\gamma_i\} \quad \text{at} \quad \{\gamma_i\} = \{\gamma_i^*\} \tag{7}$$

Since S_{p} increases as the segments become more oriented, we have the first conclusion from eq 7, without entering the detailed discussion, that the total entropy should be larger than expected from the DiMarzio theory in which the ΔS term was neglected, and the segments should be more oriented than expected from the gaslike theory.

Our concern now is to estimate the ΔS function using an appropriate model and obtain the equilibrium point given by eq 5. To be consistent with the lattice theory eq 2, we employ the lattice-walk model to represent the single chain as well as the network. Two types of walks are considered. One is *the random lattice-walk model,* and the other is *the restricted lattice-walk model* in which immediate reversals are restricted. The restricted walk is more favorable, since the lattice theory is of this type,[4–7] but it cannot be easily handled mathematically. We first examine the random walk and then try to deduce the properties of the other. For numerical simplicity, we choose the three-dimensional simple-cubic lattice (i.e., the coordination number Z is 6) with the three allowed directions equal to the principal directions of deformation (X_1, X_2, X_3), and we consider only uniaxial deformations. Then, the single parameter γ_1 which is the fraction of the segments (links) lying in the X_1 direction is sufficient to specify the segment distribution due to a stretch α given in that direction. In order to obtain some general information, we also examine the freely jointed chain originally due to Kuhn.[3] The model may be regarded as a lattice-walk model with $Z = \infty$.

Entropy of a Single Chain and the ΔS Function. In order to estimate the ΔS function, we have first to know the entropy of a single chain as a function of the chain end-to-end vector and the intrachain segment vector distribution. In general, the important parameter which characterizes the extent of segment orientation is p given by

$$p = \langle \cos^2 \theta \rangle = M^{-1} \sum_i m_i \cos^2 \theta_i \tag{8}$$

$$\sum_i m_i = M \tag{9}$$

where θ_i is the angle between the ith direction and a given direction, say the stretching direction X_1, fixed in the system, and m_i is the number of segments in that direction. Here the summations extend over all the allowed directions. For our model, $i = \pm X_1$, $\pm X_2$, and $\pm X_3$, and p is the fraction of segments in the X_1 direction. In this case, the algebraic average of p over all the chains in the network, which we denote by $\overline{p}$, coincides with γ_1.

The probability that a certain distribution $\{m_i\}$ occurs is proportional to W given by

$$W(\{m_i\}) = M!\Big(\prod_i f_i^{m_i}\Big) \Big/ \Big(\prod_i m_i!\Big) \tag{10}$$

where f_i is the a priori probability that the segment lies in the ith direction. The entropy s of a chain can be evaluated through maximizing eq 10 under the restrictions imposed on the chain. This is the method of Kuhn and Grün,[3] who obtained the inverse Langevin equations expressing s and p of the freely jointed chain with the X_1 component of the chain vector fixed. For consistency with the previous definitions, we denote the p and s of the chain with *only* the chain vector $\mathbf{R}$ fixed as p^* and s^*, respectively.

The entropy s of the chain with *both* $\mathbf{R}$ and p fixed can be evaluated similarly through maximizing eq 10 under the restrictions on $\mathbf{R}$ plus p. As shown in Appendix I, we can cast the result in the following general form;

$$\Delta s = s - s^* = -kfMq^2 \tag{11}$$

$$q = p - p^* \tag{12}$$

where f is a constant which depends on the model. For our random walk model (Appendix I),

$$f = 9/4 \tag{13}$$

and for our restricted walk model (Appendix II),

$$f = 27/8 \tag{14}$$

It is noted that eq 11 is valid only when q is small and $|\mathbf{R}|$ is small as compared with the contour length of the chain. In other words, the entropy change Δs due to changing the segment distribution by a small amount q is independent of the chain vector (and hence of p^*), so far as a small deformation is considered.

In this case, the entropy change ΔS of the network system due to changing the overall distribution by a small amount $\overline{q} = \overline{p} - \overline{p}^*$ is obviously independent of the chain vector distribution. It can be shown that when Δs is given by eq 11, ΔS may be given as the sum of the entropy changes of the individual chains with a uniform change $\overline{q}$, i.e.,

$$\Delta S(\overline{q}) = N\Delta s(\overline{q}) = -kfMN\overline{q}^2 \tag{15}$$

This additivity of entropy does not generally hold, when the functional form of eq 11 is different.

Orientation of Segments in the "Actual" Network. We now turn to our main problem. For our models, the packing entropy eq 2 is given by

$$\begin{aligned} -S_{\mathrm{p}}(\overline{p})/k = {} & N_0 \ln V_0 + N \ln (V/M) \\ & - (N_0 + MN)\{(1 - \overline{p}V) \ln (1 - \overline{p}V) \\ & + 2[1 - (1 - \overline{p})V/2] \ln [1 - (1 - \overline{p})V/2]\} \end{aligned} \tag{16}$$

where we have set $M - 1 \sim M \sim M + 1$. The equilibrium value of $\overline{p}$ ($= \overline{p}^* + \overline{q}$) is obtained from eq 5, which now reads

$$[\partial \Delta S(\overline{q})/\partial \overline{q}] + [\partial S_{\mathrm{p}}(\overline{p})/\partial \overline{q}] = 0 \tag{17}$$

Inserting eq 15 and 16 in eq 17, we have

$$2f\overline{q} = \ln [1 - (1 - \overline{p})V/2] - \ln (1 - \overline{p}V) \tag{18}$$

from which $\overline{q}$ is determined as a function of $\overline{p}^*$. As $\overline{p}^*$ is close to $1/3$ for small deformations, we may expand the logarithms in eq 18 to have the following solution valid for small deformations and large M;

$$\overline{q} = G(\overline{p}^* - 1/3) \tag{19}$$

$$G = [4f(3 - V)/(9V) - 1]^{-1} \tag{20}$$

The quantity $\overline{p}^* - 1/3$ represents the amount of segment orientation due to a stretch α in the gaslike system. Hence, G represents the relative increase in orientation due to the packing effect. Figure 1 shows the plot of G against V. We see that G is surprisingly large when $V = 1$, or in other words, the system is dry (and has no free volume), although its magnitude depends on the model, i.e., $G = 1.0$ and 0.5 for the random and restricted walks, respectively. As V decreases, or the system is swollen, the effect diminishes, but not perfectly unless $V = 0$.

It is noted that $\overline{p} - 1/3$ is proportional to the so-called stress–optical coefficient C or an equivalent $\Delta\Gamma$, the optical anisotropy of Kuhn's equivalent segment. Hence, the quantity

$$\Lambda = 1 + G \tag{21}$$

is the correction factor which multiplies C^* or $\Delta\Gamma^*$ derived from the gaslike theory, i.e.,

$$C = \Lambda C^* \quad \text{and} \quad \Delta\Gamma = \Lambda\Delta\Gamma^* \tag{22}$$

Stress–Strain Relation. In order to discuss the stress–strain relation in the "actual" system, it is necessary to know

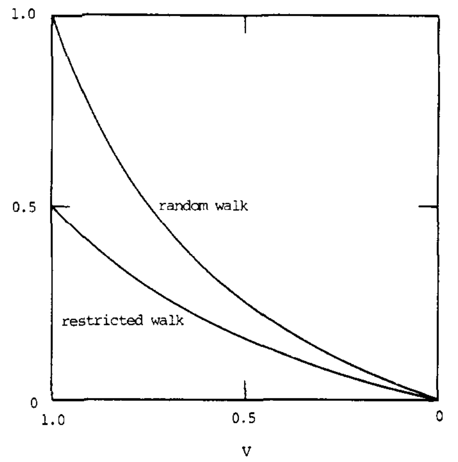

Figure 1. Plots of the parameter G vs. volume fraction of polymer V for the two lattice-walk models.

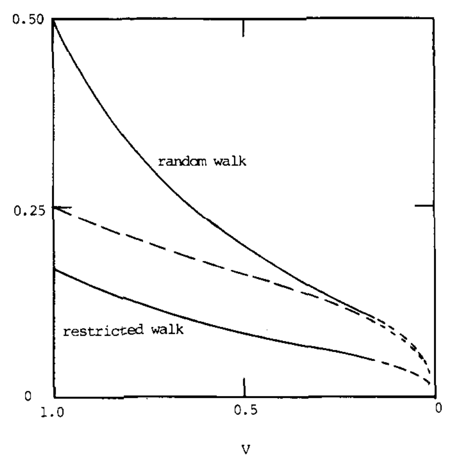

Figure 2. Plots of the parameter A vs. volume fraction of polymer V for the two lattice-walk models. The dotted curve represents the DiMarzio theory.

$\bar{p}^*$ as a function of α. As shown in Appendix III, $\bar{p}^*$ is generally given, for small deformations and large M, by

$$\bar{p}^* - \tfrac{1}{3} = g(MV^{2/3})^{-1}(\alpha^2 - \alpha^{-1}) \tag{23}$$

where g is a constant dependent on the model and α is the stretch ratio with the swollen state as the reference state. For our random and restricted walk models, g is estimated to be

$$g = \tfrac{1}{3} \quad \text{and} \quad \tfrac{2}{9} \tag{24}$$

respectively (see Appendix III).

The retractive force F is obtained from

$$F = -T(\partial S/\partial \alpha)_{T,\overline{V}} = F^* + F_{\mathrm{p}} \tag{25}$$

$$S = S^* + \Delta S(\bar{q}) + S_{\mathrm{p}}(\bar{p}^* + \bar{q}) \tag{26}$$

where $\overline{V}$ is the specific volume of the system and T is the temperature. In eq 25, F^* and F_{p} are the forces due to the gaslike theory S^* and the packing effect $\Delta S + S_{\mathrm{p}}$, respectively. From eq 15, 16, 19, 23, 25, and 26, we have

$$F_{\mathrm{p}} = -(NkT/V^{2/3})(\alpha - \alpha^{-2})(A/M)(2\alpha^2 + \alpha^{-1}) \tag{27}$$

$$A = (g^2/V^{2/3})[\tfrac{9}{2}(1 + G)^2V/(3 - V) - 2fG^2] \tag{28}$$

Thus, the packing effect results in a negative correction term which becomes larger in magnitude with the increase of α. Figure 2 shows the plot of A against V, for the two models. For $V = 1$, we have $A = \frac{1}{2}$ and $\frac{1}{6}$ for the random and restricted walks, respectively.

Obviously eq 27 and 28 with $G = 0$ (i.e., $\bar{q} = 0$) corresponds to the DiMarzio theory. The present treatments show that his correction term should be exactly doubled for $V = 1$, if the same model as his (random walk on the cubic lattice) is employed.

Discussion

We have seen above that a simple set of self-consistent models led to the indication that the segments in a stretched polymer network order along the stretching direction to a considerably higher extent than expected from the gaslike theory, and this effect resulted in a negative correction term to the stress–strain curves which is larger than estimated by DiMarzio. In the above discussion, the cross-linking effects appeared only implicitly through the parameter $\bar{p}^*$. Thus, the same phenomena can be likewise expected to occur and affect other properties of polymer chains in bulk and in concentrated solution such as stretch-induced crystallization, streaming birefringence, or whatever properties in which chain orientation matters, irrespective of chains being cross-linked or not.

However, the amount of the extra orientation represented by the parameters G or Λ differed for the random and restricted walks. If we employ some other lattice, the results should be different. In fact, the restricted walk on the two-dimensional square lattice leads to the indication that $\Lambda = \infty$, showing that Λ is model dependent. We can expect that as the coordination number Z increases (which, in reality, may correspond to the increase in chain flexibility), the ordering would become less significant. According to Flory's analysis[5] on the entropy of fusion of various polymer crystals, the value 6 for Z appears to be the best choice, or at least, a representative one. This would put some justification on our choice of the lattice. The reason why the restricted walk is more justifiable has been pointed out. Thus, it may be possible to regard the value of Λ for this model (e.g., $\Lambda = 1.5$ for $V = 1$) as a guide value representing the extent of the ordering which is expected to occur when a network is stretched. However, in view of the defects inherent in the lattice theory, it is quite difficult to judge the validity of the present theory even in its qualitative aspects. Below, we make some comparisons with experimental situation. However, this is done just to point out what could be and could not be explained by the present theory, and with no other intention.

Stress–Optical Coefficient. According to Gent and Vickroy,[9] the observed optical anisotropy $\Delta\Gamma$ of an amorphous polyethylene network swollen as highly as $V = 0.135$ was 3.9×10^{-24} cm^3 at 138 °C, while that of dry samples was 8.5×10^{-24} cm^3 on average at a similar temperature, 150 °C. Nagai[10] has calculated $\Delta\Gamma$ of polyethylene using his general theory[10–12] to obtain a value close to that of the swollen sample and suggested the presence of a short-range order in dry polyethylene networks. If we apply the above experimental values to eq 20–22, we have $\Lambda = 2.2$ for polyethylene around 150 °C. This value is similar in order of magnitude to our estimation above.

Another observation which could be explained by the present theory may be that $\Delta\Gamma$ of unswollen polyethylene networks decreases markedly with the increase of temperature,[9,13] while that of swollen samples shows little temperature dependence.[9] The observed temperature coefficient for an unswollen sample from Figure 5 of ref 9 is

$$\mathrm{d} \ln \Delta\Gamma/\mathrm{d}T = -5.5 \times 10^{-3}\ \mathrm{deg}^{-1} \quad \text{at} \quad 150\ °\mathrm{C}$$

According to Nagai's calculation,[10] it is

$$\mathrm{d} \ln \Delta\Gamma^*/\mathrm{d}T = -1.6 \times 10^{-3}\ \mathrm{deg}^{-1} \quad \text{at} \quad 150\ °\mathrm{C}$$

This value was read from Figure 1 of ref 10, assuming $E_g = 800$ cal mol^{-1} and the tetrahedral bond angle, as suggested by the author. The discrepancy is far beyond the experimental and theoretical ambiguities. From the present point of view, the discrepancy is attributed partly to the volume expansion of the system (which corresponds to the increase of free volume, and hence the decrease of V) and partly to the increase of chain flexibility with temperature. Both lead to the decrease of $\Delta\Gamma$. For practical purpose, eq 21 with eq 20 may be rewritten as

$$\Lambda = 1 + [f'(3 - V)/V - 1]^{-1} \tag{29}$$

where $f' = 4f/9$, but if we redefine f' as an adjustable parameter, eq 29 would serve as a semitheoretical equation. The parameter f' can be determined by measuring $\Delta\Gamma$ at different degrees of swelling. From eq 22 and 29, we have

$$\mathrm{d}\ln\Delta\Gamma/\mathrm{d}T = \mathrm{d}\ln\Delta\Gamma^*/\mathrm{d}T - 3(3 - V)^{-1}[f'(3 - V)/V - 1]^{-1}(\mathrm{d}\ln\overline{V}/\mathrm{d}T) - [f'(3 - V)/V - 1]^{-1}(\mathrm{d}\ln f'/\mathrm{d}T) \tag{30}$$

where $\overline{V}$ is the specific volume as before. The first term in the rhs of eq 30 corresponds to the gaslike theory, the second to the volume expansion of the system, and the last to the temperature variation of chain flexibility. There is no theoretical basis to estimate V, especially of dry samples. If we assume that $V = 1$ for dry polyethylene around 150 °C, we have $f' = 0.87$ from the above data of Gent and Vickroy. With this value and the known expansion coefficient of a branched polyethylene at 150 °C,[14] i.e., $\mathrm{d}\ln\overline{V}/\mathrm{d}t = 0.75 \times 10^{-3}$ deg^{-1}, the second term is estimated to be -1.5×10^{-3} deg^{-1}. This value is increased to -2.7×10^{-3} deg^{-1}, if we assume that $V = 1$ at 25 °C (crystalline state), and hence $V = 0.86$ at 150 °C.[15] It is not possible to estimate the last term quantitatively, but it is expected to be negative, too. The polymer chain usually becomes more flexible with the increase of T, which, in the lattice-walk model, could be associated with the increase of the coordination number Z. The increase of Z would result in larger f and hence f'. We recall that the freely jointed chain has f much larger than the random walk chain on the cubic lattice (see Appendix I). After all, most of the discrepancy could be thus explained.

Observations on $\Delta\Gamma$ are not few which suggest the presence of certain short-range orders in other polymer networks also.[16–21] Many of them could be likewise explained, at least qualitatively.

Stress–Strain Relation. The correction term to the stress–strain curves has been extensively discussed by DiMarzio.[4] We have not much to add except that his correction term should be doubled. The DiMarzio theory as well as the present one gives a negative correction term, which is in qualitative agreement with observations, i.e., the Mooney–Revlin term. Jackson et al.[22] have derived an equation formally the same as ours, based on the same model but from a different approach. However, a rather fatal defect of all these theories may be that the correction term is inversely proportional to M (see eq 27), indicating that the Mooney–Revlin term becomes trivial for weakly cross-linked networks. In reality, this is not necessarily the case.[2,9] It would be fair to emphasize that only a part of the Mooney–Revlin term could be explained from the lattice theory approach.

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Appendix

(I) Entropy of the Random Lattice-Walk Chain. In order to survey the general aspects of the problem, we first examine the freely jointed chain with fixed p and x, the X_1 component of the chain vector, given by

$$x = \sum_i m_i b \cos\theta_i \tag{A1}$$

where b is the length of links. Under the restrictions of eq 8, 9, and A1, eq 10 is maximized using the Lagrange method of undetermined multiplier and the Stirling approximation to have the distribution $m_i{}^0$ which would realize

$$m_i{}^0 = f_i \exp(\lambda)\exp(\mu b\cos\theta_i)\exp(\beta\cos^2\theta_i) \tag{A2}$$

where $f_i \propto \sin\theta_i$ in a polar coordinate system. The multipliers β, λ, and μ corresponding to eq 8, 9, and A1, respectively, are determined from the relations,

$$M = (e^{\lambda}/2)\int_{-1}^{1}\exp(\mu bt)\exp(\beta t^2)\,\mathrm{d}t \tag{A3}$$

$$p = \left[\int_{-1}^{1} t^2\exp(\mu bt)\exp(\beta t^2)\,\mathrm{d}t\right] \Big/ \left[\int_{-1}^{1}\exp(\mu bt)\exp(\beta t^2)\,\mathrm{d}t\right] \tag{A4}$$

$$x/Mb = \left[\int_{-1}^{1} t\exp(\mu bt)\exp(\beta t^2)\,\mathrm{d}t\right] \Big/ \left[\int_{-1}^{1}\exp(\mu bt)\exp(\beta t^2)\,\mathrm{d}t\right] \tag{A5}$$

where we have replaced the summations by integrals and the integral variable θ_i by $t = \cos\theta_i$. The entropy s of the chain may be given by

$$s = k\ln W(\{m_i{}^0\}) \tag{A6}$$

from which, using eq 8–10, A1, and A2, we have

$$s/k = M\ln M - \lambda M - \mu bx - \beta pM \tag{A7}$$

Differentiating eq A7 with respect to p with fixed x and using eq A3, A4, and A5, we have

$$(\partial s/\partial p)_x = -k\beta M \tag{A8}$$

When there is no restriction on p, which corresponds to setting $\beta = 0$, we recover, from eq A2, A3, and A5–A7, the equations obtained by Kuhn and Grün[3] previously, i.e.,

$$s^* = -\int_0^x [(k/b)L^{-1}(x/bM)]\,\mathrm{d}x + \text{const.} \tag{A9}$$

$$p^* = 1 - (2x/bM)/L^{-1}(x/bM) \tag{A10}$$

where L^{-1} is the inverse Langevin function. When β is nonzero, on the other hand, both β and μ depend on both p and x but cannot be expressed by known functions. Expanding eq A4 and A5 around $\mu = \beta = 0$ and solving them for β, we have

$$\beta = {}^{45}\!/_4(p - {}^1\!/_3) - {}^9\!/_2(x/bM)^2 + 0[(p - {}^1\!/_3)^2, (x/bM)^4, (p - {}^1\!/_3)(x/bM)^2] \tag{A11}$$

Inserting eq A11 in A8 and integrating it with respect to p from $p = p^*$ to p ($\beta = 0$ to β), we have, with the aid of eq A10, the entropy s given by

$$s/kM = -{}^{45}\!/_8 q^2 + 0[q^3, q^2(x/bM)^2] + C(x)/kM \tag{A12}$$

$$q = p - p^* \tag{A13}$$

where $C(x)$, a function only of x, can be identified with s^* given by eq A9. That is, the relation

$$\Delta s = s - s^* = -{}^{45}\!/_{8} kMq^2 \qquad \text{(A14)}$$

holds for small x/bM and q.

It is possible to extend this method to the general case in which the other two components of the chain vector **R** are also fixed. However, we may deduce from the above result that Δs is independent of **R** for small $|\mathbf{R}|/bM$ and q and that Δs is given by the same equation, A14. It is also noted that when we impose no restriction on **R**, Δs is given again by eq A14 with $p^* = 1/3$. In other words, to calculate Δs for small q we do not have to deal with the chain vector simultaneously as we have done above. Just as the proportionality of the mean-square $|\mathbf{R}|$ to M is a general law, this feature of the freely jointed chain may be accepted as a statistical law valid for any model (including the random and restricted lattice-walk models) which is composed of a large number of links, and we can expect that Δs is given in the form,

$$\Delta s = -kfMq^2 \qquad \text{(A15a)}$$

with the numerical constant f dependent on the model.

It is easy now to evaluate f for our random lattice-walk model. Through maximizing eq 10 with the restrictions of eq 8 and 9, we find

$$f = 9/4 \qquad \text{(A15b)}$$

(II) Entropy of the Restricted Lattice-Walk Chain. Here we have to consider a correlated process, for which a somewhat different approach is required: Expressing the X_1 direction by 1 and the other two by 2, our process is characterized by the transition matrix **Q** given by

$$\mathbf{Q} = \begin{vmatrix} t/(Z-1) & (Z-2)/(Z-1) \\ 2t/(Z-1) & (Z-3)/(Z-1) \end{vmatrix} \qquad \text{(A16)}$$

where $Z = 6$ in our case, and t is a dummy variable. The element Q_{ij} with $t = 1$ is the probability that we have a step in direction j following one in direction i ($i, j = 1$ or 2). From eq A16, we have a set of recursion equations relating the elements of $\mathbf{Q}^{M-1}$ and those of $\mathbf{Q}^{M}$, the solution of which gives a generating function $G(t)$. The coefficient of t^m in $G(t)$ is the fraction of the configurations in which a total of m steps lie in direction 1, i.e., X_1.

Although they are not reproduced here, we notice that the recursion equations are formally the same as those appearing in the kinetics of binary copolymerization.[23,24] In fact, the problem of finding the compositional distribution in copolymers is mathematically the same as ours. Stockmayer[24] has treated mathematically the rigorous solution[23] of the recursion equations which is not of practical use and expressed it in a simple form. Thus, we may cite his result directly: The distribution $w(q)$, where q ($= p - p^*$) is the difference of composition p from the average p^* in the original paper, is given by

$$w(q) = \text{const.} \times \exp[-Mq^2/2p^*(1-p^*)\kappa] \qquad \text{(A17)}$$

$$\kappa = [1 - 4p^*(1-p^*)(1-k_1k_2)]^{1/2} \qquad \text{(A18)}$$

Here, k_1 and k_2 are the reactivity ratios, which can be correlated to the elements of **Q** with $t = 1$ as

$$k_1 = Q_{11}/Q_{12} \quad \text{and} \quad k_2 = Q_{22}/Q_{21} \qquad \text{(A19)}$$

The entropy difference Δs is obtained from

$$\Delta s = k \ln [w(q)/w(0)] = -{}^{27}\!/_{8} kMq^2 \qquad \text{(A20)}$$

where we have set $p^* = 1/3$ (see Appendix I) and $Z = 6$. That is, $f = 27/8$ for this model. As is obvious from its derivation,[24] eq A17 and hence A20 are exact only for small q.

(III) Relation between $\bar{p}^*$ and α. We first consider our random walk model. By maximizing eq 10 with the chain vector fixed at (x_1, x_2, x_3), we have the distribution $M_i^0 = m_{+i}^0 + m_{-i}^0$ ($i = 1$, 2, and 3) which would realize, i.e.,[22]

$$(M_i^0)^2 = \tau + x_i^2 \qquad \text{(A21)}$$

where the Lagrange multiplier τ is determined from eq 9. For simplicity, we have assumed that the links are of unit length. At this stage, we take the averages of both sides of eq A21 over all the chains in the network;

$$\overline{(M_i^0)^2} = \bar{\tau} + \overline{x_i^2} \qquad \text{(A22)}$$

Approximating[25] $\overline{(M_i^0)^2}$ by $(\overline{M_i^0})^2$ and setting $\overline{M_2^0} = \overline{M_3^0} = (M - \overline{M_1^0})$ and $\overline{x_2^2} = \overline{x_3^2}$, we have

$$\bar{p}^* = \overline{M_1^0}/M = -1/3 + 2/3[1 + (3/M^2)(\overline{x_1^2} - \overline{x_2^2})]^{1/2} \qquad \text{(A23)}$$

For an affine deformation with respect to $\overline{x_i^2}$,[26] i.e., $\overline{x_i^2} = \alpha_i^2(M/3)V^{-2/3}$, where α_i is the deformation in direction i with the swollen state as the reference state, and a constant volume, i.e., $\alpha_1\alpha_2\alpha_3 = 1$, eq A23 reads

$$\bar{p}^* = -1/3 + 2/3[1 + (MV^{2/3})^{-1}(\alpha^2 - \alpha^{-1})]^{1/2} \qquad \text{(A24)}$$

$$(\alpha = \alpha_1)$$

For small deformation and large M, eq A24 converges to[27]

$$\bar{p}^* - 1/3 = g(MV^{2/3})^{-1}(\alpha^2 - \alpha^{-1}) \qquad \text{(A25)}$$

$$(g = 1/3)$$

Equation A25 is expected to be generally valid, with the numerical constant g dependent on the model. We can see that the value of g for the freely jointed chain model is 2/15.[3]

Rigorous calculation of g for our restricted walk model is not easy. However, it is worth noting that the product fg is the same for our random walk and freely jointed chain models, i.e., $fg = 3/4$ (see above). This should not be fortuitous, since both f and g are parameters concerning chain flexibility. Thus, although the proof is lacking, we may assume that this is generally the case. This gives $g = 2/9$ for the restricted walk model.

References and Notes

(1) (a) Kyoto University; (b) Imperial College.
(2) (a) See, e.g., L. R. G. Trelore, "The Physics of Rubber Elasticity", Oxford University Press, London, 1958; (b) See, e.g., K. Dušec and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).
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(8) It seems that there is a misprint in the original equation, eq 6 of ref 4.
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(25) This approximation is fully justified for small deformations and large M.
(26) See, e.g., F. T. Wall, *J. Chem. Phys.*, **10**, 485 (1942).
(27) DiMarzio's equation also converges to eq A25 but is different from eq A24 for large deformations and small M. Equation A24 does not include the contradictions which his equation does for large deformations (see eq 10 of ref 4).