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EFFECTS OF DILUTION DURING CROSSLINKING ON STRAIN-INDUCED CRYSTALLIZATION IN *CIS*-1,4-POLYISOPRENE NETWORKS. II. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

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**EFFECTS OF DILUTION DURING
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EXPERIMENTAL RESULTS WITH THEORY**

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ABSTRACT

Modern rubber elasticity theory was applied to the strain-induced crystallization results summarized for *cis*-1,4-polyisoprene in the preceding paper. The calculations adopted the basic assumptions made in the Flory crystallization theory, in some cases retaining the original affine elasticity model and in others adopting the new constrained-junction model. Of the two sets of theoretical stress-strain isotherms thus obtained, those from the constraint theory gave a good account of the experimental results. One major accomplishment was documenting the expected decrease in the constraint parameter κ with increase in dilution during crosslinking. This decrease is due to the fact that the diluting solvent decreases chain interpenetration, which in turn decreases entanglement constraints on the junction fluctuations.

Key Words: Constrained-junction theory; Polyisoprene; Entangling; Supercontraction

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INTRODUCTION

Stress-strain isotherms for solution crosslinked polymers have been successfully interpreted using constrained-junction theory [1] and constrained-chain theory [2], but not for the case of elastomers undergoing strain-induced crystallization. Similarly, there has been some interpretation of strain-induced crystallization in networks [3, 4], but not for any that had prepared in the diluted state and then deswollen. The primary purpose of the present investigation was therefore to use the constrained-junction theory [5] to interpret the results on strain-induced crystallization of solution crosslinked *cis*-1,4-polyisoprene, as described in the preceding paper [6] and elsewhere [7].

The increase in modulus at higher elongations in crystallizable networks is attributed to the formation of crystallites upon the orientation of neighboring chains in the network structure. In order to interpret this behavior, a theory of strain-induced crystallization was first developed by Flory using a statistical mechanical procedure [8]. Recently, the application of the constrained-junction theory [3, 4] to elastomeric networks undergoing strain-induced crystallization considerably improved the molecular understanding of such type of behavior. All of these networks, however, had been prepared in the dry state.

The purpose of the present investigation was therefore to apply the constrained-junction theory to the strain-induced crystallization exhibited by *cis*-1,4-polyisoprene (PIP) networks formed in solution, and to compare the results with Flory's theory of strain-induced crystallization [8] and with experimental results. Specifically, the experimental data were those on PIP networks crosslinked at different degrees of dilution and then studied in the deswollen state [6, 7].

Molecular Theories of Strain-Induced Crystallization

Flory Affine Theory

A statistical thermodynamic theory for strain-induced crystallization was first developed by Flory [8]. This theory is applicable only under conditions of incipient equilibrium crystallization, and is facilitated by several assumptions and approximations. It is assumed that the possibly small entropy changes associated with the formation of nuclei are negligible, and that the crystallites formed are parallel to the direction of stretch. Furthermore, it is assumed that the chains are Gaussian and deform affinely, and that each chain traverses the crystallite only once, i.e., there is no chain folding within the crystallite. This statistical theory of strain-induced crystallization unveiled the relationship between the incipient crystallization temperature and

elongation, the degree of crystallinity ω with elongation and temperature, and the retractive force at crystallization equilibrium with elongation at constant temperature.

The degree of crystallization [8] is given by:

$$\omega = 1 - \{[3/2 - \varphi(\alpha)](3/2 - \theta)\}^{1/2} \quad (1)$$

where:

$$\varphi(\alpha) = (6/\pi n)^{1/2} \alpha^2/2 + \alpha^{-1}/n \quad (2)$$

and:

$$\theta = \left(\frac{H_f}{R}\right) \left(\frac{1}{T_m^0 - \frac{1}{T}}\right) \quad (3)$$

Here, λ is the elongation in simple tension (which is the ratio of deformed length to the length at the state of formation of the network), and n is the number of statistical segments in a freely-jointed chain, H_f is the molar heat of fusion per segment, and T_m^0 is the incipient crystallization temperature of the undeformed polymer. The melting point elevation with strain is given by [8]:

$$1/T_m = 1/T_m^0 - (R/H_f)\varphi(\alpha) \quad (4)$$

when the equilibrium degree of crystallinity is very small, at low elongations. As a result of the approximation in which each chain is assumed to traverse the crystallite in the direction of the displacement of its ends with respect to the z-axis, T_m does not coincide with T_m^0 at $\lambda = 1$, as it should.

The nominal stress f^* at equilibrium in a stretched polymer network is expressed as [8]:

$$f^* = \nu RT[(\alpha - \alpha^{-2}) - (6n/\pi)^{1/2}\omega]/(1 - \omega) \quad (5)$$

where ν is the number of moles of network chains per unit volume.

Constrained-Junction Theory

Recently, the constrained-junction theory was applied to polymer networks undergoing strain-induced crystallization and the results compared with those from Flory's theory and from experiment [3]. In this treatment, the constrained-junction theory was treated in a way similar to that in Flory's theory, with the same assumptions. In addition, it was assumed that the parameters κ and ζ remain constant during the strain-

induced crystallization, in part because their dependence on degree of crystallization is unknown. The melting point T_m was not found to be equal to T_m^0 for the undeformed network in this treatment, as is also true in Flory's theory. A similar study was performed using the constrained-chain theory [4]. These applications of the constrained-junction theory and constrained-chain theory to strain-induced crystallization considerably improved the predictions of Flory's theory for this important reinforcing effect in elastomers.

Analysis of Strain-Induced Crystallization

The constrained-junction model [1] and constrained-chain model [2] have been applied to networks crosslinked in solution. These theories are based on the fact that the deviation from phantom behavior is due to the severity of the interpenetration or entanglements of the network chains, and how they change with deformation or swelling [5, 9–11]. In these studies, the constraint parameter κ was found to be related to the volume fraction v_{2c} of polymer chains in the system being cross linked which are successfully incorporated into the network structure by:

$$\kappa = A(2C_1)^{-1/2}(v_{2c})^{(4/3+m)} \quad (6)$$

where m takes into account the heterogeneities in the network structure.

In these applications of constrained-junction theory, the coefficient A was determined to be 2, and the values of m ranged from 2/3 and 8/9, although the value $m=0$ is expected from theory [1]. The decrease in κ with a decrease in v_{2c} (increases in dilution during crosslinking) indicates that the larger the amount of solvent present during crosslinking, the smaller the chain interpenetration and, thus, the less severe the entanglement constraints. This parameter also decreases with increase in crosslinking (increase in the elasticity constant $2C_1$) [7], due to decrease in interpenetration as the network chain length decreases. In addition, the heterogeneity parameter ζ strongly increases with a decrease in v_{2c} , possibly indicating increased heterogeneity in the networks crosslinked in solution.

The analysis of the same experimental results using the subsequent constrained-chain model [2] gave values of κ that were significantly smaller than those from the constrained-junction model [1]. Presumably, this is due to the constraints being imposed along the chains and not only at the junctions. According to this latter investigation, $A=2.9$ and $m=0.385$.

Present Application of the Theory

The density of the polymer during cross-linking is given by [12]:

$$d = \left(\frac{\nu M_c}{N_A} \right) \left(\frac{1}{V_o} \right) \quad (7)$$

where N_A is Avogadro's number, M_c is the number-average molecular weight of the network chains, and V_o the volume of the reference state (i.e., the volume during network formation). Substituting $\nu = \xi / (1 - 2/\phi)$ into Eq. 7, and rearranging [7] gives:

$$d = \left[\frac{\xi}{(1 - \frac{2}{\phi})} \right] \left(\frac{M_c}{N_A} \right) \left(\frac{1}{V_d} \right) \left(\frac{V_d}{V_o} \right) \quad (8)$$

where V_d is the volume of the extracted dried network.

In the case of crosslinking in solution, V_o is the total volume of the polymer plus solvent during crosslinking. Therefore, $V_d/V_o = V/V_o = \nu_{2c}$. Substituting this into Eq. 8 gives $d = d_o \nu_{2c}$, where d_o is the density of the dried network. Also, the cycle rank density is:

$$\frac{\xi}{V_o} = \left(1 - \frac{2}{\phi} \right) d \frac{N_A}{M_c} = (\xi/V_d) \nu_{2c} \quad (9)$$

The modulus for a phantom network can be generalized to:

$$[J_{ph}^*] = \left(\frac{\xi k T}{V_d} \right) (\nu_{2c})^{2/3} \quad (10)$$

for a phantom network crosslinked in solution. In the limiting case of a perfect network crosslinked in the undiluted state $\nu_{2c} = 1$. Usually $\nu_{2s} > \nu_{2c}$ for a real network. According to the Mooney-Rivlin equation, $2C_1$ can be taken as the phantom modulus at very high elongation ($\alpha^{-1} \rightarrow 0$). Therefore, Eq. 10 can also be written

$$2C_1 \cong \left(\frac{\xi k T}{V_d} \right) (\nu_{2c})^{2/3} \quad (11)$$

In the theory, the parameter κ serves as a measure of the severity of the entanglement constraints relative to those imposed by a "phantom network," where such constraints are absent [13]. If κ is taken to be proportional to the

degree of interpenetration of chains and junctions, then for a tetrafunctional network [14]:

$$\kappa = I \left(\frac{\langle r^2 \rangle_0}{M} \right)^{3/2} M_c^{3/2} \frac{\xi}{V_0} \quad (12)$$

where I is the interpenetration proportionality constant, $\langle r^2 \rangle_0$ the mean square end-to-end distance of the unperturbed network chains, and M the molecular weight per skeletal bond. If the molecular weights of the network chains are not too small, the quantity $(\langle r^2 \rangle_0/M)^{3/2}$ may be taken to be constant for a given polymer. For a tetrafunctional network [14], $M_c = V_0 N_A d / 2\xi$. Then [7]

$$\kappa = I \left(\frac{N_A d_0}{2} \right)^{3/2} \left(\frac{\langle r^2 \rangle_0}{M} \right)^{3/2} \left(\frac{kT}{[2C_1]} \right)^{1/2} v_{2c}^{4/3} \quad (13)$$

$$= A(2C_1)^{-1/2} v_{2c}^{4/3} \quad (14)$$

This predicts how κ should vary with the concentration of polymer present during cross-linking. It is advantageous to generalize the above equation to the form given in Eq. 6 [1].

In the present study of the strain-induced crystallization, incipient equilibrium crystallization was considered. It was assumed that entropy changes associated with the formation of nuclei are negligible and the crystallites formed are oriented parallel to the direction of stretch. Each chain is assumed to traverse the crystallite only once. In addition, the parameters κ and ζ were assumed to be remained constant during the strain-induced crystallization.

If a network chain consists of n statistical chain segments, and η number of segments crystallize due to the stretching, the relative number of segments left in the amorphous regions of the chain is $\gamma = (n - \eta)/n$.

The retractive force for a stretched network at constant γ is given by [3, 4, 7].

$$f = \left(\frac{\partial A}{\partial \alpha} \right)_\gamma = \left\{ \frac{\partial A}{\partial \Lambda_x^2} \frac{\partial \Lambda_x^2}{\partial \alpha} + \frac{\partial A}{\partial \Lambda_y^2} \frac{\partial \Lambda_y^2}{\partial \alpha} + \frac{\partial A}{\partial \Lambda_z^2} \frac{\partial \Lambda_z^2}{\partial \alpha} \right\}_\gamma \quad (15)$$

Here, A is the free energy of the system with respect to a totally crystalline chain, and Λ_t^2 is the microscopic deformation tensor with $t = x, y, z$. For the constrained-junction theory Λ_t^2 can be written [15]:

$$\Lambda_t^2 = (1 - 2/\phi)\gamma_t^2 + (2/\phi)1 + B_t \quad (16)$$

where B_t is given by the general form:

$$B_i = \frac{(\lambda_i - 1)(1 + \lambda_i - \zeta\lambda_i^2)}{(1 + g_i)^2} \quad (17)$$

with

$$g_i = \lambda_i^2[\kappa^{-1} + \zeta(\lambda_i - 1)] \quad (18)$$

Also of use will be the derivatives:

$$\dot{B}_i = B_i \left\{ [2\lambda_i(\lambda_i - 1)]^{-1} + (1 - 2\zeta\lambda_i)[2\lambda_i(1 + \lambda_i - \zeta\lambda_i^2)]^{-1} - 2\dot{g}_i(1 + g_i)^{-1} \right\} \quad (19)$$

and:

$$\dot{g}_i = \kappa^{-1} - \zeta \left(1 - \frac{3\lambda_i}{2} \right) \quad (20)$$

For a uniaxially stretched network, the principle extensions λ_t relative to the state of reference can be defined [3] in terms of the uniaxial elongation at by $\lambda_t = (V/V_o)^{1/3}\alpha_t$, assuming that the network is isotropic in the undistorted state. Here, V is the volume of the initial state before the application of deformation.

For a network crosslinked in solution and deformed in dried state, $V_d/V_o = V/V_o = v_{2c}$, and $\lambda_t = \alpha_t v_{2c}^{1/3}$. For uniaxial deformation in the z direction, $\lambda_1 = \lambda_z = \alpha_z v_{2c}^{1/3}$. Assuming that the volume of the dried network remains constant upon stretching, $\alpha_x = \alpha_y = \alpha_z^{-1/2}$, and $\lambda_2 = \lambda_x = \lambda_y = \alpha_z^{-1/2} v_{2c}^{1/3}$. It follows that:

$$\frac{\partial \Lambda_1^2}{\partial \alpha} = 2 \left[\frac{\varphi - 2}{\varphi} + \frac{2}{\varphi} \dot{B}_1 \right] v_{2c}^{2/3} \alpha \quad (21)$$

with a similar equation for Λ_2 [7], and with $\Lambda_1 = \Lambda_z$ and $\Lambda_2 = \Lambda_x = \Lambda_y$.

The free energy change of the system with respect to a totally crystalline chain is $\Delta A = \Delta H - T\Delta S$, and the heat of fusion ΔH of $(n - \eta)$ segments of n chains is given by [7] $\Delta H = v h_f (n - \eta)$, where h_f is the heat of fusion per segment. The total entropy change is $\Delta S = \Delta S_a + \Delta S_b$, where ΔS_a is the entropy change due to the melting of $(n - \eta)$ segments of each of the chains [3], and ΔS_b is the entropy change due to the change in the chain length distribution in the amorphous regions [as a result of the melting of the $(n - \eta)$ segments [3]. These entropy changes are given by $\Delta S_a = \Delta(n - \eta)s_f$, and:

$$\Delta S_b = -vk \left[\frac{n\beta^2\eta^2 l^2}{(n-\eta)} - \frac{2\beta\eta l}{\pi^{1/2}} \frac{n}{(n-\eta)} \Lambda_z + \frac{n}{2(n-\eta)} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) - \frac{3}{2} \right] \quad (22)$$

where $\beta = (3/2n)^{1/2}/l$, with l being the length of a segment. Therefore,

$$\Delta S = vk \left[\frac{n-\eta}{k} s_f - (\beta l \eta)^2 \frac{n}{(n-\eta)} + \frac{2(\beta l \eta)n}{\pi^{1/2}(n-\eta)} \Lambda_z - \frac{n}{2(n-\eta)} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) + \frac{3}{2} \right] \quad (23)$$

Assuming that the change in chain length distribution is not accompanied by a change in internal energy,

$$A = vkT \left[\eta \left(\frac{s_f}{k} - \frac{h_f}{kT} \right) + (\beta l \eta)^2 \frac{n}{(n-\eta)} - \frac{2(\beta l \eta)n}{\pi^{1/2}(n-\eta)} \Lambda_z + \frac{n}{2(n-\eta)} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) - n \left(\frac{s_f}{k} - \frac{h_f}{kT} \right) - \frac{3}{2} \right] \quad (24)$$

This can be written in molar terms as:

$$A = vRT \left[n\theta(1-\gamma) + (\beta l \eta)^2 \frac{(1-\gamma)^2}{\gamma} - \frac{2(\beta l \eta)(1-\gamma)}{\pi^{1/2}} \frac{1-\gamma}{\gamma} \Lambda_z + \frac{1}{2\gamma} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) - n\theta - \frac{3}{2} \right] \quad (25)$$

with $\gamma = (n-\eta)/n$, and $\theta = (s_f/k - h_f/kT)$. The molar value of θ assumes the form:

$$\theta = \frac{H_f}{R} \left(\frac{1}{T_m^0} - \frac{1}{T} \right) \quad (26)$$

Here, H_f is the molar heat of fusion.

Using these relationships [7], the retractive force for the uniaxially stretched network can be written:

$$f = vRT \left\{ \left[-\sqrt{\frac{6n}{\pi}} \frac{(1-\gamma)}{\gamma} \Lambda_1^{-1} + \frac{1}{\gamma} \right] \left(\frac{(\varphi-2)}{\varphi} + \frac{2}{\varphi} \dot{B}_1 \right) v_{2c}^{2/3} \alpha - \frac{1}{\gamma} \left(\frac{(\varphi-2)}{\varphi} + \frac{2}{\varphi} \dot{B}_2 \right) v_{2c}^{2/3} \alpha^{-2} \right\} \quad (27)$$

The force f becomes the stress f^* when v is a density, specifically the number of \dot{B}_2 network chains per unit volume of the dried network.

The modulus in uniaxial elongation is defined by $[f^*] = f^* v_2^{1/3} / (\alpha - \alpha^{-2})$, where v_2 is the volume fraction of polymer during the deformation. For a network stretched in undiluted state, $v_2 = 1$. Accordingly,

$$[f^*] = [vRTv_{2c}^{2/3} / \gamma(\alpha - \alpha^{-2})] \{ [-(6n/\pi)^{1/2}(1 - \gamma)\Lambda_1^{-1} + 1] \\ \times [(\varphi - 2)/\varphi - 2/\varphi] B_1 \alpha \} - [(\varphi - 2)/\varphi + (2/\varphi) B_2] \alpha^{-2} \quad (28)$$

The condition for equilibrium with respect to the longitudinal growth of the crystallites can be expressed as $(\frac{\partial A}{\partial \eta})_{\Lambda_x, \Lambda_y, \Lambda_z} = 0$. This then gives [7]:

$$\left(\frac{1}{vkT} \right) \left(\frac{\partial A}{\partial \gamma} \right)_{\Lambda_x, \Lambda_y, \Lambda_z} = - \left[n\theta + (\beta ln)^2 \left(\frac{1}{\gamma^2} - 1 \right) - \frac{2(\beta ln)}{\pi^{1/2} \gamma^2} \Lambda_z \right. \\ \left. + \frac{1}{2\gamma^2} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) \right] \quad (29)$$

which, on equating to zero gives:

$$\theta_\gamma^2 + n\beta^2 l^2 (1 - \gamma^2) = \Phi(\Lambda_x, \Lambda_y, \Lambda_z) \quad (30)$$

where

$$\Phi(\Lambda_x, \Lambda_y, \Lambda_z) = \frac{2\beta l}{\pi^{1/2}} \Lambda_z - \frac{1}{2n} (\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) \quad (31)$$

Substituting $\beta = (3/2n)^{1/2} / l$ into this equation yields:

$$\Phi(\Lambda_x, \Lambda_y, \Lambda_z) = \left(\frac{6}{\pi n} \right)^{1/2} \Lambda_z - \frac{(\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2)}{2n} \quad (32)$$

Solving for equilibrium value of γ then gives [7]

$$\gamma = \frac{[\frac{3}{2} - \Phi(\Lambda_x, \Lambda_y, \Lambda_z)]^{1/2}}{[\frac{3}{2} - \theta]^{1/2}} \quad (33)$$

Finally, the degree of crystallinity of the κ chains under consideration is defined as $\omega = 1 - \gamma$.

This development is reasonably satisfactory for low degree of crystallinity. In reality, a given chain may pass through several crystalline regions, because of the simultaneous occurrence of nucleation and the growth of already-existing crystalline regions. Generally, these several crystalline regions will not be co-linear, and at relatively high values of ω additional x and y restraints may consequently be imposed. However, the above calculations should represent useful approximations.

Flory's theory is a useful approximation at relatively small values of ω . At $\gamma = 1$, $T = T_m$, and Eq. 30 can be written:

$$\theta = \left(\frac{H_f}{R} \right) \left(\frac{1}{T_m^0} - \frac{1}{T_m} \right) = \Phi(\Lambda_x, \Lambda_y, \Lambda_z) \quad (34)$$

The dependence of crystallization temperature on elongation can be expressed as:

$$\frac{1}{T_m} = \frac{1}{T_m^0} - \frac{R}{H_f} \Phi(\Lambda_x, \Lambda_y, \Lambda_z) \quad (35)$$

At higher elongations, $\Phi(\Lambda_x, \Lambda_y, \Lambda_z)$ can be approximated as:

$$\Phi(\Lambda_x, \Lambda_y, \Lambda_z) \cong \left(\frac{6}{\pi n} \right)^{1/2} \Lambda_z - \frac{1}{2n} \Lambda_z^2 \quad (36)$$

For the undeformed network, T_m is not equal to T_m^0 in the present treatment of constrained-junction theory as is also true in Flory's theory, because $\phi(\Lambda_x, \Lambda_y, \Lambda_z)$ is identical to $\Phi(\gamma)$ for the undeformed network.

Numerical Calculations

Theoretical stress-strain isotherms based on the constrained-junction theory were generated using Eq. 28. The functionality ϕ and the quantity m were taken to be equal to 4 and 7/9, respectively [1]. For all the PIP networks, values of H_f and T_m^0 used in calculations were 1040 cal/mol of repeat units [16] and 232 K [17], respectively. It was assumed that the number of statistical chain segments were equal to the number of repeat units, and the density of the networks were taken as 0.9421 g/cm³. The best theoretical fit for each experimental stress-strain isotherm was obtained using a global-search method [18]. In this method, the cumulative squared error between the theoretical and experimental stress-strain isotherms was minimized by varying ν , κ , n and A . The values of these parameters which gave this minimum error were taken as the most reliable values.

RESULTS AND DISCUSSION

Figures 1 through 4 show some comparisons among stress-strain isotherms based on the constrained-junction theory, Flory's original theory, and experiment [6, 7]. Additional results are shown elsewhere [7]. Comparisons between Fig. 1 and Fig. 2 show that the isotherms are only slightly changed in going from the lowest degree of crosslinking to the highest, in the case of

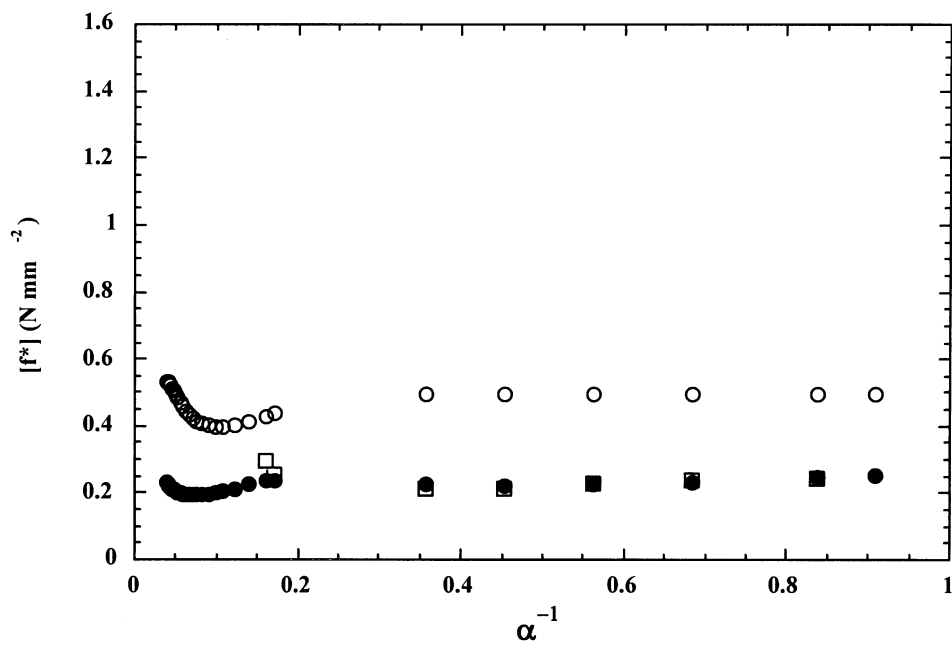


Figure 1. Comparison of stress-strain isotherms obtained from the constrained-junction theory (●) and Flory's theory (○) with experimental results (□) for the *cis*-1,4-polyisoprene sample cross linked at the dilution $v_{2s} = 1.0$ for 1 hour.

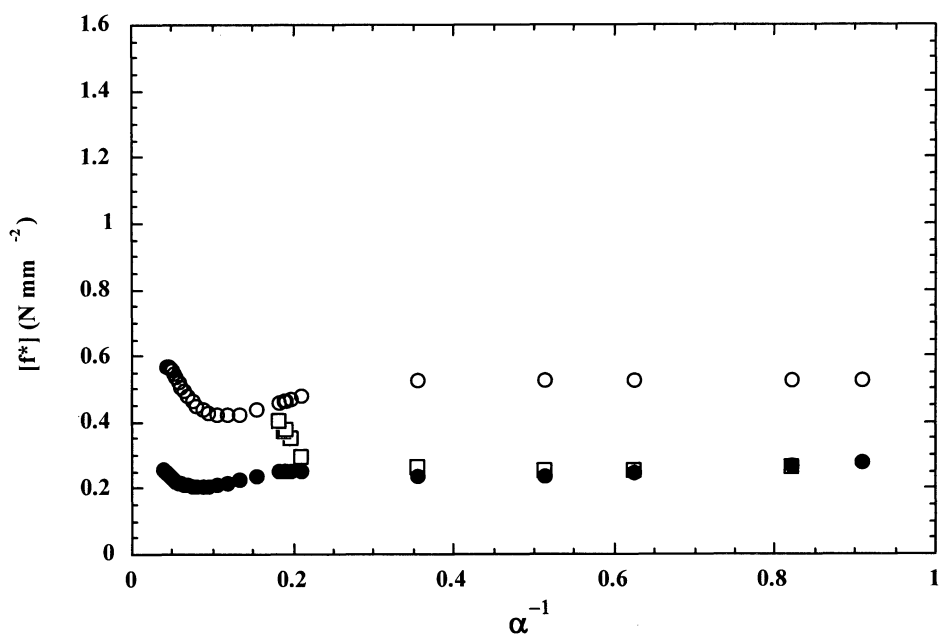


Figure 2. Same as in Fig. 1, but for 3 hours.

the chains crosslinked in the unswollen state. On the other hand, Figs. 3 and 4 shows similar results for the networks prepared at the highest degree of dilution, $v_{2s} = 0.4$. As expected, both Flory's theory and the present application of the constrained-junction theory showed upturns in modulus at high elongations. There is a downturn in modulus just prior to its upturn in the isotherms based on Flory's theory and the constrained-junction theory. The corresponding experimental stress-strain isotherms do not exhibit such downturns, which is consistent with previous experimental stress-strain isotherms obtained for peroxide-cured networks at low temperatures [19, 20]. According to the previous experimental studies [19, 20], a downturn in modulus in the linear portion of the stress-strain isotherms appeared only at moderate temperatures for peroxide-cured networks. This behavior was explained by the fact that there was straightening and aligning of the network chains [5], due to strain-induced crystallization. This would cause decreases in the deformation in the remaining amorphous regions, with corresponding decreases in the modulus [19, 20]. In addition, increases in modulus from the reinforcing effects of the crystallites are apparently not very large during this downturn.

Upturns in the stress-strain isotherms from the constrained-junction theory appear at higher elongations than those from Flory's theory. This is due to the fact that the microscopic deformation Λ_Z in the constrained-junction theory is less than the macroscopic deformation λ_Z . Stress-strain

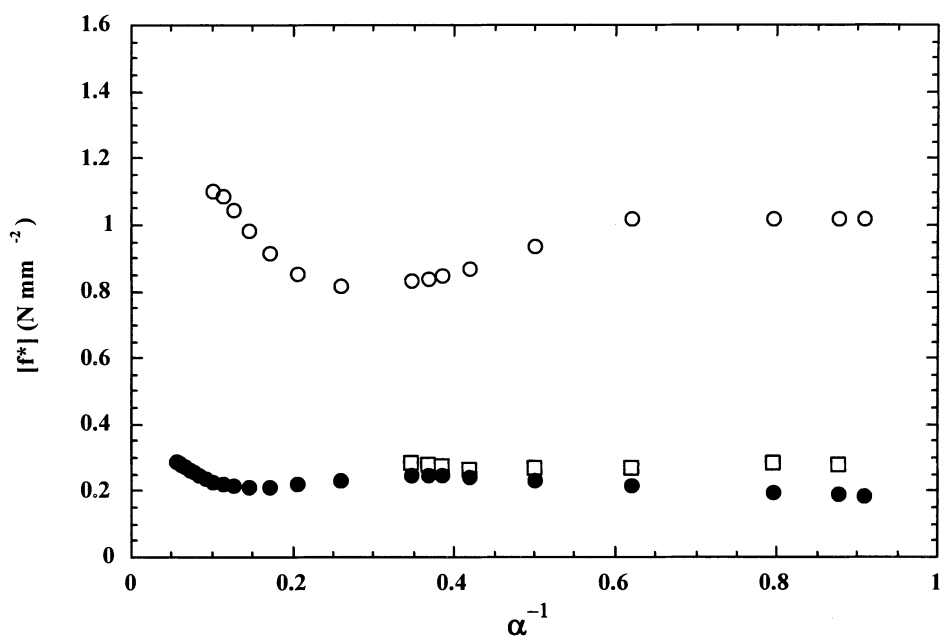


Figure 3. Same as Fig. 1, but for $v_{2s} = 0.4$ and 3 hours.

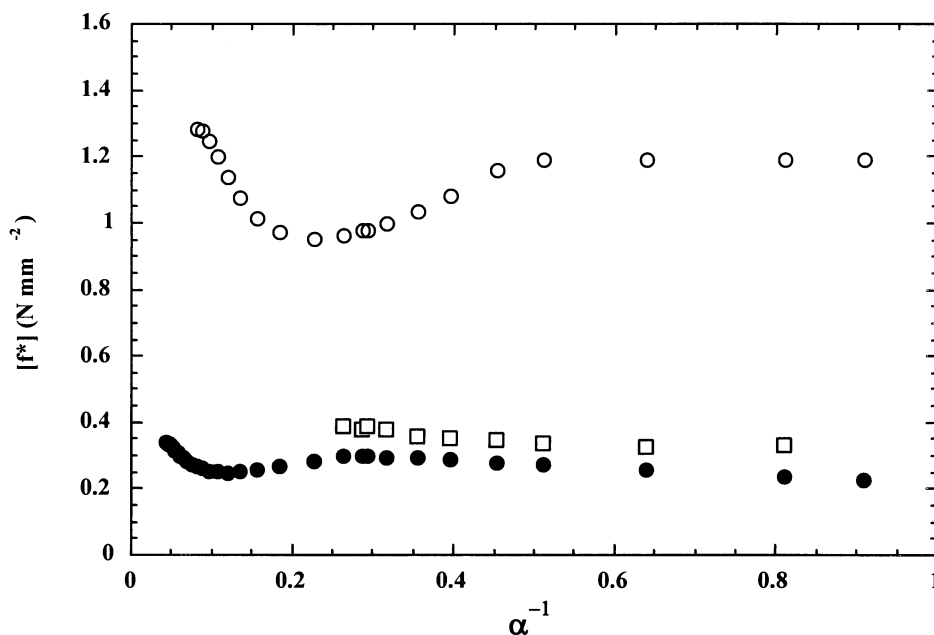


Figure 4. Same as Fig. 1, but for $v_{2s} = 0.4$ and 7 hours.

isotherms obtained from Flory's theory are higher in modulus compared with the corresponding experimental stress-strain isotherms. This is due to the fact that Flory's theory for strain-induced crystallization is based on the affine theory and calculated values of the modulus according to this theory correspond to the affine limit.

The stress-strain isotherms for the networks crosslinked at different dilutions show that the present application of the constrained-junction theory is in at least qualitative agreement with the experimental results. The upturns in the theoretical stress-strain isotherms in the present study also appear at higher elongations than those in corresponding experimental stress-strain isotherms, however. This is attributed to the fact that these theories are based on Gaussian chains. Furthermore, the minima in the resulting theoretical isotherms appear at elongation ratios smaller than the maximum elongation ratio α_{\max} for freely-jointed chains ($\alpha_{\max} \propto n^{1/2}$). Accordingly, it can be concluded that these theoretical upturns in the modulus are probably due to strain-induced crystallization. However, a theory based on a non-Gaussian distribution should yield better agreement with the experimental results. Specifically, the non-Gaussian effects caused by the shortening of the network chains from the strain-induced crystallization should affect the experimental results.

In Flory's theory and in the present application of the constrained-junction theory, the incipient crystallization is assumed to occur under

equilibrium conditions, which would correspond to the network being stretched above its T_m and then slowly cooled to temperatures below T_m (without further stretching). Under these equilibrium conditions, the development of crystallinity results in a reduction of the tensile force by an amount greater than that predicted from rubberlike elasticity theory [5]. It is important to emphasize here that the experimental stress-strain isotherms used in the present investigation were obtained by a step-wise stretching of the networks at a constant temperature of 5°C, which is higher than T_m . Therefore, the incipient crystallization occurs under non-equilibrium conditions. According to Flory, under non-equilibrium conditions, ζ increases with increase in heterogeneity in the network structure [13], but is generally quite small [14, 21]. Interestingly, in the present investigation the values for ζ in all the samples were found to be equal to zero.

Results shown in Table 1 and Fig. 5 document the dependence of κ on ν_{2c} , specifically showing that κ decreases markedly with increase in ν_{2c} , as expected. This is mainly due to the fact that crosslinking in solution decreases the chain interpenetration and, hence, decreases entanglement constraints on junction fluctuations [5]. Accordingly, the value of κ should be decreased [14], and the present results establish the magnitudes involved. This conclusion is also supported by the observation that the average value of $2C_2/2C_1$ decreased with decrease in ν_{2s} , due to decreases in chain entanglements.

Table 1. Network Characteristics and Constrained-Junction Theory Parameters for the Interpretation of the Experimental Results

| Sample | κ | A |
|--------|----------|-----|
| B-1 | 3.48 | 1.6 |
| B-2 | 3.76 | 1.8 |
| B-3 | 3.65 | 1.8 |
| S.8-1 | 3.21 | 3.0 |
| S.8-2 | 3.00 | 2.6 |
| S.8-3 | 3.09 | 2.8 |
| S.8-4 | 3.03 | 2.8 |
| S.6-1 | 1.65 | 3.0 |
| S.6-2 | 1.81 | 3.0 |
| S.6-3 | 1.84 | 3.0 |
| S.6-4 | 1.72 | 3.0 |
| S.6-5 | 1.53 | 3.0 |
| S.4-1 | 0.279 | 1.0 |
| S.4-2 | 0.273 | 1.0 |
| S.4-3 | 0.267 | 1.0 |
| S.4-4 | 0.251 | 1.0 |
| S.4-5 | 0.239 | 1.0 |

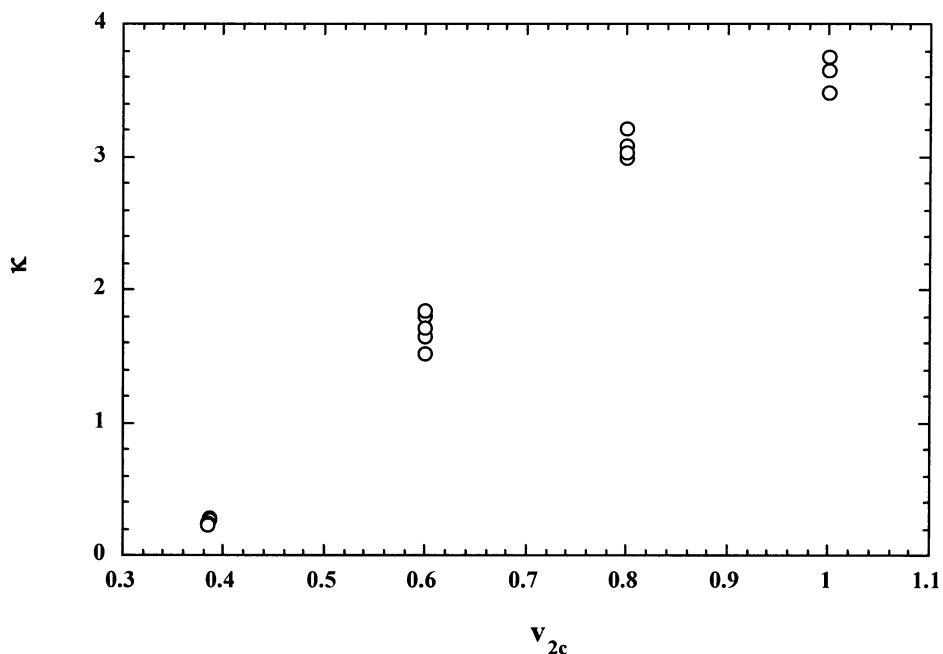


Figure 5. The dependence of κ on v_{2c} obtained from the constrained-junction theory for PIP networks crosslinked at various dilutions. The set of values of κ that are the highest are for the B series, the next highest for the S.8, series the next highest for the S.6 series, and the lowest for the S.4 series. Detailed specifications are given in Table 1.

As shown in Table 1 and Fig. 6, κ strongly decreases with increase in network chain density (degree of crosslinking). This reflects the fact that increases in v/V_d correspond to decreases in network chain lengths, which decrease chain interpenetration and thus lower the values of κ . These variations in κ are consistent with the previous experimental results [16]. It should be mentioned here that the crystallites being formed in a crystallizable network upon stretching may also increase the constraints on junction fluctuations, leading to higher values of κ .

The dependences of the degree of crystallinity ω on α calculated from the constrained-junction theory are shown in Figs. 7 and 8, and elsewhere [7]. All the networks cross linked at the various dilutions show an increase in ω with increase in α . The elongation for the onset of crystallization based on the constrained-junction theory is higher than that in the experimental results. This is not surprising, since the constrained-junction theory assumes that the network chains are Gaussian. The dependences of the melting temperature calculated according to constrained-junction theory are shown in Figs. 9 and 10, and additional similar results are shown elsewhere [7]. The T_m increases with increasing elongation in all cases.

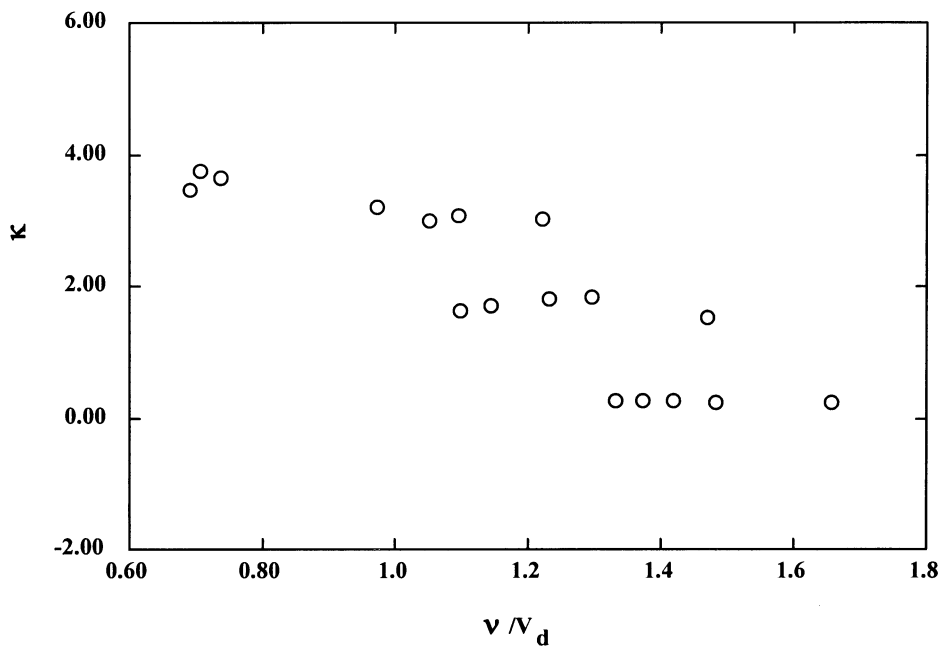


Figure 6. Same as Fig. 5, but showing the dependence of κ on v/V_d .

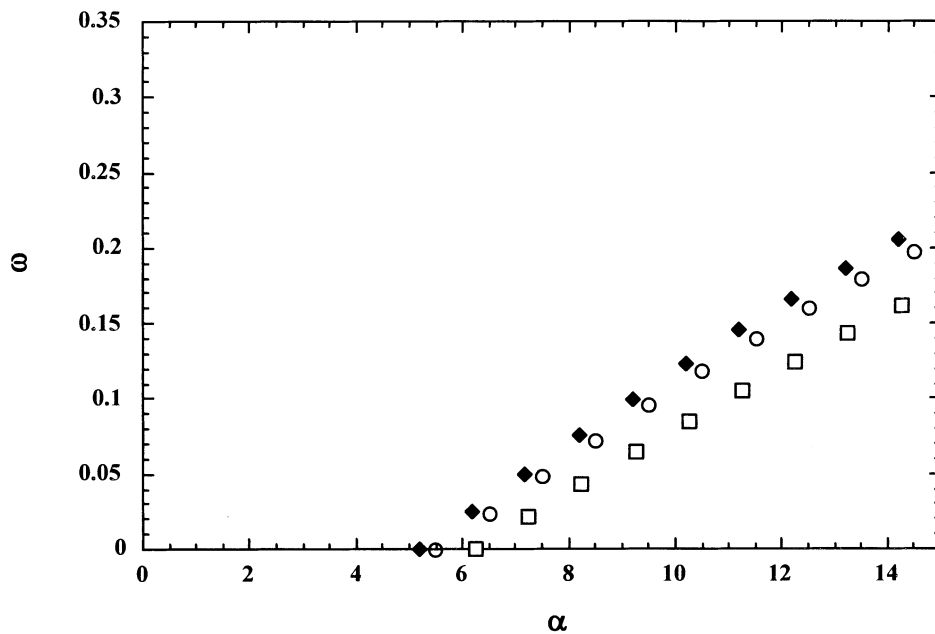


Figure 7. The dependence of the degree of crystallization on elongation obtained from the constrained-junction theory for PIP networks cross linked at $v_{2s} = 1.0$, for 1 hour (□), 2 hours (◆), and 3 hours (○).

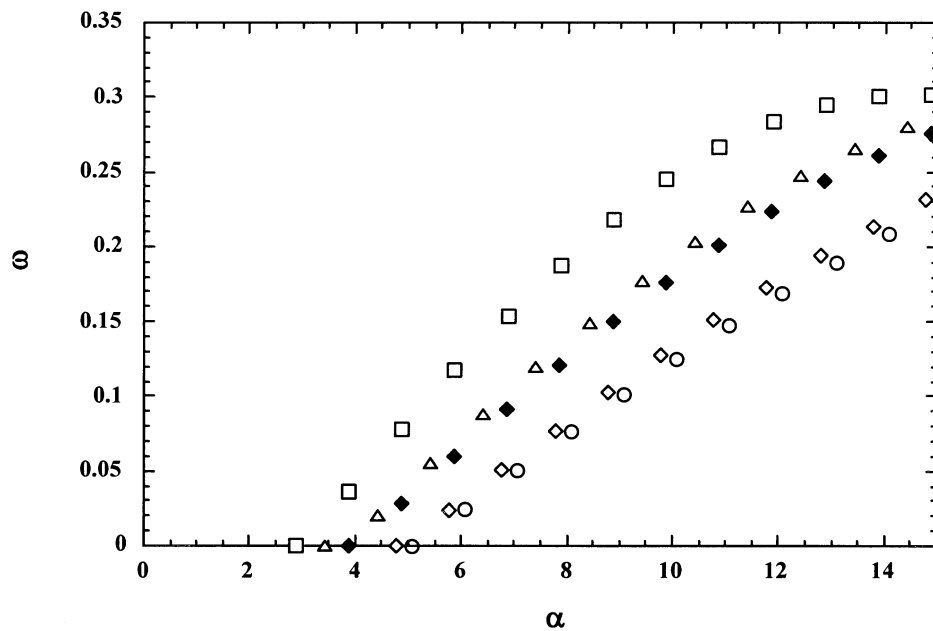


Figure 8. The dependence of degree of crystallization on elongation for $v_{2s} = 0.4$, and 3 hours (\square), 4 hours (\blacklozenge), 5 hours (\circ), 6 hours (\diamond), and 7 hours (\triangle).

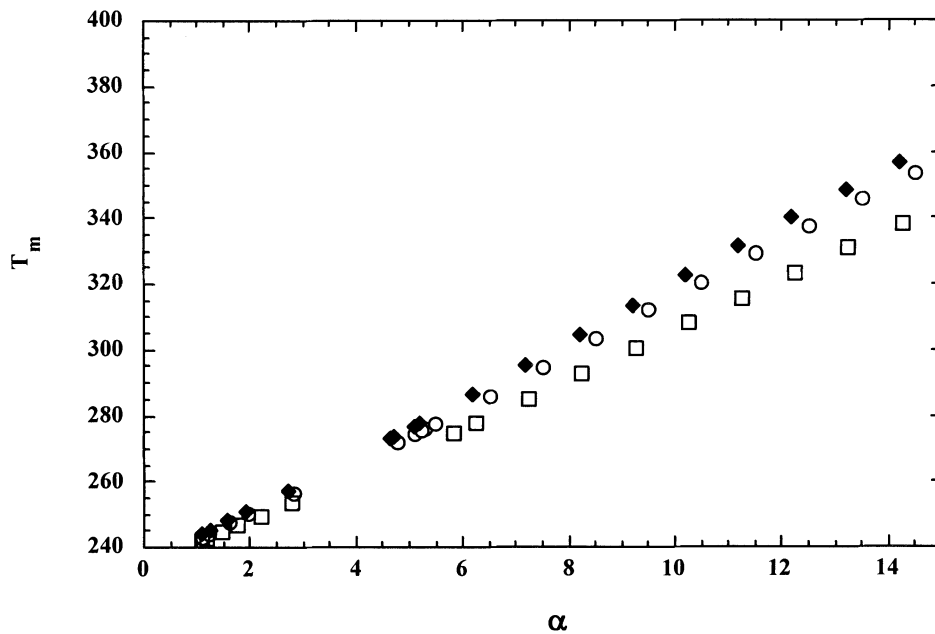


Figure 9. The dependence of crystallization temperature on elongation obtained from the constrained-junction theory for PIP networks cross linked at $v_{2s} = 1.0$, for 1 hour (\square), 2 hours (\blacklozenge), and 3 hours (\circ).

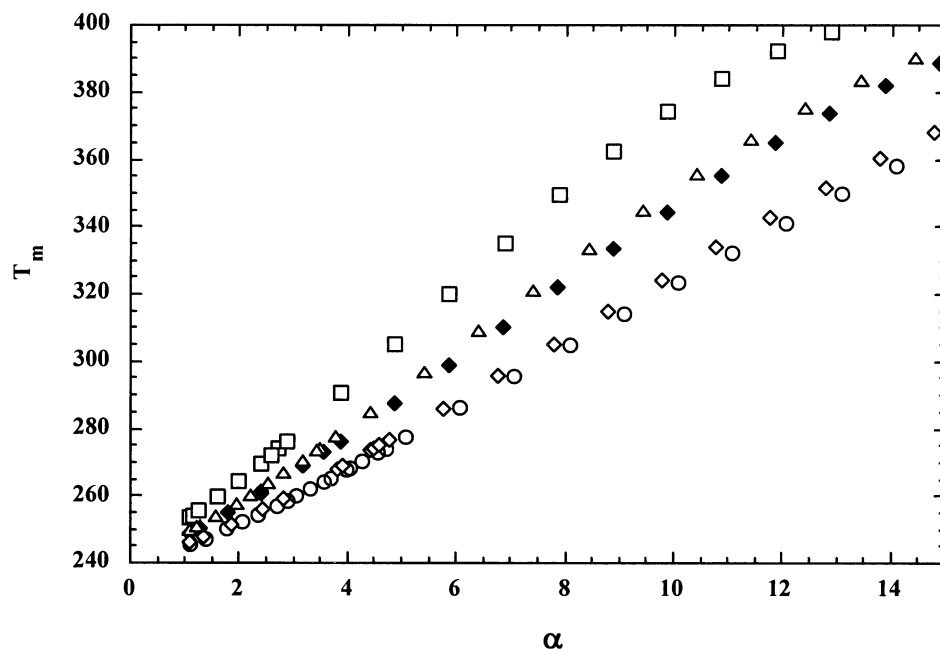


Figure 10. The dependence of crystallization temperature on elongation for $v_{2s} = 0.4$, at 3 hours (□), 4 hours (◆), 5 hours (○), 6 hours (◇), and 7 hours (△).

There is no correlation between the quantity A (Table 1) and the value of v_{2c} , and the average value of A calculated for these networks was found to be 1.95.

The present analysis is thus seen to give a very reasonable interpretation of the experimental results on how crosslinking in solution affects strain-induced crystallization.

This experimental and theoretical study of crosslinked elastomers should encourage similar studies of other unusual network structures, for example those prepared by crosslinking chains in the deformed state [9].

CONCLUSION

Stress-strain isotherms generated for crystallizable networks cross linked in solution using the constrained-junction theory and standard assumptions from Flory's theory of strain-induced crystallization are in a satisfactory agreement with experiment. The parameter κ measuring the severity of constraints of chain entanglements on junction fluctuations decreased with increase in the dilution at which the networks were formed,

as expected. This is mainly due to the fact that the higher the dilution at which the networks were formed, the fewer the chain entanglements. The present treatment of the constrained-junction theory considerably improves the theoretical analysis of strain-induced crystallization in elastomeric networks, particularly those cross linked at different dilutions. However, a non-Gaussian theory which takes into account the shortening of network chains due to the formation of crystallites should give even better agreement between theory experiment.

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REFERENCES

1. Erman, B.; Mark, J.E. *Macromolecules* **1987**, *20*, 2892.
2. Erman, B.; Mark, J.E. *Macromolecules* **1992**, *25*, 1917.
3. Sharaf, M.A.; Kloczkowski, A.; Mark, J.E.; Erman, B. *Comput. Polym. Sci.* **1992**, *2*, 84.
4. Kloczkowski, A.; Mark, J.E.; Sharaf, M.A.; Erman, B. In *Synthesis, Characterization, and Theory of Polymeric Networks and Gels*; Aharoni, S.M., Ed.; Plenum Press: New York, 1992.
5. Erman, B.; Mark, J.E. *Structures and Properties of Rubberlike Networks*; Oxford University Press: New York, 1997.
6. Premachandra, J.K.; Mark, J.E., *Journ. Mac. Sci., Pure & Appl. Chem.* **2002**, *A39* (4).
7. Premachandra, J.K. Ph.D. Thesis, The University of Cincinnati, 1998.
8. Flory, P.J. *J. Chem. Phys.* **1947**, *15*, 397.
9. Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
10. Flory, P.J. *Proc. Roy. Soc. London, Ser.* **1976**, *A351*, 351.
11. Mark, J.E. In *Physical Properties of Polymers*, 2nd Edn., Mark, J.E.; Eisenberg, A.; Graessley, W.W.; Mandelkern, L.; Samulski, E.T.; Koenig, J.L.; Wignall, G. D. American Chemical Society: Washington, DC, 1993.
12. Flory, P. J.; Rabjohn, N.; Schaffer, M.C. *J. Polym. Sci.* **1949**, *4*, 435.
13. Flory, P.J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
14. Erman, B.; Flory, P.J. *Macromolecules* **1982**, *15*, 806.
15. Erman, B.; Flory, P.J. *Macromolecules* **1983**, *16*, 1601.
16. Roberts, D.E.; Mandelkern, L. *J. Am. Chem. Soc.* **1955**, *77*, 781.
17. Smith, K.J., Jr.; Green, A.; Ciferri, A. *Kolloid Z-Z. Polym.* **1964**, *194*, 49.

18. Gottfried, B.S.; Weisman, J. *Introduction to Optimization Theory*; Prentice-Hall: Englewood Cliffs, New Jersey, 1973.
19. Su, T.K.; Mark, J.E. *Macromolecules* **1977**, *10*, 120.
20. Chiu, D.S.; Su, T.K.; Mark, J.E. *Macromolecules* **1977**, *10*, 110.
21. Brotzman, R.W.; Mark, J.E. *Macromolecules* **1986**, *19*, 667.

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