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

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ABSTRACT

Preparing an elastomer by crosslinking polymer chains in solution and then drying the resulting network should have at least two major effects. Specifically, there should be fewer entanglements, and the drying part of the process should compress the chains into a "supercontracted" state. The former effect would be expected to increase crystallization and the latter to reduce it. The present study was conducted to investigate these opposing effects on strain-induced crystallization in *cis*-1,4-polyisoprene chains that had been crosslinked by peroxide thermolysis in decalin solutions, and subsequently dried. The initiation of crystallization was taken to be the elongation at which an upturn in the modulus became discernible. Higher elongations were required for the networks prepared at higher dilutions, suggesting that with regard to strain-induced crystallization, the compressed states of the chains is more important then their reduced entangling. It is likely that quantitative comparisons are complicated by non-Gaussian effects. In addition to the qualitative insights obtained, the results should be useful for evaluations of the theories of rubberlike elasticity and strain-induced crystallization, as is illustrated in the following paper of this two-part series.

Key Words: Polyisoprene; Solution crosslinking; Modulus; Strain-induced crystallization

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INTRODUCTION

One of the main goals in studying the elastomeric properties of rubber-like materials is to characterize their structures [1−6]. Several of these experiments involve the use of solvents, and it is useful to summarize them, to put the present investigation into context. In one type of experiment, the elastomer is prepared by crosslinking in the dry state; it is then placed into a solvent, and the extent to which it swells is measured. The resulting equilibrium extent of swelling occurs when the free energy increase for the dilational stretching of the chains is balanced by the free energy decrease from the mixing of the solvent with the chains. If the effect of the latter contribution can be estimated from thermodynamic interaction parameters, then one can get structural information on the network, such as the molecular weight M_c between crosslinks [4−6].

In a second variety of experiment, the network is again prepared by crosslinking in the dry state but it is then swelled (not generally to equilibrium) with a non-volatile solvent which remains present during typical stress-strain measurements [2, 4, 6]. Application of equations from the molecular theories of rubberlike elasticity then yields the desired structural information. The role of the solvent in this case is to facilitate the approach to elastic equilibrium, but it also provides the bonus of giving stress-strain isotherms that are closer in form to those expected from the simplest molecular theories of rubberlike elasticity.

The final type of experiment is the one relevant here, and involves crosslinking the chains in solution but then drying the network before the stress-strain measurements [7−13]. Again, there is a faster approach to equilibrium and the isotherms are closer to the expected form. The new feature of interest is the fact that such networks are "supercontracted" by the deswelling process, and this in turn makes them super-extensible [14−20]. This is illustrated schematically in Fig. 1.

The present investigation [21] focuses on determination of the effects of this supercontraction on the strain-induced crystallization in such elastomeric materials.

Theory

Characterization of Network Structure

A network chain of molecular weight M_c is defined as that portion of a polymer chain extending between crosslinking points of functionality φ [4]. Additionally, the structure of a network can be described by the number of network chains ν, number of junctions μ, or cycle rank ξ (the number of chains that have to be cut in order to reduce the network to a tree with no
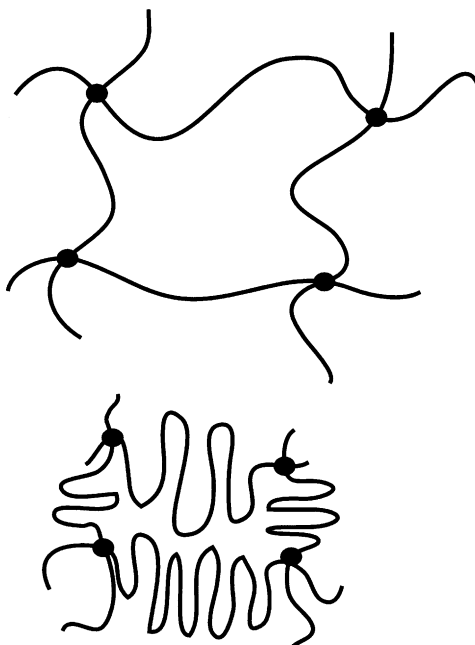
Figure 1. Highly simplified sketches showing the supercontracting of network chains upon preparing a network by crosslinking the chains in solution (upper portion of the figure), and then drying the network (lower portion). The dots represent crosslinks.

closed cycles) [6]. One elastomeric property of importance in this investigation is the modulus defined by [6]

$$[f^*] \equiv f v_2^{1/3}/[A^*(\alpha - \alpha^{-2})] \tag{1}$$

where f is the equilibrium force, v_2 the volume fraction of polymer in the network during the deformation, $\alpha = L/L_i$ the relative length or elongation, and A^* the undeformed cross sectional area of the dry sample. According to the simplest molecular theories [4, 6], it is given by

$$[f^*] = (\nu/V_d)kTv_{2c}^{2/3} \tag{2}$$

where V_d is the volume of the dried network, k the Boltzmann constant, T the absolute temperature, and v_{2c} the volume fraction of the polymer chains in the system being crosslinked which are successfully incorporated into the network structure. Although these theories predict that the reduced stress to be independent of elongation for a given network at constant temperature, experimental results show that $[f^*]$ decreases significantly with increase in α. In the region of low and moderate elongations, the relationship can be represented by the Mooney-Rivlin phenomenological equation [2, 22–24]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{3}$$

where $2C_1$ and $2C_2$ are constants independent of α [24]. The ratio $2C_2/2C_1$, which represents the constant $2C_2$ normalized to constant crosslink density, is a measure of the deviation of an observed stress-strain relationship from that predicted by the simplest molecular theories [24]. The ratio $2C_2/2C_1$ is thought to characterize increase in non-affineness of the deformation with increase in elongation [4, 6].

Molecular Theories of Rubberlike Elasticity

Development of the molecular theories of rubberlike elasticity [1, 2, 25−30] has been based on a number of important postulates. According to the affine network theory, junctions are frozen into the network with the complete suppression of their fluctuations and, therefore, the end-to-end chain vectors transform affinely with the applied macroscopic deformation [1, 2, 25−27]. For uniaxial deformation parallel to the z-axis, the equilibrium retractive force for the affine deformation is:

$$f_{\text{aff}} = \left(\frac{\nu kT}{L_{i,z}}\right)\left(\frac{V}{V_o}\right)^{2/3}[\alpha - \alpha^{-2}] \tag{4}$$

where L_o and V_o are the length and volume of the undeformed network, and L and V are the corresponding quantities after deformation.

In the phantom network theory [4, 6, 28−30] all junctions within the network fluctuate freely around their time-averaged positions. These fluctuations of the junctions are strain independent, but the time-averaged vectors are transformed affinely in the presence of an applied macroscopic deformation. It is also assumed that the only contribution to the elasticity of the network is from the network connectivity. According to the network theory, the equilibrium retractive force f_{ph} under uniaxial deformation is given by:

$$f_{\text{ph}} = \left(\frac{\xi z kT}{L_o}\right)\left(\frac{V}{V_o}\right)^{1/3}[\alpha - \alpha^{-2}] \tag{5}$$

The behavior of a real network falls between phantom and affine extremes [6, 31, 32]. The transition of the real networks from affine limit to phantom limit is achieved by diminishing chain-junction entanglements with increase in elongation or dilution. These ideas lead to a workable theory of real networks which has later been referred to as the constrained-junction model [6]. In this theory, the impediment on the fluctuations of the network junctions are attributed to the entanglements of the chains emanating from

the junctions with their neighboring chains and junctions. According to the constrained-junction theory, the elastic force can be expressed as:

$$f = f_{ph} = [1 + f_c/f_{ph}] \tag{6}$$

where f_c is the contribution to the force from the entanglements and steric constraints on junction fluctuations, and f_{ph} is the contribution of the corresponding phantom network. The relative contribution from the constraints is:

$$\frac{f_c}{f_{ph}} = \left(\frac{\mu}{\xi}\right)[\alpha K(\lambda_1^2) - \alpha^{-2} K(\lambda_2^2)](\alpha - \alpha^{-2})^{-1} \tag{7}$$

Here, the K's are complicated functions [6] of a parameter κ measuring the severity of the entanglement constraints relative to those imposed by the phantom network, and another parameter ζ measuring the possibly nonaffine nature of the transformation of the domains of constraints with increasing strain.

The theory predicts that f_c/f_{ph} decreases with increasing deformation, and the modulus approaches the phantom limit at $\alpha^{-1} \to 0$. The relative contribution from the constraints in the limit $\alpha^{-1} \to 1$ for a perfect network is predicted by the theory to be [6]:

$$\frac{f_c}{f_{ph}} = \frac{2}{(\varphi - 2)} \tag{8}$$

and should therefore vanish as the network functionality φ increases.

In later studies, the constrained-junction theory was modified by considering the effect of constraints on the points along the chains rather than on junctions only [6]. Specifically, the constraints were either placed on the centers of mass of the network chains in the "constrained-chain model," or all along the chains in the "diffused constraints" model.

Strain-Induced Crystallization

Some unfilled polymer networks show a large and rather abrupt increase in modulus at high elongations, and this is probably due to self-reinforcement from crystallites generated by strain-induced crystallization [33–47]. Since this provides such significant improvements in mechanical properties, it is important to establish its dependence on network properties, including those resulting from crosslinking in solution.

Effects of Crosslinking in Solution

A number of experimental studies have shown that values of $2C_2/2C_1$ are very small for networks formed in solution and then dried, and this effect is most significant at higher dilutions [7−12]. It was suggested that the solvent present during crosslinking disentangles the chains prior to their crosslinking, giving rise to simpler topologies in the networks [31, 33]. In such networks, crosslinks which are spatially first neighbors are more likely also to be topological neighbors than in a network prepared in the undiluted state. Furthermore, solution crosslinked networks have fewer chain-junction entanglements and fewer inter-chain entanglements [4]. Figure 1 shows the structure of a network prepared by crosslinking in solution. Since the crosslinks would be less enmeshed with surrounding chains, they would be less firmly embedded in the network structure and therefore deform more non-affinely [6]. An additional effect is the possible increased formation of loops as the extent of dilution increases.

It can be conjectured that disentangling the chains prior to network formation should facilitate strain-induced crystallization. There should be another important effect, however, namely that the drying part of the process should compress the chains into a "supercontracted" state [14−20]. The chains may therefore need more extension before their entropy is sufficiently diminished for crystallization to occur. The present study was carried out to investigate the opposing effects of these changes on strain-induced crystallization in *cis*-1,4-polyisoprene chains crosslinked by peroxide thermolysis in decalin solutions. The initiation of crystallization was taken to be the elongation at which an upturn in modulus became discernible. The subject of primary interest was whether crosslinking in solution decreases or increases the elongation at which such strain-induced crystallization occurs.

EXPERIMENTAL

Bases for Choice of System and Crosslinking Conditions

In the present study it was very important to use a network in which the crystallization is induced only upon stretching, and at a convenient temperature. *Cis*-1,4-polyisoprene (PIP) meets these conditions [48], it is a commercially important elastomer both in the synthetic form and as natural rubber, and it was therefore chosen for this investigation.

The method of crosslinking chosen was peroxide thermolysis, which is known to give single covalent bond crosslinks and low degrees of chain scission [49, 50]. In some crosslinking techniques, particularly irradiation of *cis*-polybutadiene, the *trans* form predominates in the crosslinked product, because of isomerization of the double bond. In the case of the peroxide crosslinking of *cis*-polyisoprene, however, this problem is

minimized [51]. Since increasing the degree of crosslinking significantly decreases the crystallization temperature of natural rubber and *cis*-1,4-polyisoprene [52], 5°C was chosen as the temperature for the stress-strain measurements [21].

Materials

A 1,4-polyisoprene sample of very high *cis* content (99%) and number-average molar mass of 318,000 g mol⁻¹ was generously provided by Dr. Adel Halasa of the Goodyear Tire and Rubber Company. The solvent used as diluent was decalin and the crosslinking agent was dicumyl peroxide; both were obtained from the Aldrich Chemical Company.

Preparation of Networks

The polymer-solvent mixture was prepared in a Petri dish by dissolving the required amount of PIP in a decalin solution containing the desired amount of dicumyl peroxide [21]. The values of the volume fraction v_{2s} of polymer in the system being crosslinked were 1.0, 0.8, 0.6, and 0.4. The higher the dilution, the lower the efficiency of crosslinking when networks are formed in solution [7, 9, 11]. As a consequence, the degree of crosslinking is low and the soluble fraction of polymer is high in such networks. This difficulty was minimized by using increasing amounts (1.0, 2.0, 3.0 and 5.5 wt%) of the crosslinking agent for the dilutions $v_{2s} = 1.0, 0.8, 0.6,$ and 0.4, respectively. In order to get the specified volume fractions of polymer during crosslinking, excess decalin was allowed to evaporate at room temperature from the most dilute master solution. A portion of the resulting mixture was pressed into an aluminum mold in a Carver press, and cured at 160°C. An aluminum foil gasket placed between the upper and the lower parts of the mold prevented evaporation of decalin from the sample during the procedures. At each value of v_{2s}, several networks having different crosslink densities were prepared by using different cure times.

Extraction of Samples

A small portion of each crosslinked sample was dried in air to a constant weight and then extracted with benzene at room temperature for three days [21]. The extracted samples were then deswelled with methanol and dried in air. The weights of uncrosslinked polymer thus extracted were used to determine the values of the amount of polymer successfully incorporated (v_{2c}) from the corresponding values of v_{2s}. The main portion of each

crosslinked sample was extracted in the same way, for use in the mechanical property measurements.

Stress-Strain Measurements

Equilibrium stress-strain data in uniaxial extension were obtained in the usual manner [4, 6, 11, 21], using strips (approximately 30 mm × 1.5 mm × 3 mm) cut from extracted, dried samples. The value of the force of the sample stretched to a desired length was assumed to be the equilibrium value when it became constant for at least 15 minutes. The elongations were increased until the rupture point of each strip was reached.

RESULTS AND DISCUSSION

The preparation and the characteristics of the networks prepared are described in Table 1. Networks prepared in the bulk, undiluted state ($v_{2s} = 1.0$) are denoted by B-1 to B-3. The networks prepared in solution having volume fraction v_{2s} of the polymer of 0.8, 0.6, and 0.4 were denoted by S.8, S.6, and S.4, respectively. Values of the soluble fraction ω_s of the polymer, the ratio of the weight of uncrosslinked polymer to the weight of total polymer used, and the values of v_{2s} were used to calculate the corresponding values of v_{2c} given by $(1 - \omega_s)v_{2s}$. It was assumed that the extractable uncross-linked polymer acts as additional solvent or diluent during the crosslinking process [11]. Values of v_{2c} are very close to the corresponding values of v_{2s} of these networks. As already mentioned, several networks with different crosslinking densities at each value of v_{2s} were prepared by using different cure times. Although the increase in cure time may decrease the soluble fraction of polymer, longer cure times at high temperatures may result in degradation of the polymer and the increase in soluble fraction of polymer. This could be the reason for the decrease of the values of v_{2c} with longer cure times at some values of v_{2s}.

Some typical stress-strain isotherms are shown in Figs. 2 and 3, and results obtained from the curves are given in Table 1. Similar results were obtained for the entire series of samples [21], crosslinked either in the undiluted state or in solution, and all showed upturns in modulus at high elongation. These isotherms were used to obtain values of $2C_1$, $2C_2$, the elongation α_{crst} at which the crystallization is discernible as a marked increase in modulus, a measure of the degree of crosslinking, and the increment $\Delta[f^*]$ in modulus due to strain-induced crystallization at the elongation at rupture.

The values of $2C_1$ (which is a measure of the cross-link density) increased with cure time at each value of v_{2s}. Values of $2C_1$ in the networks crosslinked in solution were somewhat higher than those in networks

Table 1.   Preparative Details and Some Properties of the Networks

Sample	v_{2s}	Cure Time (h)	v_{2c}	$2C_1$ (N mm^{-2})	$2C_2/2C_1$	α_{cryst}	$\nu/V_d \times 10^{-17}$ (Chains mm^{-3})	$\Delta[f^*]$ (N mm^{-2})
B-1	1.00	1.0	0.968	0.184	0.411	2.22	0.691	0.103
B-2	1.00	2.0	0.971	0.202	0.313	1.96	0.705	0.107
B-3	1.00	3.0	0.971	0.215	0.289	1.67	0.736	0.178
S.8-1	0.80	1.0	0.776	0.300	0.0519	2.08	0.973	0.094
S.8-2	0.80	3.0	0.779	0.262	0.305	2.08	1.05	0.090
S.8-3	0.80	4.0	0.776	0.282	0.260	1.92	1.09	0.065
S.8-4	0.80	5.0	0.774	0.290	0.364	1.85	1.22	0.098
S.6-1	0.60	3.0	0.543	0.252	0.112	2.13	1.10	0.133
S.6-2	0.60	4.0	0.569	0.253	0.283	1.96	1.23	0.175
S.6-3	0.60	5.0	0.576	0.258	0.336	1.90	1.30	0.138
S.6-4	0.60	6.0	0.569	0.282	0.0709	2.02	1.14	0.084
S.6-5	0.60	7.0	0.541	0.288	0.301	1.82	1.47	0.072
S.4-1	0.40	3.0	0.386	0.230	0.256	1.92	1.42	0.040
S.4-2	0.40	4.0	0.386	0.240	0.130	2.04	1.33	0.080
S.4-3	0.40	5.0	0.385	0.250	0.116	2.00	1.37	0.204
S.4-4	0.40	6.0	0.384	0.280	0.0754	1.82	1.48	0.156
S.4-5	0.40	7.0	0.385	0.310	0.086	1.61	1.66	0.072

crosslinked in the undiluted state. This may be due to the increased amount of crosslinking agent and the cure time employed. The ranges of values of $2C_2/2C_1$ corresponding to different values of v_{2s} overlap to some extent, as was found in a previous study [53]. However, the values of $2C_2/2C_1$ for networks prepared in the comparatively higher dilution $v_{2s} = 0.4$ were lower than those for the networks prepared in the undiluted state. More important, the average value of $2C_2/2C_1$ for each value of v_{2s} decreases markedly with decrease in the value of v_{2s} (Table 2). This is due to the fact that the increase in nonaffineness with increase in elongation is very small in dried networks crosslinked in solution, as a result of reduced chain-junction entanglements.

   As expected, the values of α_{crst} in the networks crosslinked in the undiluted state decreased with increase in cure time. The same trend in α_{crst} with cure time can be seen in the networks crosslinked in solution at each value of v_{2s}, except for the specific networks S.6-4 and S.4-1 [21].

   At low deformations ($\alpha^{-1} \rightarrow 1$) [46], the estimated network chain density ν/V_d [1,5] is given by $(2C_1 + 2C_2)/kT_{2c}^{2/3}$. Its values are tabulated in column eight of Table 1. These values increased with increase in cure time at each value of v_{2s}. Figure 4 shows the dependences of α_{crst} on ν/V_d for the undiluted state and for each dilution, and also its dependence on dilution. Increases in ν/V_d indicate decreases in network chain length. As can be seen from Fig. 4, α_{crst} decreases with increase in ν/V_d at each value of v_{2s}. This is attributed to the fact that sufficient orientation of network chains for
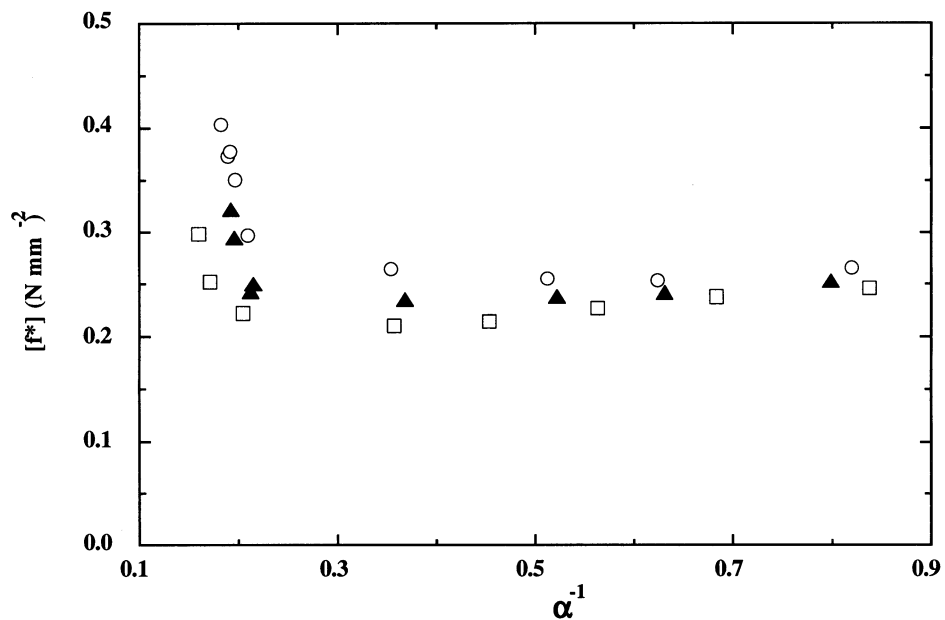
Figure 2. Stress-strain isotherms at 5°C for samples of *cis*-1,4 polyisoprene cured with 1.0% dicumyl peroxide at 160°C in decalin at the dilution $v_{2s} = 1.0$, for 1 (□), 2 (▲), and 3 (○) hours.
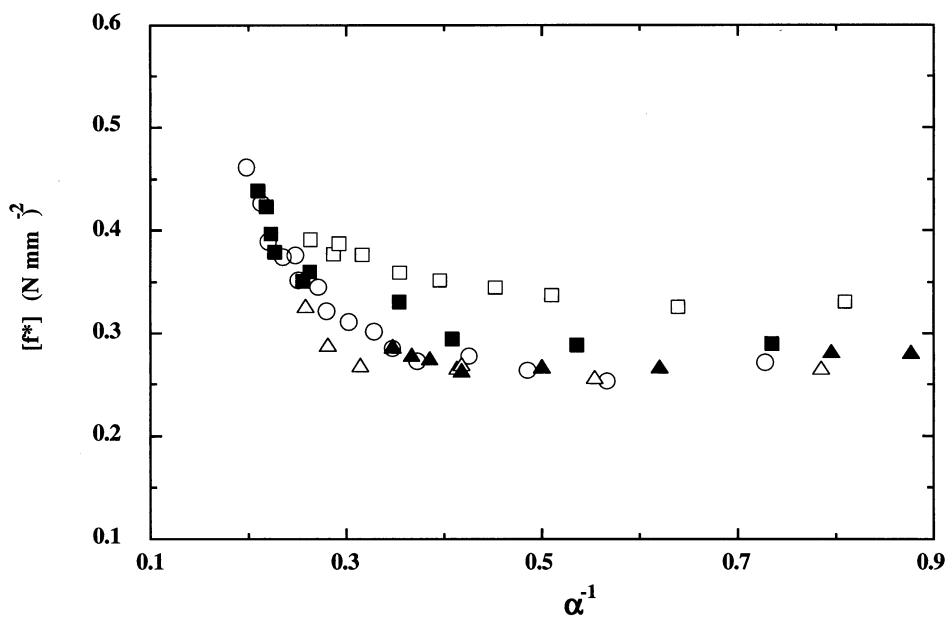

Figure 3. Stress-strain isotherms at 5°C for samples of *cis*-1,4 polyisoprene cured with 5.5% dicumyl peroxide at 160°C in decalin at the dilution $v_{2s} = 0.4$, for 3 (▲), 4 (Δ), 5 (○), 6 (■), and 7 (□) hours.

Table 2. The Dependence of $2C_2/2C_1$ on Dilution

v_{2s}	Average Value of $2C_2/2C_1$
1.0	0.338
0.8	0.245
0.6	0.221
0.4	0.133

strain-induced crystallization is achieved earlier in the elongation for short network chains than for longer network chains [36−39].

The quantity $\Delta[f^*]$ is also of interest as a measure of the crystallinity developed in these networks due to applied strain. There was no obvious trend in $\Delta[f^*]$ with v_{2s}, however. This is presumably due to the fact that its values depend on the rupture points, which are notoriously difficult to control.

Since the higher the dilution at which the network is formed, the fewer the inter-chain entanglements in the dried network, and this should lower the elongation α_{crst} for initiation of the strain-induced crystallization. On the contrary, as shown in Fig. 4, in the regions at which the different v_{2s} lines (or
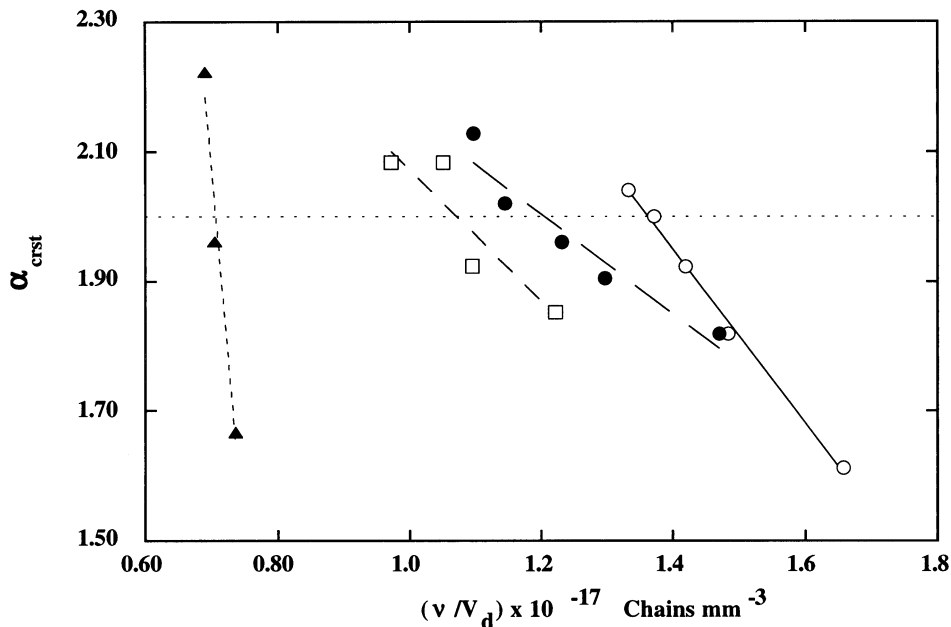
Figure 4. The elongation a_{crst} required for incipient crystallization vs. the network chain density v/V_d for dried networks crosslinked at the dilutions $v_{2s} = 0.4$ (○), 0.6 (●), 0.8 (□), and 1.0 (▲).

their extrapolations) overlap, α_{crst} at constant v/V_d generally *increases* with a decrease in v_{2s}. Thus, in brief, networks formed in solution require higher elongations to exhibit strain-induced crystallization. This is consistent with the observation that dried samples of solution crosslinked poly(dimethylsiloxane) did not crystallize at all in the undeformed state [20]. There may be another interesting parallel in the area of plant-produced polyesters such as poly(hydroxybutyrate), a highly crystalline polymer with a melting point of $178°C$ [54–56]. It must be highly amorphous in the granules in which it appears, otherwise the plant would not have access to it in its functioning as a storage device. Perhaps nature uses a similar collapsing to supercontract the chains into the small volumes they occupy in a way that avoids the crystallization that does occur once the polymer is removed from its granules.

In any case, the present results demonstrate the greater importance of increased network chain contraction upon drying from the increasingly dilute gels. An other way of making a comparison would be in terms of a constant value of α_{crst}, for example at the value 2.00 horizontally marked in Fig. 4 [21]. The results indicate that the higher the dilution at which the network is formed, the higher the network chain density (the shorter the network chains) required for crystallization to occur at this specified value of the elongation. Therefore, network chains required to exhibit the strain-induced crystallization at a specified value of elongation have to be shorter, in spite of the opposing effect of fewer chain entanglement in such a network. Therefore, with regard to strain-induced crystallization it is evident that the compressed states of network chains in the dried networks was more important than their reduced entangling.

CONCLUSION

The present study showed that the networks formed by crosslinking in solution required higher elongations to exhibit strain-induced crystallization, at a constant value of network chain density. Alternatively, the higher the dilution at which the network was formed, the higher the network chain density required for crystallization to occur by a specified value of the elongation. These observations, in turn, suggests that with regard to strain-induced crystallization, the compressed states of the chains in the dried networks was more important than their reduced entangling. In addition to these qualitative insights, the results are of considerable quantitative importance in testing various theories for rubberlike elasticity and strain-induced crystallization, as is illustrated in the following paper [57].

ACKNOWLEDGMENTS

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