Boundaries of Constrained Random Flight Polymer Chains

Robert J. Rubin

National Bureau of Standards, Washington, D.C. 20234

George H. Weiss*

National Institutes of Health, Bethesda, Maryland 20014. *Received May 15, 1978*

ABSTRACT: We call the radius of the smallest sphere which contains all segments of a random flight chain and is centered at the starting point of the chain the Hollingsworth radius of the chain R. In this paper we consider two cases in which the configurations of random flight chains are constrained. In each case we calculate the probability density of the Hollingsworth radius for the constrained chains. In the first case, the end-to-end distance of the chains is constrained to the value r. In the second case, all segments of the chain are constrained to lie on one side of an impenetrable plane through the starting point.

I. Introduction

There have been many studies of the dimensions and shapes of polymer chains. A number of these are summarized in the books of Volkenstein[1] and Yamakawa.[2] In particular Katchalsky, Kuenzle, and Kuhn[3] were the first to study the dimensions of constrained polymer chains. In their case they assumed that the two ends of the chain were separated by a fixed distance. DiMarzio and Rubin[4] have analyzed similar problems when the polymer chain is confined between parallel planes. One of the parameters of interest is the maximum extent of the polymer chain, that is, the maximum of the distances between the segments of the chain and a specified end of the chain. The distribution of this quantity for unconstrained polymer chains was first obtained by Hollingsworth.[5] Katchalsky et al.[3] derived an expression for the mean-square distance from the initial point to an arbitrary point on the chain. Their maximization of this mean is not equivalent to a calculation of the Hollingsworth radius,[5] because one would need a joint distribution of the distances to all points on the chain to calculate the maximum. In this note we present results for the Hollingsworth radius of a chain with a fixed distance between its ends, and for a chain with one of its ends on an impenetrable plane. This latter problem is of particular interest in characterizing the details of the surface structure of chain-folded polymer crystals. For example, if only part of a chain is incorporated in a polymer crystal, then the dangling end or cilium may be regarded as a polymer chain attached to an impenetrable surface. In this case, we calculate the probability density of the radius of the smallest hemisphere (centered at the point of attachment to the crystal) which contains all segments of the cilium. All of the calculations in this paper are carried out in the random flight or diffusion limit.

We assume that the chains are in a force-free field for which the dimensionless diffusion equation in spherical coordinates is

$$\frac{\partial n}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r}\right) \qquad (1)$$

To establish a correspondence between the random walk picture and the diffusion picture, the diffusion constant, D, has been replaced by $L^2/6$ where L, the length of a single bond, is set equal to unity. Further, the product Dt or DN, where N is the number of bonds, has been replaced by τ. For technical reasons in the second of the above two problems, we find it necessary to base our calculation on a solution of the diffusion equation in spherical coordinates where the initial distribution is not concentrated at the center of the spherical coordinate system. The appropriate form of the diffusion equation in this case is

$$\frac{\partial n}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial n}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 n}{\partial \varphi^2} \qquad (2)$$

II. Hollingsworth Radius of a Chain with Constrained Ends

The fraction of the ensemble of all chains whose initial point is at $r = 0$, whose maximum extension at τ is $\leq R$, and whose position at τ is in the spherical shell $(r, r + \mathrm{d}r)$ is $4\pi r^2 n_R(r,\tau)\, \mathrm{d}r$ where

$$n_R(r,\tau) = \frac{1}{4rR^2}\sum_{j=-\infty}^{\infty} j \sin\left(\frac{\pi j r}{R}\right)\exp\left(-\frac{j^2\pi^2\tau}{R^2}\right) \qquad (3)$$

A more convenient form for this expression is obtained by using a Poisson transformation[9] which yields

$$n_R(r,\tau) = \frac{1}{8\pi^{3/2}\tau^{3/2} r}\sum_{j=-\infty}^{\infty} (2jR + r)\exp\left[-\frac{(2jR + r)^2}{4\tau}\right] \qquad (4)$$

Let us denote by $S(r,R;\tau)$ the fraction of chains whose Hollingsworth radius is $\leq R$. Then $S(r,R;\tau)$ is given by

$$S(r,R;\tau) = \frac{1}{r}\sum_{j=-\infty}^{\infty} (2jR + r)\exp\left[\frac{r^2 - (2jR + r)^2}{4\tau}\right] \qquad (5)$$

and the fraction of polymer chains with Hollingsworth radius between R and $R + \mathrm{d}R$ is

$$s(r,R;\tau) = \partial S/\partial R \qquad (6)$$

It is easily verified that $S(r,r;\tau) = 0$ and $S(r,\infty;\tau) = 1$ so that $s(r,R;\tau)$ is properly normalized. Several curves of $s(r,R;\tau)$ are shown in Figure 1 plotted as a function of R/r for values of $\theta = r^2/(4\tau)$. The probability density function of the Hollingsworth radius is seen to depend sensitively on θ for $\theta \leq 1$. For larger values of θ the probability density is highly peaked at a value of R slightly greater than r.

The average Hollingsworth radius for a constrained end-to-end separation can be calculated from eq 5 and 6. The result is

$$\frac{\langle R(r)\rangle}{r} = 1 + \frac{\tau}{r^2}\left\{1 - \sum_{j=1}^{\infty}\frac{1}{j(j+1)}\exp[-j(j+1)r^2/\tau]\right\} \qquad (7)$$

We consider the value of $\langle R(r)\rangle$ in two limiting cases.

First, in the limit $(r^2/\tau) << 1$, the sum in eq 7 has the expansion (see Appendix A, eq A7)

$$\sum_{j=1}^{\infty} \frac{1}{j(j+1)} \exp[-j(j+1)r^2/\tau] \sim 1 - (\pi r^2/\tau)^{1/2} + (r^2/\tau) + \ldots \quad (8)$$

As a consequence, the average Hollingsworth radius of chains whose ends coincide is simply

$$R(0) = (\pi\tau)^{1/2} \quad (9)$$

This average constrained Hollingsworth radius should be compared with the average uncontrained radius,[5]

$$R_{\mathrm{Holl}} = (\pi/2)(\pi\tau)^{1/2} \quad (10)$$

In the second limiting case, $r^2/\tau >> 1$, the sum in eq 7 can be neglected and one obtains

$$\langle R(r)\rangle/r \simeq 1 + (\tau/r^2) \quad (11)$$

Before considering the problem of calculating the probability density of the Hollingsworth radius of a chain constrained to lie on one side of a plane through its "starting" end, we consider the problem of calculating the probability density of the Hollingsworth radius of the subset of chains whose end-to-end distance is equal to the Hollingsworth radius. This probability density is complementary to that for the Hollingsworth radius of the set of chains whose ends coincide ($r = 0$). According to eq 3, the probability density of such extended chains, $n_{\mathrm{R}}(R)$, is equal to zero. Therefore, we are forced to consider the fraction of chains whose end-to-end distance lies close to the Hollingsworth radius and to determine how this fraction approaches zero as the Hollingsworth radius is approached. Thus for $r = R - \epsilon$, we have from eq 4

$$4\pi r^2 n_{\mathrm{R}}(r;\tau) = \frac{R^2(1-\epsilon R^{-1})}{(4\pi\tau^3)^{1/2}} \sum_{j=-\infty}^{\infty} (2j+1-\epsilon R^{-1}) \times \exp[-(2j+1-\epsilon R^{-1})^2 R^2/(4\tau)] \quad (12)$$

In the limit $\epsilon \rightarrow 0$, this fraction is proportional to ϵ. In particular, the normalized fraction of chains whose end-to-end distance is equal to the Hollingsworth radius is

$$\phi(R;\tau) = C^{-1} \lim_{\epsilon\rightarrow 0} \epsilon^{-1} 4\pi(R-\epsilon)^2 n_{\mathrm{R}}(R-\epsilon;\tau) = -\frac{4R}{\pi^2\tau} \frac{\mathrm{d}}{\mathrm{d}R} \{R \sum_{n=0}^{\infty} \exp[-(2n+1)^2R^2/(4\tau)]\} \quad (13)$$

where the normalization constant is $C^{-1} = 4\tau^{1/2}\pi^{-3/2}$. The average Hollingsworth radius for these "extended" chains is

$$\langle R_{\mathrm{ext}}\rangle = \frac{16}{\pi^2}(\pi\tau)^{1/2} \sum_{n=0}^{\infty} (2n+1)^{-3} \quad (14)$$

Thus the relative values of R_{ext}, R_{Holl}, and $R(0)$ are 1.7051:1.5708:1.

III. Average Hollingsworth Radius of a Chain Attached at One End to an Impenetrable Surface

We now consider the problem of calculating the average Hollingsworth radius of a chain with one end located on an impenetrable surface. In principle the calculation is analogous to the calculations of Hollingsworth[5] and Weidmann et al.[7] However, a technical problem arises in the mathematical analysis because the chain end is located on an impenetrable surface where the solution of the diffusion equation is required to be zero.[8] We encountered a similar difficulty in treating the problem of the "extended" chains in section II and now proceed in a similar way. We assume that the equatorial plane of the spherical coordinate system coincides with the impenetrable surface and assume an initial distribution of the form

$$n(r,\theta,\phi;0) = (2\pi r^2)^{-1}\delta(r-\epsilon)[\delta(\cos\theta - 1 + \gamma) - \delta(\cos\theta + 1 - \gamma)] \quad (15)$$

where ϵ and γ are parameters that will eventually be set equal to zero. The solution to the diffusion eq 2 for the initial condition in eq 15 and the boundary condition $n(R,\theta,\phi;\tau) = 0$ automatically satisfies the boundary condition

$$n(r,\pi/2,\phi;\tau) = 0 \quad (16)$$

on the impenetrable plane. We show in Appendix B that the limit function

$$v(r,\theta,\phi;\tau) = \lim_{\epsilon\rightarrow 0}\lim_{\gamma\rightarrow 0} \epsilon^{-1} n(r,\theta,\phi;\tau) = \left(\frac{2}{\pi^3 R^7}\right)^{1/2} \cos\theta \sum_{i=1}^{\infty} \frac{s_i^{1/2}}{r^{1/2}} \frac{J_{3/2}(s_i r/R)}{[J_{3/2}'(s_i)]^2} \exp(-s_i^2\tau/R^2) \qquad 0 \le \theta \le \pi/2 \quad (17)$$

is proportional to the probability density of the position of the end of a polymer chain at time t in the case where no step lies at a distance greater than R from the origin and where the random flight chain starts immediately above the origin. In eq 17, $J_{3/2}(x)$ is the Bessel function of the first kind of order $^3/_2$,

$$J_{3/2}(x) = \left(\frac{2}{\pi x}\right)^{1/2}\left(\frac{\sin x}{x} - \cos x\right) \quad (18)$$

$J_{3/2}'(x)$ denotes the derivative, $(\mathrm{d}/\mathrm{d}x)\, J_{3/2}(x)$; and s_i denotes the ith positive root of $J_{3/2}(x) = 0$, i.e., the ith positive root of $x = \tan x$.

The normalized integral over the hemisphere

$$\psi(R,\tau) = c^{-1} \int_0^R r^2\,\mathrm{d}r \int_0^{\pi/2} \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} v(r,\theta,\varphi;\tau)\,\mathrm{d}\varphi \quad (19)$$

is the fraction of all chains which start at the origin, are of length τ, and are contained in the hemisphere or radius R. The value of $\psi(R,\tau)$ is

$$\psi(R,\tau) = \frac{1}{Rc} \sum_{i=1}^{\infty} \left(\frac{2}{\sin^2 s_i} - \frac{2}{s_i \sin^2 s_i} - \frac{s_i}{\sin s_i}\right) \times \exp(-s_i^2\tau/R^2) \quad (20)$$

where the normalization constant, c, is

$$c = \lim_{R\rightarrow\infty} \psi(R,\tau) \quad (21)$$

The probability density of the maximum distance, R, of any segment in the chain from the starting point (the point of attachment of the chain to the impenetrable surface) is

$$p(R,\tau) = \frac{\partial\psi}{\partial R}(R,\tau) \quad (22)$$

The probability density, $p(R,\tau)$, has been calculated numerically from eq 20–22 and is plotted in Figure 2 as the solid curve. For comparison, we have also plotted, as a dashed curve, the probability density function of Hollingsworth[5] to show the effect of the introduction of an impenetrable surface just below the starting point of a free chain. The first and second moments obtained by numerical integration from eq 20–22 are

$$\langle R\rangle = 3.204\tau^{1/2}$$

and

$$\langle R^2\rangle = 10.926\tau$$

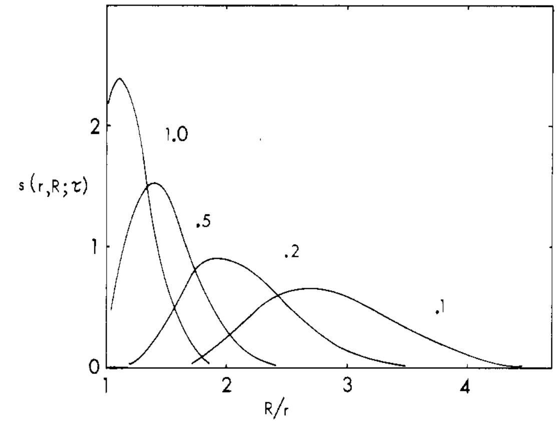

Figure 1. Probability density $s(r,R;\tau)$ as a function of R/r for several values of $\theta = r^2/(4\tau)$.

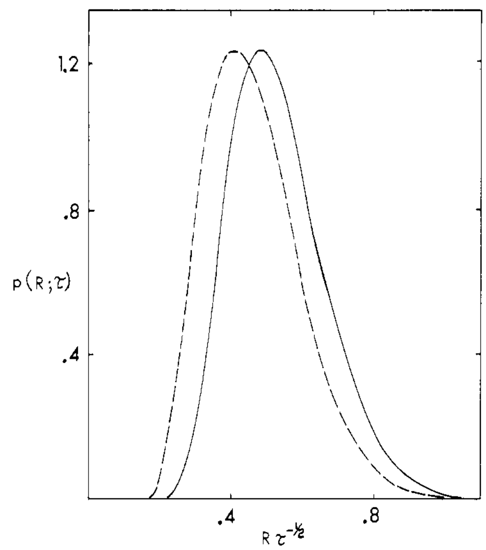

Figure 2. Probability density $p(R;\tau)$ of the Hollingsworth radius of a chain attached to an impenetrable surface as a function of $R\tau^{-1/2}$ (solid curve). For comparison the probability density of the Hollingsworth radius of a chain is also shown as a function of $R\tau^{-1/2}$ (dashed curve).

For comparison, the mean and the mean-square values of the Hollingsworth radius[5] are

$$\langle R_{\rm Holl}\rangle = \frac{\pi}{2}(\pi\tau)^{1/2} = 2.784\tau^{1/2}$$

and

$$\langle R_{\rm Holl}^2\rangle = 8\tau\sum_{n=0}^{\infty}(2n+1)^{-3} = 8.414\tau$$

The mean-square value of the end-to-end distance of the unconstrained random flight chain in the same units is

$$\langle r^2\rangle = 6\tau$$

Appendix A. Evaluation of $R(r)$ in Equation 7 when $r^2/\tau << 1$

Consider the sum

$$S(v) = \sum_{n=1}^{\infty}\frac{1}{n(n+1)}e^{-\pi v n(n+1)} \quad \text{(A1)}$$

The derivative

$$-\frac{1}{\pi}\frac{dS}{dv} = \sum_{n=1}^{\infty}e^{-\pi v n(n+1)}$$

can be expressed in terms of a θ function[9] as

$$-\frac{1}{\pi}\frac{dS}{dv} = \frac{1}{2}e^{\pi v/4}\theta_2(0,iv) - 1 \quad \text{(A2)}$$

where

$$\theta_2(0,iv) = 2\sum_{n=0}^{\infty}e^{-\pi v(n+(1/2))^2} \quad \text{(A3)}$$

In the limit of interest, $r^2/\tau = \pi v << 1$, the appropriate form of the θ function in eq A2 is[9]

$$\frac{dS}{dv} = \pi - \frac{\pi}{2v^{1/2}}e^{\pi v/4}\theta_0(0,i/v) \quad \text{(A4)}$$

where

$$\theta_0(0,i/v) = 1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-\pi n^2/v} \quad \text{(A5)}$$

Integrating both sides of eq A4 with respect to v and noting that $S(0) = 1$, we obtain

$$S(v) = 1 + \pi v - \frac{\pi}{2}\int_0^v \frac{dx\, e^{\pi x/4}}{x^{1/2}}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-\pi n^2/x}\right] dx \quad \text{(A6)}$$

In the limit $v << 1$, we obtain the following approximate expression for $S(v)$, retaining only the dominant contribution from the integral in (A6)

$$S(v) \simeq 1 + \pi v - \pi v^{1/2} \quad \text{(A7)}$$

Substituting (A7) for the sum in eq 7, with $r^2/\tau = \pi v$, we obtain

$$\langle R(r)\rangle \simeq (\pi\tau)^{1/2} \qquad r^2/\tau << 1$$

Appendix B. Solution of the Diffusion Equation 2 for the Initial Condition 15

The general solution of the diffusion eq 2 with the boundary condition $n(R,\theta,\varphi;\tau) = 0$ is[10]

$$n(r,\theta,\varphi;\tau) = \sum_{n=0}^{\infty}\sum_{\alpha}\sum_{m=0}^{n}(\alpha r)^{-1/2}e^{-\alpha^2\tau}J_{n+(1/2)}(\alpha r)P_m^{\ n}(\cos\theta)\times(A_{nm\alpha}\cos m\varphi + B_{nm\alpha}\sin m\varphi) \quad \text{(B1)}$$

where the summation index α denotes the positive roots of $J_{n+(1/2)}(\alpha R) = 0$, where $J_{n+(1/2)}(x)$ is a Bessel function of the first kind of order $n + (1/2)$, $P_n^{\ m}(\cos\theta)$ is an associated Legendre function, and the coefficients $A_{nm\alpha}$ and $B_{nm\alpha}$ are determined by the initial condition. In the present case where the initial condition 15 is symmetric around the polar axis and antisymmetric in the equatorial plane,

$$A_{nm\alpha} = B_{nm\alpha} = 0 \qquad \text{for all } m > 0$$

and

$$A_{n0\alpha} = \frac{(2n+1)\alpha^{1/2}}{2\pi R^2}\Big/\frac{1}{[J_{n+(1/2)}'(\alpha R)]^2}\int_0^R r^{3/2}J_{n+(1/2)}(\alpha r)\,dr \times\int_0^{\pi}\sin\theta\, P_n(\cos\theta)\,d\theta\int_0^{2\pi}n(r,\theta,\varphi;0)\,d\varphi \quad \text{(B2)}$$

Thus the solution of eq 2 for the initial condition 15 is

$$n(r,\theta,\varphi;\tau) = \sum_{n\ \rm odd}\sum_{\alpha}\left(\frac{2n+1}{\pi R^2(r\epsilon)^{1/2}}\right)e^{-\alpha^2\tau}\times\frac{J_{n+(1/2)}(\alpha\epsilon)J_{n+(1/2)}(\alpha r)}{[J_{n+(1/2)}'(\alpha R)]^2}P_n(\cos\theta)P_n(1-\alpha) \quad \text{(B3)}$$

In the limit of small ϵ and γ, the initial condition is concentrated just above (and below) the center of the sphere of radius R. As $\epsilon \to 0$ with $0 \le \gamma < 1$, the solution $n(r,\theta,\varphi;\tau)$ approaches zero proportional to ϵ because the equatorial plane is equivalent to an absorbing plane. For this reason, we form the limit function

$$v(r,\theta,\varphi;\tau) = \lim_{\epsilon\to 0}\lim_{\gamma\to 0} \epsilon^{-1} n(r,\theta,\varphi;\tau) = \left(\frac{2}{\pi^3 R^7}\right)^{1/2} \cos\theta \sum_{i=1}^{\infty} \left(\frac{s_i^3}{r}\right)^{1/2} \frac{J_{3/2}(s_i r/R)}{[J_{3/2}'(s_i)]^2} e^{-s_i^2\tau/R^2} \quad \text{(B4)}$$

In the limit $\epsilon \to 0$ in eq B3, only the terms with $n = 1$ survive. The sum on α is replaced by an equivalent sum on i where s_i denotes the ith positive root of $J_{3/2}(x) = 0$. The limit function $v(r,\theta,\varphi;\tau)$ is proportional to the probability density of the location of the chain end at r,θ,φ (in the hemisphere of radius R above the impenetrable equatorial plane) for those chains of length τ which start immediately above the origin and never wander outside the hemisphere of radius R. The integral over the hemisphere,

$$\psi(R,\tau) = \int_0^R \mathrm{d}r \int_0^{\pi/2} \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\varphi/v(r,\theta,\varphi;\tau) = \frac{1}{R}\sum_{i=1}^{\infty}\left(\frac{2}{\sin^2 s_i} - \frac{2}{s_i \sin s_i} - \frac{s_i}{\sin s_i}\right) e^{-s_i^2\tau/R^2} \quad \text{(B5)}$$

is proportional to the fraction of all chains which start at the origin, are of length τ, and are contained in the hemisphere of radius R above an impenetrable surface. The normalized fraction is

$$\Psi(R,\tau) = c^{-1}\psi(R,\tau)$$

where

$$c = \lim_{R\to\infty} \psi(R,\tau)$$

References and Notes

(1) M. V. Volkenstein, "Configuration Statistics of Polymeric Chains", Interscience, New York, N.Y., 1963, Chapter 4.
(2) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter 2.
(3) A. Katchalsky, O. Kuenzle, and W. Kuhn, *J. Polym. Sci.*, **5**, 283 (1950).
(4) E. A. DiMarzio and R. J. Rubin, *J. Chem. Phys.*, **55**, 4318 (1971).
(5) C. A. Hollingsworth, *J. Chem. Phys.*, **16**, 544 (1948).
(6) M. J. Lighthill, "Fourier Analysis and Generalized Functions", Cambridge Univesity Press, New York, N.Y., 1958, pp 67–71.
(7) The explicit result in eq 10 was obtained independently by J. J. Weidmann, H. Kuhn, and W. Kuhn, *J. Chim. Phys. Phys.-Chim. Biol.*, **50**, 226 (1953).
(8) The results reported here were announced in R. J. Rubin and G. H. Weiss, *Bull. Am. Phys. Soc.*, **21**, 374 (1976).
(9) P. M. Morse and M. Feshbach, "Methods of Theoretical Physics", Vol. 1, McGraw-Hill, New York, N.Y., 1953, p 489.
(10) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", 2nd ed, Oxford University Press, London, 1959, p 250.

Notes

Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. 6. The Second State of Ease

HSIN-CHIA KAN and JOHN D. FERRY*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received May 30, 1978*

The cross-linking of 1,2-polybutadiene strained in simple extension has been described in previous papers of this series.[1-3] When a strained sample with stretch ratio λ_0 is cross-linked with γ irradiation near the glass transition temperature (T_g), the resulting cross-link network traps the entanglements originally present; after release and warming, the sample seeks a state of ease with stretch ratio λ_s in which the forces associated with the cross-links and the trapped entanglements act in opposite directions. From λ_0 and λ_s, together with stress–strain measurements in small extensions from the state of ease, or simply from the equilibrium stress at λ_0, the concentration of trapped entanglement strands ν_N can be calculated; the proportion of entanglements trapped, T_e, can be compared[3] with the theory of Langley.[4]

It was recognized when these experiments were undertaken[5,6] that untrapped entanglements might at first contribute to the retractive force toward the original unstrained state so that a first state of ease λ_s' would be reached followed by partial reversal of the retraction to a second state of ease λ_s as the strands terminated by untrapped entanglements rearrange their configurations. Until recently, only one state of ease was observed; ordinarily, the retraction kinetics and the relaxation of untrapped entanglement strands involve similar time scales and are not distinguishable.[3] However, if the degree of cross-linking is very slight, and precise length measurements are made, a reversal of retraction can be observed, as described in the present note.

A 1,2-polybutadiene with 96% vinyl microstructure, number-average molecular weight 96 000, T_g −10 °C, generously supplied by Dr. G. G. A. Böhm of Firestone Tire and Rubber Company (previously[3] identified as Polymer C), was strained in simple extension to a stretch ratio λ_0 of approximately 1.9 and cross-linked by γ irradiation as previously described.[1-3] Distances between fiducial marks on the sample strip were measured by a travelling microscope before irradiation. During irradiation, the sample was attached to a steel band,[3] and after irradiation the stretched length was measured on the band. Finally, the sample was released and flattened on a base of Teflon; distances were measured again by a travelling microscope, first at 0 °C, then at higher temperatures where the relaxation processes are faster. All lengths were corrected for thermal expansion with a linear expansion coefficient of 2.5×10^{-4} deg^{-1} to a reference temperature of 23 °C. Only the last portion of the retraction is measured by this procedure, since 80% of it or more occurs before the first measurements are taken.

From the values of λ_0 and λ_s, the ratio $R_0' = \nu_x/\nu_N$ can be calculated, where ν_x is the concentration of network strands terminated by cross-links, by use of a three-constant Mooney–Rivlin formulation.[2] With additional data on stress–strain relations in deformation from the state of ease, both ν_x and ν_N can be calculated, and from them the average number of cross-link points per original molecule (γ) and the experimental fraction of entanglements trapped (T_e). For one sample, these quantities were estimated from other data on a sample with similar thermal history and irradiation dose. All values are summarized in Table I for these experiments.

0024-9297/78/2211-1049$01.00/0