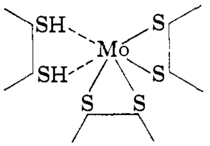
The specific extinction coefficients used for these calculations are

	Mo(VI) complex	Mo(IV) complex
680 mμ	41.6 cm.²/mg.	8.35 cm.²/mg.
510 mμ	8.16 cm.²/mg.	18.6 cm.²/mg.

Discussion

The green complex formed as one of the products when molybdenum(V) reacts with dithiol is identified as $Mo^{VI}Di_3$ by its spectral characteristics. Because formation of molybdenum(VI) by air-oxidation is believed to be ruled out, disproportionation must occur and the red complex is a compound of molybdenum(IV).

The red complex shows a S/Mo ratio of 5.95 and therefore contains 3 dithiol radicals per molybdenum atom. Three possible structures suggest themselves, disregarding coördinated water molecules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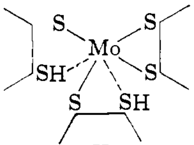
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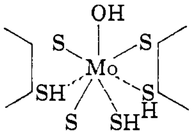
III

The calculated percentage compositions and the analytical values for the red complex are

	C, %	H, %	S, %	Mo, %
$MoDi_2(H_2Di)$ or $MoDi(HDi)_2$	45.0	3.60	34.32	17.11
$MoOH(HDi)_3$	43.6	3.83	33.2	16.59
Red complex	47.1	3.7	34.0	17.1

Because of the difficulties in the C and H determinations, values for these are of little significance. The Mo and S values give some support for formulas I and II.

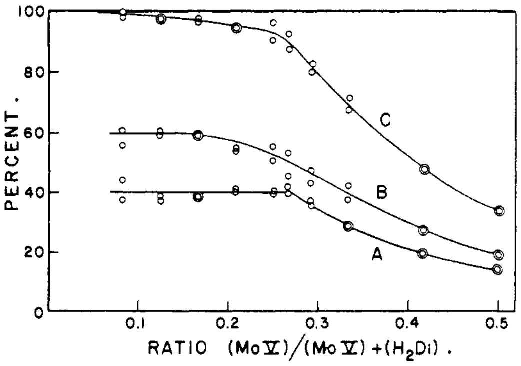

Fig. 4.—Proportions of green (Mo(VI)) and red (Mo(IV)) complexes formed by reaction of Mo(V) in 8 *N* sulfuric acid at different ratios of Mo/dithiol ($[Mo(V)] + [H_2Di] = 2.4 \times 10^{-4}$ *M*; phase ratio, benzene/aqueous = 1/1): A, per cent. of total Mo in form of extracted Mo(VI) complex; B, per cent. of total Mo in form of extracted Mo(IV) complex; C, sum of A and B.

The disproportionation is accompanied by side reactions so that equal amounts of Mo(IV) and Mo(VI) complexes are not formed, nor is all of the original molybdenum necessarily transformed into dithiolates. The greater proportion of the Mo(IV) complex formed in 8 *N* sulfuric acid (Fig. 4) can be ascribed to some reduction of Mo(V) by dithiol. As the excess of dithiol becomes smaller, complete formation of the dithiolates does not occur. Mo(IV) not combined with dithiol disproportionates in the aqueous phase to Mo(V) and Mo(III). Dithiol does not react with Mo(III). Especially at high acid concentrations the formation of Mo(IV) is impeded or prevented entirely, as postulated by the reaction

$$3Mo(V) + 6H_2Di \longrightarrow 2MoDi_3 + Mo(III) + 12H^+$$

In 12 *N* hydrochloric acid, the formation of the red Mo(IV) complex seems to be suppressed completely, but the green Mo(VI) complex still is formed.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

The Melting Temperature of Natural Rubber Networks

BY D. E. ROBERTS AND L. MANDELKERN

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The isotropic melting temperatures T_m[1] of natural rubber networks which were formed either by chemical reaction or by the action of ionizing irradiation were determined by dilatometric techniques. Substantial depression of the melting temperature with increasing amounts of crosslinking was observed for networks formed from randomly coiled chains irrespective of the method by which the crosslinks were introduced. It is also found that the melting temperatures of networks formed from highly ordered chains are substantially higher than those of corresponding networks formed from random chains. The difference in melting temperatures for these two types of networks can be quantitatively attributed to the decrease in configurational entropy of the former type networks which occur as a consequence of the chain disposition at the time of their formation.

Introduction

It has been shown recently that in accord with the theoretical predictions of Flory[1] many of the properties of polymer networks will depend on the relative arrangement of the chain units at the time of network formation.[2-4] In particular, if the network being studied is crystallizable its

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[1] P. J. Flory, THIS JOURNAL, **78**, 5222 (1956).

[2] D. E. Roberts, L. Mandelkern and P. J. Flory, *ibid.*, **79**, 1515 (1957).

[3] D. E. Roberts and L. Mandelkern, *ibid.*, **80**, 1289 (1958).

[4] L. Mandelkern, D. E. Roberts, J. C. Halpin and F. P. Price, *ibid.*, **82**, 46 (1960).

isotropic melting temperature T_m^i will be sensitive to the presence or absence of any orientation of the chain elements prior to network formation. Quantitative predictions[1] as to the magnitude of this effect have been made and experiments reported to date[3,4] have given qualitative support to these concepts. It has not been possible, however, to make rigorous quantitative comparison between theory and experiment. In the case of the natural rubber networks previously studied[3] the melting temperatures were not determined by reliable methods nor were the required careful annealing procedures followed during the melting process.[5] Thus the melting temperatures reported did not represent equilibrium melting. Though the melting temperatures of the polyethylene networks were determined under conditions approaching equilibrium, the orientation of the chain units in this case could not be quantitatively described.[4]

In the present work, the melting temperatures of the natural rubber networks have been reexamined using experimental techniques and procedures designed to yield data that could be quantitatively compared with theoretical expectations. The isotropic melting temperatures of networks formed by subjecting the polymer, when in the amorphous state or when in a state of high axial orientation, to the action of ionizing radiation of gamma rays from a Co^{60} source, were determined. In addition the melting temperatures of networks formed from random chains by chemical methods also were determined.

Experimental

Materials.—The networks formed by the irradiation of both amorphous and fibrous natural rubber were identical with those previously reported.[3] The method used to determine the fractions of the units crosslinked for these networks has been described. Natural rubber vulcanizates were prepared by conventional techniques. The recipe was: smoked sheet (Tensosheet) 100; zinc oxide 1; zinc dibutyl dithiocarbamate 0.5; and sulfur 0.5, 1.0, 1.5, or 2. The compounds were cured at 116°; the first two for 60 min. and the other two for 120 min. Deproteinized pale crepe was vulcanized with di-*tert*-butyl peroxide and the fraction of units crosslinked determined by chemical means.[6,7]

Methods.—The density of the specimens was determined at 25.0° by the method of hydrostatic weighings.[8] The melting temperatures of the chemically crosslinked networks were determined by conventional dilatometric techniques using mercury as a confining fluid.[9] Crystallinity was developed in these specimens by maintaining the dilatometers at −30° for 75 days. Subsequent to the development of crystallinity the fusion process was studied employing slow heating rates. At the lower temperatures, the temperature was raised at the rate of about 1–2° per day; this rate was decreased gradually to 1° in five days at temperatures slightly below 0° and decreased to 1° every ten days as the melting point was approached. The typical partial melting and recrystallization that are invariably observed during the fusion of polymeric systems also were noted during the fusion of the partially crystalline networks when the aforementioned heating rates were employed.

Because of the small quantity (0.025–0.16 g.) available of each of the irradiated networks and the relatively small volume change that is observed on melting, it was necessary to construct extremely sensitive dilatometers in order to determine the melting temperatures accurately. The bulb of each dilatometer was made of Pyrex glass tubing fabricated so as to approximate closely the shape and size of the specimen. The excess space beyond that occupied by the polymer sample was filled with fine glass beads of 0.1–0.2 mm. diameter. The capillary part of the dilatometer was constructed of 0.3–0.8 mm. precision bore Pyrex tubing and the capillary height measured by means of a travelling microscope to 0.001 mm. Crystallization of these specimens was effected at −20°, and a heating rate similar to that employed in studying the fusion of the chemically formed networks was adopted. Similar partial melting and recrystallization were also observed in these specimens. By utilizing this technique melting points for these small samples could be determined to within 1°.

Wide angle flat plate X-ray diffraction patterns of the rubber-sulfur networks were taken at −60° after crystallization at −20°.

Results

Chemically Crosslinked Networks.—The dependence of the specific volume on temperature for the four rubber-sulfur networks is plotted in Fig. 1. From plots of this type the melting temperature, taken as the temperature at which crystallinity completely disappears, can be easily determined. The most significant result is the fact that when the fusion process is carried out under conditions approaching that of equilibrium an appreciable decrease in the melting temperature is observed with increasing crosslinking density. Thus for the network containing about 2% sulfur, where from the equilibrium swelling measurement it is estimated that slightly more than 1% of the units are crosslinked, the melting point is depressed by 26°. Distinct differences in the nature of the fusion process also can be discerned for the various networks illustrated. For the polymer containing the fewest crosslinks, the melting is relatively sharp and the transformation terminates rather abruptly. However, as the amount of crosslinking is increased in the specimens, the melting range is progressively broadened with a definite rounding of the curves occurring in the vicinity of the melting temperature. Melting curves of this type are reminiscent of the fusion of random copolymers.[10,11] In the liquid state, though the volume-temperature coefficients are essentially independent of the number of crosslinks introduced, a decrease in specific volume with increased sulfur content is observed in accord with previous reports.[12] The natural rubber networks prepared by reaction with *t*-butyl peroxide show a similar melting behavior both as to the depression of the melting point and broadening of the melting range with increased crosslinking.

Fig. 2 illustrates the manner in which the isotropic melting temperature of the chemically crosslinked networks depends on ρ, the fraction of the units crosslinked. For both types of networks the melting temperature depends solely on ρ and is independent of the nature of the crosslinking process. The melting temperature progressively decreases as ρ is increased and a substantial depression of this temperature is achieved in the

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(5) D. E. Roberts and L. Mandelkern, THIS JOURNAL, **77**, 781 (1955).

(6) C. G. Moore and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).

(7) We are indebted to Dr. C. G. Moore of the British Rubber Producers' Research Association for providing us with these samples and the chemical analyses.

(8) L. A. Wood, N. Bekkedahl and F. L. Roth, *J. Research Natl. Bur. Standards*, **29**, 391 (1942).

(9) P. J. Flory, L. Mandelkern and H. K. Hall, THIS JOURNAL, **73**, 2532 (1951).

(10) P. J. Flory, *Trans. Farad. Soc.*, **51**, 848 (1955).

(11) L. Mandelkern, M. Tryon and F. A. Quinn, *J. Polymer Sci.*, **19**, 77 (1956).

(12) G. M. Martin and L. Mandelkern, *J. Research Natl. Bur. Standards*, **62**, 141 (1959).

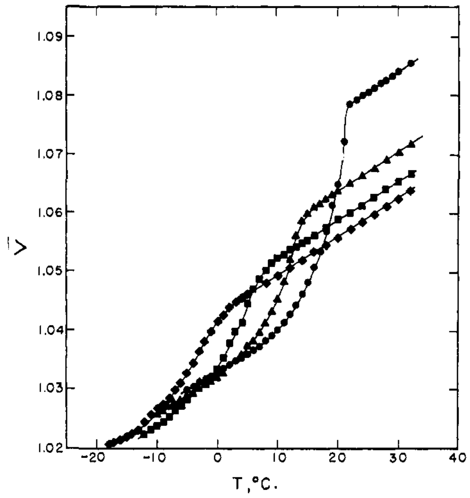

Fig. 1.—Plot of specific volume, $\bar{V}$, against temperature for natural rubber networks formed by reaction with sulfur: 0.5% sulfur ●; 1% sulfur ▲; 1.5% sulfur ■; 2% sulfur ◆.

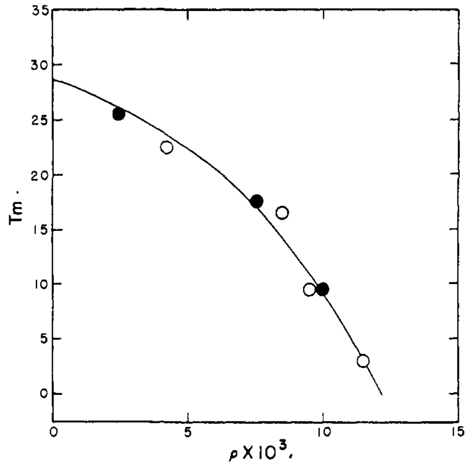

Fig. 2.—Plot of isotropic melting temperature of chemically formed natural rubber networks against fraction of the units crosslinked. Formed by reaction with sulfur O; formed by reaction with di-tert-butyl peroxide ●.

crosslinking range that is commonly encountered. The smooth curve drawn through the experimental data extrapolates to 28–29° for ρ equal to zero. This temperature is in very close accord with the equilibrium melting temperature of non-crosslinked natural rubber previously reported.[5]

Networks Formed by Irradiation.—When natural rubber is subjected to the action of high energy ionizing radiation, it has been demonstrated[3,13] that the predominant effect is crosslinking, chain scission processes occurring only to a very small extent. This relatively simple and convenient crosslinking technique offers the advantage that the arrangement of the polymer chain units at the time of network formation can be altered. We therefore consider the effect of crosslinking on the melting temperature of two types of networks formed in this manner. In one case the chains at the time of crosslinking are randomly arranged while in the other they are in a state of high axial orientation.[3]

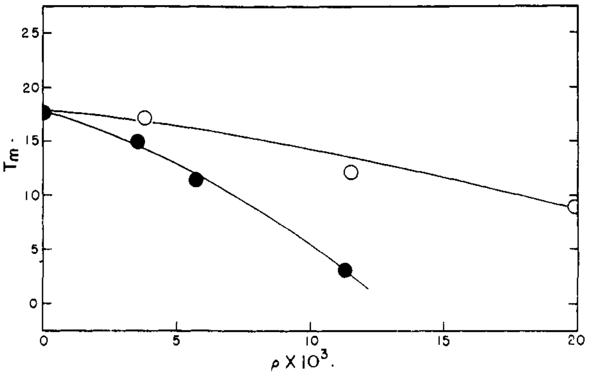

Fig. 3.—Plot of isotropic melting temperature of natural rubber networks formed by irradiation. Chains random ●; chains oriented O.

The dependence of the melting temperature on the fraction of the units crosslinked for networks formed by irradiating random chains is illustrated by the lower curve of Fig. 3. These results are qualitatively the same as those previously reported for similar networks. The melting temperatures previously reported, however, were substantially lower at all crosslinking levels. This difference can be attributed to the fact that in the previous work rapid heating rates were employed and the melting points determined by subjective visual observations. The present dilatometric studies utilizing slow heating rates are deemed more reliable For networks of this type a substantial depression of the melting temperature again is observed. The magnitudes of the depressions are quantitatively almost identical with those observed for the chemically crosslinked polymer. The melting point of the non-crosslinked rubber is somewhat lower than expected for the equilibrium melting temperature of the polymer.

The upper curve of Fig. 3 represents the dependence of the isotropic melting temperature on crosslinking for networks formed when the polymer chains were in a highly oriented state. Prior to determining the melting temperature, the oriented crosslinked networks were rendered amorphous by heating. The samples then were allowed to recrystallize merely by cooling as previously described. Subsequently the fusion process was studied and the melting temperature determined. For these networks the melting temperatures decrease only slightly with increasing crosslinks as can be seen in Fig. 3. At comparable crosslinking levels the melting points of networks formed from the ordered chains are substantially greater than corresponding networks formed from random chains. Thus for example at $\rho = 1.0 \times 10^{-2}$ the difference in melting temperatures is about 10°. While a network formed from ordered chains with a value of $\rho = 2 \times 10^{-2}$ crystallizes readily on cooling, a corresponding network formed from random chains has not crystallized after 18 months at −30°.

(13) A. Charlesby and D. Groves, "Proc. Third Rubber Technology Conference," W. Heffer and Sons, Ltd., Cambridge, England, 1954, p. 317.

Qualitative indication of the difference in melting temperatures has been given[3] previously; the conclusions are now substantiated by the more quantitative determination of the melting temperatures under conditions approaching equilibrium.

Discussion

Networks from Random Chains.—The experimental results show that regardless of the details of the nature of the crosslinking process substantial reduction in the melting temperature occurs when the chain units are randomly coiled at the time of network formation. Similar results have been reported[4] for polyethylene networks formed by irradiating the polymer at temperatures above its melting temperature. The observation of a large depression of the melting temperature with crosslinking therefore appears to be a characteristic property of polymer networks formed from random chains.

When crosslinks are introduced at random into a collection of randon polymer chains the units that are paired are thus selected at random. Therefore, the configurational entropy of the chain units in the liquid state remains unaltered by this process. However, the crosslinking of a fraction ρ of the units effects a compositional change in the system. For this reason the entropy of the liquid should be increased by the amount $R\rho$. If the crosslinked units are prevented from participating in the crystallization for steric reasons and if equilibrium conditions prevail, then the melting temperature should be depressed by an amount given by the relation

$$1/T_m{}^i - 1/T_m{}^0 = (R/\Delta H_u)\rho \qquad (1)$$

where $T_m{}^i$ is the isotropic melting temperature of the network, $T_m{}^0$ that of the non-crosslinked polymer, R is the gas constant and ΔH_u the heat of fusion per mole of crystallizing unit. Utilizing the previously determined value of ΔH_u,[5] equation 1 predicts only a trivially small depression of $T_m{}^0$ for the crosslinking densities encountered in this work. A similar conclusion was reached for polyethylene networks formed from amorphous chains.[4] It is clear then that the units involved in crosslinkages depress the melting temperature by an amount much greater than would be expected if they behaved solely as non-crystallizing copolymeric units randomly distributed along the chain.

It has been emphasized[4,10,14] that the use of equation 1 or its counterparts in analyzing experimental data requires that the melting temperatures be determined under equilibrium conditions. This requires not only the adoption of slow heating rates but also the unrestricted development of the lateral growth of the crystallites, with the longitudinal development being impaired only by the presence of the non-crystallizing crosslinked units. Thus the perfection of the crystallinity that must be developed in a network to appropriately utilize equation 1 must be comparable to that which occurs in the annealed non-crosslinked polymer.

It has been reported,[4] for networks prepared from random chains of polyethylene, that after crystallization and annealing the {110} reflection of the wide angle X-ray pattern continuously broadens with the introduction of increasing amounts of crosslinkages. This observation can be interpreted as being due to restrictions on crystallite size or the development of imperfections or strain. It has also been shown[15] recently that when polyethylene fibers are crosslinked, melted and then recrystallized the meridional X-ray diffraction maxima that are observed at low angles decrease in magnitude with increased crosslinking, indicating that as perfect crystallinity cannot be developed in crosslinked systems as in non-crosslinked systems.

Similar effects are also shown by the natural rubber-sulfur networks studied here. Photometer traces of the wide angle X-ray diffraction patterns taken at −60° after crystallization at −20° show progressive broadening of the {120}, {201} and {200} reflections with increasing sulfur content, with the {201} reflection being broadened most severely. Thus again for natural rubber networks crystallinity cannot be developed which is comparable in perfection to that of the non-crosslinked polymer. This behavior appears to be typical of crystallized networks formed from random chains, irrespective of the nature of the polymer and the large depression of the melting temperatures that are observed can be attributed to this cause. Only when the specific nature of the imperfections are known can a quantitative estimate of the effect of crosslinking on the melting temperature be made.

The fact that the introduction of crosslinks severely depresses the melting temperature of a network has an important bearing on the analysis of the mechanism and rates of crystallization from the melt for such systems. For natural rubber networks it is well known[16,17] that the introduction of crosslinks severely retards the crystallization rate at a given temperature. It has been tacitly assumed[17] that this effect is due solely to the reduction in the mobility of the crystallizing chain segments which in turn retards the rate of the transformation. More definitive conclusions could be reached when comparison is made at the same value of undercooling rather than at the same temperature. Such experiments, which would account for the differences in melting point that occur on crosslinking, would more properly assess the role played by nucleation processes in the development of crystallinity. In fact, Price[18] recently has reported that the rate of growth of spherulites in polyethylene networks formed from random chains is independent of the number of crosslinks when comparison of the different networks is made at the same value of undercooling. Thus for this polymer, when the observed differences in melting temperature are properly accounted for, the rate of spherulitic growth is unaffected by crosslinking.

Networks from Oriented Chains.—In contrast to the formation of networks from random chains, the introduction of crosslinks into a system of axially ordered chains affects the configurational entropy

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(14) P. J. Flory and L. Mandelkern, *J. Polymer Sci.*, **21**, 345 (1956).

(15) A. S. Posner, L. Mandelkern, C. R. Worthington and A. F. Diorio, *J. Appl. Phys.*, **30**, in press (1959).

(16) N. Bekkedahl and L. A. Wood, *Ind. Eng. Chem.*, **33**, 381 (1941).

(17) A. N. Gent, *J. Polymer Sci.*, **18**, 321 (1955).

(18) F. P. Price, Abstract of paper presented before the meeting of the American Chemical Society, Boston, Mass., April, 1959.

of the units in the liquid state.[1] This occurs because crosslinking in this state requires that the unit of one molecule be joined to a neighboring predetermined unit, because of the order imposed on the system and maintained during the crosslinking. Thus, even if the crosslinks are randomly distributed in space, an order will be imposed on the system which will be maintained after the transformation to the liquid state as long as the points of crosslinkage are not destroyed. A decrease in the configurational entropy of the liquid occurs because of this ordering effect. According to Flory[1] this change in entropy can be expressed as

$$\Delta S = R\nu\ [(1/2)\ln C - 9/4 + (3/4)\ln(\nu/N_{\mathrm{S}})] \quad (2)$$

where ν is the number of chains in the network, N_{S} the number of statistical units in the system and C a dimensionless quantity of the order of unity. The decrease in the configurational entropy of the liquid must result, of course, in a decrease in the entropy of fusion. If the alteration of the entropy of fusion were the sole effect of crosslinking oriented chains, then under equilibrium conditions the isotropic melting temperature should obey the relation[4]

$$(1/T_{\mathrm{m}}^{0} - 1/T_{\mathrm{m}}^{\mathrm{i}}) = (R\nu/N_{\mathrm{S}}\Delta h')[9/4 - 3/4\ln(\nu/N_{\mathrm{S}})] \quad (3)$$

where $\Delta h'$ is the heat of fusion per mole of statistical elements. According to equation 3 the isotropic melting temperatures of networks fulfilling the above conditions should be greater than that of the non-crosslinked system from which they are formed and should progressively increase with increasing values of ρ.

The results of Fig. 3 show that contrary to these expectations a slight decrease occurs in the isotropic melting temperature of the networks formed from fibrous natural rubber. However, the melting temperatures decrease only slightly with ρ and are greater in magnitude than those of corresponding networks formed from random chains. It can be assumed that the presence of crosslink units again prevents the development of the required more perfectly crystalline order that can be attained in the non-crosslinked system.[4] Hence the expected increase in $T_{\mathrm{m}}^{\mathrm{i}}$ on crosslinking oriented chains, caused by the decrease in chain configurational entropy, can be offset by the other effects of crosslinking which limit the perfection of the crystallinity developed. It therefore appears reasonable, in making quantitative comparison between the two types of networks, to assume that the non-configurational effects of crosslinking on the melting temperature are the same for both cases. When this condition is invoked equation 3 can be rewritten as

$$1/T_{\mathrm{m,r}}^{\mathrm{i}} - 1/T_{\mathrm{m,o}}^{\mathrm{i}} = (R\rho/\Delta H_{\mathrm{u}})[9/4 - 3/4\ln(\rho k)] \quad (4)$$

where $T_{\mathrm{m,r}}^{\mathrm{i}}$ and $T_{\mathrm{m,o}}^{\mathrm{i}}$ are the melting points of the networks formed from random and oriented chains, respectively, and ΔH_{u} is the heat of fusion per mole of repeating unit. The parameter k represents the number of chain repeating units equivalent to one statistical segment.[19]

In Table I comparison is made between the observed values of the quantity $(1/T_{\mathrm{m,r}}^{\mathrm{i}} - 1/T_{\mathrm{m,o}}^{\mathrm{i}})$ as determined from the smoothed data of Fig. 3 and the same quantity calculated from equation 4 with k being assigned values of one and three, respectively.

TABLE I

COMPARISON OF ISOTROPIC MELTING TEMPERATURES OF NATURAL RUBBER NETWORKS

	$(1/T_{\mathrm{m,r}}^{\mathrm{i}} - 1/T_{\mathrm{m,o}}^{\mathrm{i}}) \times 10^3$		
		Theoretical	
$\rho \times 10^3$	Obsd.	$k = 1$	$k = 3$
5.0	0.049	0.062	0.052
7.5	.080	.084	.073
10.0	.110	.109	.093
12.5	.163	.133	.113
15.0	.180	.155	.131

The data in this table show that when comparison is made at the same values of ρ, the differences observed in the melting temperature of the two types of networks are in good accord with theoretical expectations over the crosslinking range in which it is possible to prepare crystallizable networks. Very good agreement is obtained when 1% or less of the units are crosslinked. The slight deviations that occur for the higher values of ρ indicate a greater observed difference in $T_{\mathrm{m}}^{\mathrm{i}}$ than is expected. This can be attributed to the large melting point depression observed for the networks formed from random chains in this range. Thus quantitative support is given to the concept that there is a significant decrease in configurational entropy in the liquid state when networks are formed from axially oriented chains. Qualitatively similar effects are shown for networks formed from highly crystalline but unoriented chains.[4] In this instance the microscopic order between chains in the crystalline state is sufficient for the effect to be observed.

WASHINGTON, D. C.

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[19] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 399 ff.