FeX_4^{--} would be paramagnetic with four unpaired electrons. The existence of perchlorate and fluoroborate salts of the $M_2(PAA)_3(X)_4$ type also militates against structure VI, since these anions have only very slight tendencies to coördinate with metal ions.

A reasonable structure for the $[M_2(PAA)_3]^{+4}$ ion is one in which each of the three ligand molecules acts as a bidentate group toward each of the two metal ions. If all four nitrogen atoms of each ligand are coördinated, the twelve apices of the octahedra around the two metal ions are filled. The resulting structure would be similar to the $W_2Cl_9^{-3}$ ion,[13] in which the two octahedra have one face in common, except that, in this case, the two adjacent faces are separated by the N–N bond distance. It can be shown, using models, that each of the three ligands will remain nearly planar, thus contributing to the stability of this structure. Earlier workers have prepared $(M_2trien_3)^{n+}$ compounds, where "trien" is the tetradentate triethylenetetramine,[14] but the nature of the preparations indicates that only one ligand acts as a bridge, with the other two ligands behaving as tetradentate chelating agents toward single metal ions. Such a structure does not seem reasonable for the compounds reported here, since pyridinaldazine cannot chelate in a tetradentate manner.

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[13] A. F. Wells, "Structural Inorganic Chemistry," Second Edition, Oxford University Press, London, 1950, p. 295.

[14] F. Basolo, THIS JOURNAL, **70**, 2634 (1948); H. B. Jonassen and B. E. Douglas, *ibid.*, **71**, 4094 (1949).

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

Some Properties of Polymer Networks Formed from Oriented Chains of Natural Rubber

BY D. E. ROBERTS AND L. MANDELKERN

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Highly oriented natural rubber samples prepared by a modification of the racking process described by Feuchter were cross-linked by means of γ-radiation. Some of the physical properties of the networks prepared in this manner were studied and compared with networks formed from chains which were randomly arranged prior to the introduction of the cross links. In accord with the theoretical considerations of Flory it was found that the swelling behavior, isotropic length, and isotropic melting temperature of the networks depend not only on the fraction of units cross-linked but also very markedly on the arrangement of the chains prior to network formation. It also was observed that the crystalline oriented racked rubber was cross-linked twice as effectively by γ-radiation as was the amorphous rubber.

Introduction

A three-dimensional polymer network can be formed from an assemblage of individual polymer chains by the intermolecular linking of a sufficient number of chain elements. This intermolecular linking process is termed cross-linking and can be carried out by a variety of chemical methods and in favorable cases by the use of high energy radiation. The network that is formed differs in many of its properties from the original system of polymer chains. A polymer network is characterized by its insolubility, although it has the ability to imbibe many times its volume of liquid when immersed in a good solvent. A non-network collection of polymer chains, on the other hand, will completely dissolve under the same conditions. In the absence of crystallinity a polymer network is also characterized by its long range elasticity at temperatures above its glass temperature. Thus a network has the capacity to support a relatively large stress and to return to its original dimensions when the stress is removed.

In considering the physical and mechanical properties of polymeric networks, from both theoretical[1] and experimental[2] points of view, it always has been assumed that the cross-linking is a random process, *i.e.*, units of different molecules are paired together in an uncoördinated and random manner, and furthermore that the polymer chains are in a randomly coiled configuration. The requirement that chain segments be randomly disposed prior to network formation is obviously a stringent limitation on the types of networks that can be formed. It is well known, for example, that many of the fibrous proteins occur naturally in a state of high orientation and cross-links if not already present can be introduced without disrupting the characteristic order of the system. Similarly, by a suitable mechanical and thermal treatment many of the more flexible chain-type molecules can be brought to states of high order and orientation and subsequently cross-linked. In a recent theoretical paper Flory[3] has considered the problem of how the properties of a network will depend on the relative arrangement of the chains prior to network formation. In this very general treatment the previous results for the more usual type network are deduced as a special case. The other extreme that can be conveniently considered is the case where the chains are perfectly axially oriented. It was found[3] that the properties to be expected in a network depend not only on the fraction of the units that are randomly cross-linked but also, in a significant manner, on the disposition of the chains prior to network formation. These theoretical deductions are important in efforts to explain the behavior and physical properties of both protein and non-protein macromolecular systems, and it is therefore of interest to assess, by experimental studies, their general validity.

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[1] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 464 ff.

[2] P. J. Flory, ref. 1, p. 577 ff.

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

The present paper is concerned with an investigation and comparison of the properties of two types of natural rubber networks. One type of network is the usual type which is obtained when the chains are randomly coiled prior to cross-linking. The other type of network, which has not been heretofore studied, is that formed from chains originally in a highly axially oriented state. Natural rubber was selected for this initial study since it can be cross-linked easily by the action of γ-rays and a great deal of physico-chemical information concerning this polymer is available. The physical properties of the network selected for study were the isotropic melting temperature, the isotropic length and the equilibrium swelling ratio. The manner in which these properties depend on the fraction of the units cross-linked and the mode of network formation were investigated. A preliminary report, which discussed the changes that occur in the isotropic length of a network when it is cross-linked already has been communicated.[4]

Experimental

Materials.—The natural rubber used in this work was obtained from the original latex which contained ammonia as a preservative. Films ranging in thickness from 0.5 to 2.0 mm. were prepared in the conventional manner by casting the latex on clean glass plates and allowing it to air-dry for 15 days, during which time the sheet was turned over once or twice to expose both surfaces to air. As would be expected[5] films prepared in this manner were not completely soluble in good solvents such as benzene or toluene, even at elevated temperatures. About 35% of the polymer film thus prepared was found to be insoluble. When immersed in benzene the insoluble gel portion swells to about sixty times its original volume, indicating that the fraction of the units cross-linked is relatively small. However, since the slight amount of cross-linking that is present is a very desirable feature in the subsequent treatment of the film, no effort was made to remove or prevent the formation of gel. The density of the dried latex film was determined by the method of hydrostatic weighings[6] and found to be 0.910 g./cc. at 25° which is in accord with the accepted value for natural rubber in the amorphous state.[7] There was no evidence of orientation or crystallization in these films as determined by X-ray diffraction. This material was then used to prepare networks of the type whose chains were in the randomly coiled configuration and also served as the starting material for preparing the highly oriented systems.

Racking Process.—The highly oriented state of the rubber molecules was obtained by a modification of the "racking process" originally developed and described by Feuchter.[8] The term racked is applied to a polymer sample stretched well beyond its normal limit of extensibility and being capable of maintaining this state without the application of any external force. In this procedure a narrow strip of the latex film is subjected to a very rapid elongation while being held at an elevated temperature and is then quickly cooled to about 20°. Crystallization ensues rapidly at the lower temperature and, when the external force is removed, the specimen remains in the crystalline and elongated condition. By successively repeating the heating, stretching and cooling operations enormous extensions can be reached with natural rubber, elongations as high as 10,000% being reported.[9] However, it is found that the ratio of the extended or racked length to the retracted length of the specimen continually decreases with each successive racking operation, the maximum in this ratio being achieved after the first step. It appears that continually racking the sample introduces irrecoverable increases in length which may be attributed to such processes as chain rupture or flow. Because of these considerations the oriented samples prepared for study were limited to only one racking cycle.

The maximum extended length that could be attained in one cycle is also strongly influenced by the temperature at which the stretching takes place. For the natural rubber latex films that were used here the optimum temperature was found to be 80°, and a maximum ratio of racked length to retracted length of about eleven was achieved in the specimens used. Extensions of this order are much larger than that usually achieved by subjecting natural rubber to a simple tensile force. Solubility studies indicate that during the one-cycle racking process no change occurred in the proportion of the material that was gel. These high extensions could be obtained by us only when the lightly cross-linked latex film was used. Attempts at racking rubber from other sources as smoked sheet and pale crepe were not nearly as successful. It would appear that a necessary requirement for obtaining high elongation is that the polymer be either lightly cross-linked or be of very high molecular weight.

The wide-angle X-ray pattern of the racked rubber[9] is a characteristic fiber-type diagram with a large number of sharp reflections indicative of high axial orientation. However, an amorphous halo still persists. This latter observation is in accord with our measured density of 0.938 g./cc. for the racked rubber, which indicates that though highly oriented only about 35% of the material is in the crystalline state.[10] The highly oriented condition of racked rubber is maintained without the application of any external force at temperatures up to and including 42°. At this temperature the rubber shrinks very quickly to its original length and reverts to the disordered state. Both the original latex rubber and the racked specimens can be cross-linked when exposed to the action of γ-rays from a Co^{60} source. As the density of cross-links in the oriented material is increased, the temperature at which retraction occurs decreases progressively until a point is reached where the samples will retract at room temperature while being irradiated. Despite this limitation on the amount of cross-linking that can be introduced into racked rubber, a sufficient fraction of the units can be interlinked without significant shrinkage occurring, so that the properties of interest and their dependence on cross-linking can be studied.

Cross-linking Procedure.—Both a 50-curie and a 200-curie Co^{60} source located at the National Bureau of Standards were used for the irradiations. The specimens being irradiated were contained in a sealed and evacuated 20-mm. Pyrex tube, the flat bottom of which was placed a fixed distance above the source. Prior to being subjected to the action of the γ-rays each strip of racked rubber was split in half along the longitudinal direction, and one of the halves, which served as a control for the length measurements, was not irradiated. The strips to be irradiated were wrapped into coils to fit the inner diameter of the Pyrex tube, and alternate layers of the amorphous unoriented rubber and the racked coils were placed in the tube, and the distance of each sample from the bottom of the tube was noted. The number of samples in a given tube usually ranged from six to ten, and the tube and its contents were subjected to the action of the γ-rays for a predetermined time. Exposure times for the experiments reported here ranged from 6 to 1000 hr. The appropriate dose rate for each sample was determined from its distance from the bottom of the tube, the distance of the bottom of the tube from the source and a previous calibration[11] relating dose rate and distance from the source. Thus, for a given total exposure time for the entire tube, each sample can be characterized by an equivalent exposure time which is proportional to the radiation dose received. In a typical experiment, if the total exposure time of the tube was 600 hr., the equivalent exposure time of the individual rubber specimen would range from 600 hr. to about 100 hr.

Length Measurements.—Subsequent to the introduction

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[4] D. E. Roberts, L. Mandelkern and P. J. Flory, THIS JOURNAL, **79**, 1515 (1957).

[5] E. M. Bevilacqua, *Science*, **123**, 1123 (1956).

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

[7] L. A. Wood and N. Bekkedahl, *J. Appl. Phys.*, **17**, 362 (1946).

[8] H. Feuchter, *Kautschuk*, **1**, 6 (1925); **4**, 8, 28 (1928).

[9] See chapter by G. S. Whitby in C. C. Davis and J. T. Blake, "The Chemistry and Technology of Rubber," Reinhold Publ. Corp., New York, N. Y., 1937, for a more detailed discussion of the properties of racked rubber.

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

[11] L. A. Wall and D. W. Brown, *J. Phys. Chem.*, **61**, 129 (1957).

of the cross-linkages each of the racked samples and its corresponding control was immersed in boiling water for a half minute. The shrinkage of both specimens occurred very rapidly under these conditions. The specimens were dried in air for 24 hr. at 25° and the lengths measured using a scale which could be read to 0.1 mm. The non-cross-linked control specimens always returned to approximately their original length, which was of the order of one centimeter. This length, characteristic of the material which had been racked but had not been cross-linked, is designated as L_0. A maximum increase of length due to the racking process itself of about 5% was observed. To minimize the effect that any slow relaxation processes might have, the lengths of the specimens which had been cross-linked in the oriented condition were redetermined after swelling in benzene and redrying *in vacuo*. This length, characteristic of the retracted material which had been cross-linked in the oriented state, is designated as L_{i}. In the subsequent discussion, in order to account for the slight increase in length caused by the racking process itself, the ratio L_{i}/L_0 for each specimen will be considered.

Sol–Gel Ratio and Equilibrium Swellings.—To determine the fraction of the material partitioned between the sol and gel portions after irradiation, the original unoriented samples and the retracted oriented samples were weighed and immersed in freshly distilled benzene at 25°. Swelling occurred during this process as well as dissolution of the sol fraction. The benzene was replaced every 48 hr. and this process was continued for five to ten days. After this period of extraction it was found that the dried insoluble or gel portion had attained a constant weight which did not change on further extraction. To assess the reliability of this method in a few experiments, the total benzene supernatant was evaporated to dryness and the amount of soluble material determined. It was found that the total weight of the sol and the gel portion agreed with the original weight of the material to within 1%. The fraction of sol in these studies ranged from 0.65 for the original material to 0.015 for the most highly irradiated specimens.

After the sol portion had been extracted, the dried and weighed gel was reimmersed in a closed tube containing a large excess of benzene, and the system was thermostated in a water-bath maintained at 25 ± 0.1°. Preliminary experiments indicated that the swelling equilibrium was attained in seven days since no significant change of weight occurred in the swollen system after this time. After the establishment of equilibrium, the swollen gel was transferred to a weighing bottle and the contents weighed after the liquid adhering to the polymer surface was removed by brief contact with paper. The equilibrium swelling ratio of the network, which is defined as the ratio of the volume of the swollen network to the volume of the dry network, was computed from the above weight, the weight of the dried gel, and the known densities of natural rubber and benzene at 25°.

It must be emphasized that in order to obtain swelling equilibrium measurements that are of physical significance it is mandatory that all the sol be removed from the sample. Besides the obvious correction to the weight of the system that must be made if sol is present, a small amount of soluble polymeric material will drastically alter the chemical potential of the swelling liquid. Since the equations governing swelling equilibria, particularly the relation between swelling ratio and the fraction of the units cross-linked, are derived on the basis of the swelling in a pure liquid, corrections would have to be applied. The necessary corrections are difficult to introduce in a general way and would require an independent thermodynamic study. The error involved when the above-mentioned precaution is not taken can be quite serious and leads in some cases to an apparent increase in the swelling ratio as the fraction of the units cross-linked increases.[12]

Melting Point Determination.—Following the determination of the equilibrium swelling ratio the dried gel portions were placed in small stoppered tubes and the tubes were maintained at temperatures ranging from −18° to −36° for several weeks. Under these conditions of storage the crystallization of both types of polymer networks ensued, as evidenced by the development of turbidity and loss of the characteristic rubber-like elasticity. After the development of an adequate amount of crystallinity the tubes were heated at the rate of 3–4° per hour, and the temperature at which the sample became transparent was taken as the melting point. This temperature could be determined reproducibly to within 1°. The relatively rapid heating rate employed[10,13] is not conducive to the formation of the most stable crystallites, and hence this type of observation does not allow the determination of the equilibrium melting temperature. However, this procedure should be adequate for comparing the melting temperature of the different type networks. For present purposes the determination of the relative melting temperatures is all that is required.

Results and Discussion

The Cross-linking Process.—In order to describe adequately the determination of the fraction of units cross-linked in each type of network, it will be necessary to discuss briefly the theory of cross-linking and gel formation in polymers. When polymer materials are subject to the effect of high-energy radiation, either cross-linking or chain scission reactions or both usually occur.[14,15] In the case of natural rubber, Charlesby and Groves[12] have demonstrated that the predominant effect is cross-linking and the amount of chain fracture that occurs is very small. When the units of a polymer are cross-linked at random, regardless of the mechanism of the cross-linking process, Flory[16] and Stockmayer[17] have shown that certain critical conditions must be fulfilled in order for gelation to occur. They have shown that for any initial molecular weight distribution, gelation will occur when the fraction of the units in the entire system that are cross-linked ρ_t is equal to the reciprocal of the weight-average degree of polymerization. The further introduction of additional cross-links after the gel point has been reached will cause a systematic decrease in the fraction of the polymer that is soluble. In the absence of chain scission reactions, a point eventually will be reached where a sufficient number of cross-links have been introduced to render the whole material insoluble. However, if the cross-linking is accompanied by chain scission processes then complete insolubility of the material will not be attained.

A quantitative description of the partitioning of the polymer material between sol and gel in the post gelation region has been given by Flory[18] in 1947. Under the assumptions that chain units are paired at random and that chain scission reactions are absent, he found that the fraction sol of the material W_s can be expressed as

$$W_s = \sum_{y=1}^{\infty} w_y \left[1 - \rho_t(1 - \phi_s)\right]^y \qquad (1)$$

where w_y is the weight fraction of chains in the original polymer consisting of y repeating units, and ϕ_s is the probability that a non-cross-linked chain unit selected at random will be part of the sol. This equation is valid for any initial molecular weight distribution of the primary molecules. ϕ_s can be related to W_s by the relation

$$W_s/\phi_s = 1 - \rho_t(1 - \phi_s) \qquad (2)$$

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[12] A. Charlesby and D. Groves, "Proc. Third Rubber Tech. Conf.," W. Heffer and Sons, Ltd., Cambridge, England, 1954, p. 317.

(13) L. Mandelkern, *Chem. Revs.*, **56**, 903 (1956).

(14) A. Charlesby, *J. Polymer Sci.*, **11**, 513 (1953).

(15) A. R. Shultz and F. A. Bovey, *ibid.*, **22**, 485 (1956).

(16) P. J. Flory, THIS JOURNAL, **63**, 3097 (1941).

(17) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(18) P. J. Flory, THIS JOURNAL, **69**, 30 (1947).

When ρ_t is small, ϕ_s in equation 1 can, with negligible error, be identified with W_s, and the equation reduces to the more useful form of

$$W_s = \sum_{y=1}^{\infty} w_y[1 - \rho_t W_g]^y \qquad (3)$$

where W_g is the weight fraction of the gel.

With the recent renewed interest in cross-linking processes in polymers, due to the availability of high energy radiation sources, equation 3 has been rederived by Baskett,[19] and an approximate version also has been given by Charlesby.[20] Equations 1 and 2 or their approximate version equation 3 indicate how the primary molecular weight distribution, characterized by w_y, can be obtained from a knowledge of the dependence of the sol–gel ratio on the fraction of the units cross-linked.[18] Flory[18] has also shown that for low values of ρ_t the fraction of the units in the sol that are cross-linked ρ'

$$\rho' = \rho_t W_s \qquad (4)$$

while ρ, the fraction of the units in the gel that are cross-linked, can be expressed approximately as

$$\rho = \rho_t(1 + W_s) \qquad (5)$$

In order to apply these considerations to situations where chain scission processes occur concurrently with cross-linking, as often happens when the sample is exposed to high energy radiation, it is only necessary to specify the change that occurs in w_y as a consequence of the degradation process. For many types of initial distribution the new distribution that results from the random fraction of a given number of bonds can be computed.[21] If the above conditions prevail and the number of fractures is proportional to the radiation dose, the distribution consistent with a given radiation dose, in the absence of cross-linking, can be specified. Similarly if ρ_t is also proportional to the radiation dose, the fraction sol can be expressed in terms of the radiation dose and the two above-mentioned proportionality factors. Charlesby[20] has considered in detail the situation where a polymer subject to high energy irradiation initially possesses a "most probable" molecular weight distribution, and the number of cross-links introduced and the number of bonds broken are each proportional to the radiation dose. He found that the manner in which W_s varies with radiation dose will depend very markedly on the ratio of the number of bonds broken to the number of cross-links formed per unit dose. The limiting value of W_s at high radiation dose reflects the magnitude of this ratio for this type of initial molecular weight distribution. Qualitatively similar results should be expected for other types of initial molecular weight distributions.

In the present work very lightly cross-linked chains in either the disoriented or racked condition were further cross-linked by the action of γ-rays. To study adequately and compare the properties of the resulting networks, it is required that the fraction of the units in the gel that are cross-linked ρ be specified. This quantity, for the networks formed from disoriented chains, can be obtained in a relatively simple manner from the equilibrium swelling ratio in a suitably chosen solvent by use of the conventional swelling equations.[22,23] Unfortunately this procedure is not directly applicable to networks formed from highly oriented chains (see discussion of swelling below) since the appropriate swelling equation contains a parameter which depends on the disposition of the chains prior to cross-linking and this parameter has not as yet been susceptible to calculation.

In order to circumvent this difficulty, advantage can be taken of the fact that in a series of experiments it was found that for both the disoriented chains and the racked chains the limiting value of W_s ranges between 0.015 to 0.020. Thus following Charlesby's analysis we can conclude that the ratio of the number of bonds broken to the number of cross-links formed per unit radiation dose is the same in the two cases and that the cross-linking process is by far the predominant effect. Since both types of chains possess the same initial molecular weight distribution, the variation of W_s with radiation dose should be identical in the two cases provided only that the same proportionality exists between ρ_t and radiation dose. If, however, the above-mentioned proportionality is different in the two cases, then the fraction of sol will not be the same at a given radiation dose. From any observed differences that may occur in the fraction of sol, the relative amounts of cross-linking in the two cases can be deduced. Since for the network formed from random chains an absolute value of ρ can be obtained from swelling equilibrium and ρ_t obtained by application of equation 5, knowledge of the relative efficiency of cross-linking will enable ρ_t to be determined from the network formed from ordered chains.

To evaluate the relative efficiencies of the cross-linking process, the fraction sol of each type of network was determined at various radiation dosages so chosen that W_s ranged from 0.65 to 0.20. The results of these experiments are illustrated in Fig. 1, where the sol fraction is plotted against radiation dose, the dosage being expressed in terms of the equivalent time of exposure. The solid curve is drawn through the experimentally observed points representing the results for cross-linking chains in the highly oriented state, while the open circles represent the fraction sol obtained when the random chains were cross-linked. Under corresponding conditions the fraction sol obtained from the oriented chains is always less than when the chains are arranged at random. Since chain scission processes are small and in the same proportion to cross-linking in both cases the plot in Fig. 1 indicates that for any given radiation dose cross-linking is more effective in the racked system. The dashed curve in this plot is obtained from the solid curve by multiplying the abscissa corresponding to a given W_s by a factor of two. The dotted curve adequately represents the data for the networks formed from the collection of randomly coiled chains. It can thus be concluded that the cross-

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(19) A. C. Baskett, *La Ricerca Scientifica*, Supplement A, page 379 (1955).

(20) A. Charlesby, *Proc. Roy. Soc.* (*London*), **A222**, 542 (1954).

(21) N. Grassie, "Chemistry of High Polymer Degradation Processes," Butterworths Scientific Publications, London, 1956, p. 118 ff.

(22) P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).

(23) P. J. Flory, *ibid.*, **18**, 108 (1950).

linking of the racked chains is about twice as efficient as the cross-linking of the chains **in** the disordered state.

The above analysis is probably an underestimate of the relative cross-linking efficiencies of the two cases since in highly oriented systems a greater proportion of cross-links will be between adjacent chains already cross-linked and part of the gel. Cross-links of this type will not be effective in causing additional molecules to become part of the gel and can be considered to be wasted cross-links. This effect should become more pronounced at low fraction of sol and should not seriously affect the above analysis which is limited to higher sol concentrations. The reasons for the large differences in the relative efficiencies of cross-linking in the two cases is not readily understood, nor is it clear as to whether it is due to the crystallization, the orientation or a combination of both. Though these observations are of significance in themselves, the problem has not as yet been investigated any further since it is not pertinent to the present investigation.

Swelling Behavior.—The theoretical relation derived by Flory[3] which describes the swelling equilibrium of a polymer network can be expressed as

$$[V_1\rho/\bar{v}M_0][\langle\alpha\rangle_0^2 v_2^{1/3} - v_2/2] = -[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \quad (6)$$

where v_2 is the volume fraction of polymer in the swollen gel, *i.e.*, the reciprocal of the equilibrium swelling ratio Q_m, V_1 and $\bar{v}$ are the molar volume of the swelling liquid and specific volume of the polymer, respectively, M_0 is the molecular weight of the chain repeating unit, χ_1 is the thermodynamic interaction parameter[2] and $\langle\alpha\rangle_0$ is a parameter which is dependent on the disposition of the polymer chains relative to one another prior to the random introduction of cross-links.

In considering the properties of a network, where the stipulation is not made that the chains be randomly disposed relative to one another prior to cross-linking, a reference state of the isotropic (zero force) network[3] is taken as that where the mean square components of the chain vectors are equal to each other and consequently equal to one third the mean square end-to-end distance of the unconstrained or free chain $\overline{r_0^2}/3$. Limiting considerations to networks formed at constant temperature and in the absence of diluent the mean square end-to-end distance of the chains for the isotropic network will depend on the relative disposition of the chains prior to network formation. If the mean square end-to-end distance of the chains in the network in the isotropic state at the same volume of the reference state is $\overline{r_i^2}$, then the quantity $\langle\alpha\rangle_0$ is defined[3] as $(\overline{r_i^2}/\overline{r_0^2})^{1/2}$ and measures the geometric mean of the linear dilation of the network relative to the reference state. For networks formed from chains randomly arranged $\overline{r_i^2}$ will be equal to $\overline{r_0^2}$ and $\langle\alpha\rangle_0$ will obviously be equal to unity. However, for networks formed from oriented chains the value of $\langle\alpha\rangle_0$ will depend on the details of chain dimensions and arrangements prior to cross-linking. For highly oriented chain $\langle\alpha\rangle_0$ has as yet not been susceptible to direct calculation but generally can be expected to differ from unity.[3]

When $\langle\alpha\rangle_0$ is equal to unity equation 6 reduces to the conventional or more usual equilibrium swelling relation. The resulting equation then can be used to calculate ρ for the case of the random cross-linking of random chains as long as χ_1 can be specified. However, for a network formed by the cross-linking of oriented chains, $\langle\alpha\rangle_0$ will differ from unity by an unspecified amount. Hence in this case ρ cannot be determined solely from equilibrium swelling measurements. It is this consequence of equation 6 which necessitates the adoption of the following procedure in order to determine ρ for this type network.

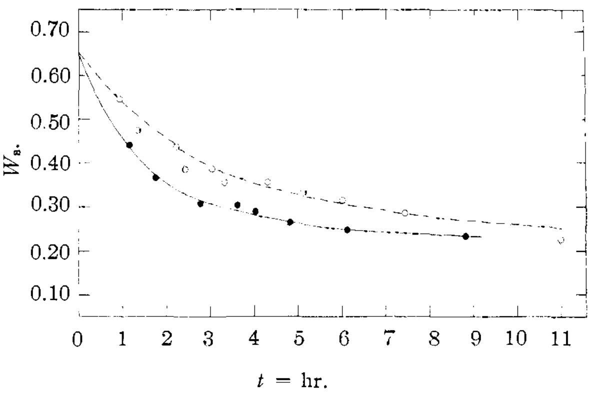

Fig. 1.—Fraction of sol, W_s, *versus* equivalent irradiation time, t: racked rubber, ●; amorphous rubber, ○.

It may be recalled that each tube that was irradiated consisted of alternate layers of amorphous unoriented rubber and of racked rubber, and each sample could be characterized by an equivalent radiation time. For the initially amorphous samples in each tube the value of ρ_t could be determined from the fraction gel and the swelling equilibrium of the gel portion in benzene by use of equation 6, ($\langle\alpha\rangle_0 = 1$) employing Gee's[24] value of 0.395 for χ_1. Though for this type of rubber ρ_t increased monotonically with the equivalent radiation time an exact direct proportionality between the two quantities was not observed. The value of ρ_t for an oriented system irradiated for a given equivalent time was obtained by first considering the appropriate value for an amorphous system under the same condition of irradiation. This latter quantity could be deduced easily by interpolation from the observed results for the amorphous system. The value appropriate to an oriented system at the same equivalent time is obtained when the relative efficiency of cross-linking of the two types of systems is accounted for. This is accomplished when the value of ρ_t for the amorphous polymer is multiplied by a factor of two. The procedure just outlined was used to determine ρ_t for the oriented systems. The value of ρ for the network formed from the oriented chains is then obtained by using equation 5.

The solid circles plotted in Fig. 2 are the experimental results obtained for the equilibrium swelling ratios of the networks obtained from the highly

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[24] G. Gee, *Trans. Farad. Soc.*, **42B**, 33 (1946); **42**, 585 (1946).

oriented specimens. A large range in cross-linking density is covered by these experiments with a maximum of 3% of the units being involved in cross-linkages. The plotted points delineate a curve indicated by the dashed curve in the figure. The shape of this curve over the complete cross-linking range is such that it cannot be exactly described by equation 6 with a fixed though arbitrary value of $<\alpha>_0$. This can be seen by comparing the plotted points with the two solid curves in the plot which were calculated from equation 6 for values of $<\alpha>_0 = 1.0$ and $<\alpha>_0 = 0.8$, respectively. The deviations from the theoretical relation are beyond the experimental errors, and if equation 6 is to apply, $<\alpha>_0$ must vary with ρ. This possibility already has been considered by Flory[3] in his original consideration of the problem. In order to satisfy the experimental results for this case, $<\alpha>_0$ would have to vary from 0.75 to 1.0 over the cross-linking range.

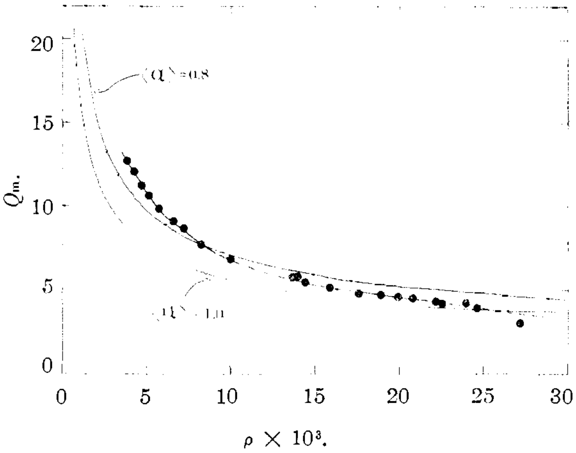

Fig. 2.—Swelling ratio, Q_m. *versus* fraction of units cross-linked, ρ. Solid lines theoretical curves calculated from equation 6 for indicated values of $<\alpha>_0$. Experimental results for networks formed from oriented chains designated by ●.

An exact quantitative comparison between theory and experiment is obviously very difficult to make because of the inherent difficulty of specifying $<\alpha>_0$ and its variation with ρ. However, the results of these experiments as illustrated in Fig. 2 indicate that the amount of liquid that a network will imbibe at equilibrium will depend markedly on the arrangement of the chains prior to network formation. This can be seen by comparing the theoretical curve representing the swelling equilibrium of networks formed from random chains with the experimental results for the networks formed from ordered chains. This fact confirms one of the major conclusions drawn from the theoretical considerations which resulted in equation 6. As a consequence of this fact appreciable error would result if the conventional swelling relation ($<\alpha>_0 = 1$) were used to determine ρ when a different value of $<\alpha>_0$ were appropriate. Thus for a network characterized by a value of $<\alpha>_0 = 0.8$ errors of the order of 30 to 50% could be expected if the aforementioned procedure were adopted.

Isotropic Length.—An interesting property of a polymer network which heretofore has received relatively slight consideration is its isotropic length. The isotropic length L_i is defined as the length of the amorphous network in the absence of any external force. From theoretical considerations Flory[3] concluded that the manner in which L_i will depend on the fraction of the units cross-linked will be largely influenced by the arrangement of the chains prior to the introduction of cross-links. He derived the relation that

$$L_i = (\nu/\sigma')(\overline{r_0^2}/3)^{1/2} <\alpha>_0 \qquad (7)$$

where ν is the number of chains in the network and σ' to a good approximation can be identified with the number of chain vectors passing through a plane transverse to the axis of the sample, it being assumed that the value of σ' at the time of network formation and in the isotropic state are identical.

If a collection of chains in the randomly coiled configuration are cross-linked then, as defined above, the resultant network will be in the isotropic state regardless of the number of cross-links introduced. The length of the network would then be L_i, and except for a very small variation due to the density change that accompanies the actual cross-linking process, would be independent of ν. The fact that a Gaussian distribution of chain end-to-end distances is maintained prior to and subsequent to the random cross-linking process requires that this condition be fulfilled. This fact is easily verified experimentally. Since $\overline{r_0^2}$ will vary inversely as ν, it can be concluded[3] from equation 7 that for a network formed in this manner σ' must increase as $\nu^{1/2}$.

This increase in σ' with cross-linking has been given qualitative explanation[3] by the fact that a plane transverse to the sample axis will be intersected many times by the segments of a given randomly coiled chain. Hence when subsequent cross-links are introduced, not only are more chain vectors added to the system but more of the vectors will intersect the plane under consideration with the resultant increase in the value of σ'. However, if the polymer chains are oriented prior to the introduction of cross-links, the number of segments of a given chain which intersect the transverse plane must necessarily decrease. Thus if the same number of new chain vectors are introduced as in the previous case, the number of these vectors which cross the transverse plane will not be as great and consequently σ' will not increase as rapidly with the cross-linking density. In the extreme case of perfect axial orientation σ' will be equal to the number of polymer molecules in a cross-section and obviously will then be independent of the amount of cross-linking. Since $\overline{r_0^2}$ will vary inversely as σ' we conclude from equation 7 that for this case L_i should increase directly as $\nu^{1/2} <\alpha>_0$. Thus the two extreme cases of chain arrangements prior to network formation lead to quite different expectations as to how the isotropic length will depend on cross-linking. If perfect axial orientation of a collection of polymer molecules could be achieved, it is implied by equation 7 that the first cross-links introduced would cause the isotropic length to shrink to zero.

Since it is well known that the cross-linking of amorphous unoriented chains does not alter the dimensions of a sample, it is of interest to investigate the dimensional changes that occur in the isotropic state of a network formed from chains which were originally oriented. It has been reported[25,26] that when stretched natural rubber networks are cross-linked, there is an increase in the length of the sample when the stress is removed. These experiments were limited, however, to cases where the cross-links were introduced into deformed systems which were still within the Gaussian range. Systematic quantitative studies, particularly at high orientations, have not been made to test adequately any of the conclusions that can be drawn from equation 7. The high orientation possessed by racked rubber specimens and the ease with which it can be quantitatively cross-linked make it a suitable polymeric system with which to study these effects.

A brief report on the change of L_i with cross-linking for racked rubber samples already has been given,[4] and reference is made to the figure contained in that communication. To account for minor variations among the different specimens the ratio of L_i to L_0 the length of the retracted but non-cross-linked specimen was considered. This ratio increased by a factor of two and a half over the fifty-fold range of cross-linking encompassed by the experiments. When the ratio L_i/L_0 is plotted against $\rho^{1/2}$, as in the figure cited,[4] it is found that for values of $\rho^{1/2}$ greater than 9×10^{-2} the data are well represented by a straight line whose slope is 15. When this straight line is drawn so as to correspond to lower values of $\rho^{1/2}$, it extrapolates almost exactly to the origin. However, the actual experimental results at the lower cross-linking densities show marked deviations from the straight line delineated by the data at the higher cross-linking densities. In fact the ratio L_i/L_0 approaches unity with an almost horizontal slope. Thus we observe that the initial introduction of cross-links causes only a slight increase in the isotropic length, but after about 1% of the chain units become involved in cross-linkages, the isotropic length increases linearly with $\rho^{1/2}$.

In order to consider these experimental results in more detail, it will be convenient to reduce equation 7 to a form which will be more appropriate for the consideration of networks formed from highly oriented chains. If V is the volume of the specimen (assumed to be the same in the retracted and the racked state) and L_r is its length in the racked state, then for perfect axial orientation the number of chains which intersect a plane transverse to the axis of the specimen can be written as

$$\sigma' = V/(L_r a) \tag{8}$$

where a is the cross-sectional area of a single chain. For a system containing N_0 units, $\nu = N_0\rho$ and since $(\overline{r_0^2})^{1/2}$ can be expressed as $(\overline{r_0^2}/M)^{1/2}(M_0/\rho)^{1/2}$, equation 7 becomes

$$L_i/L_0 = (L_r/L_0)\{[N_a a/(\sqrt{3}M_0{}^{1/2}\bar{v})](\overline{r_0^2}/M)^{1/2}\}\rho^{1/2} <\alpha>_0 \tag{9}$$

where N_a is Avogadro's number. Thus from equation 9, an estimate can be made of the slope to be expected from the linear plot of L_i/L_0 against $\rho^{1/2}$.

The two molecular quantities, $\overline{r_0^2}/M$ and a, which are needed to evaluate this slope, are available as a result of the intensive investigations of the properties of natural rubber. From the appropriate dilute solution studies of the configurational properties of natural rubber, Wagner and Flory[27] have concluded that $(\overline{r_0^2}/M)^{1/2}$ is equal to 0.83×10^{-8} cm. The extensive crystallographic studies of Bunn[28] have resulted in a detailed analysis of the structure and dimensions of the unit cell. From this work the cross-sectional area of a chain is found to be 27.8×10^{-16} cm.^{2}. The specific volume of amorphous natural rubber at 25° is 1.10 cm.^{3}/g.,[7] so that the quantity in the braces of equation 9 becomes equal to 0.89. Since in these experiments the ratio of L_r/L_0 is between eleven and twelve, and an average value of $<\alpha>_0$ can be taken as 0.9, a theoretical slope of approximately 10 is predicted from equation 9. This theoretical estimate compares favorably with the value of 15 observed for the linear portion of the plot and gives strong substantiation to the theoretical conclusions. The discrepancy between the theoretical and observed slope can be attributed in part to uncertainties in the value of a and $\overline{r_0^2}/M$, approximations in the theory and the assumed invariance of σ'.

These results show that a substantial increase in the isotropic length of a sample can be accomplished by cross-linking chains in an oriented state. The limitation imposed on the number of cross-links that can be introduced into racked rubber without retraction occurring already has been discussed. It would appear that if a higher cross-linking density could be accomplished, even larger values of the isotropic length would be attained. This phenomenon is not limited to natural rubber. It appears to be true for cross-linked (tanned) collagen fibers,[29] and preliminary experiments from this Laboratory indicate that similar effects, but of greater magnitude, occur when highly oriented polyethylene is cross-linked.

The density values of the racked rubber specimens and the wide-angle X-ray diffraction patterns indicate that though substantial orientation can be achieved by the racking process, the samples are not completely crystalline nor is the orientation perfect. Thus when cross-links are initially introduced into the system, units of disordered and partially oriented chain units will become cross-linked so that a chain direction may reverse itself several times between cross-links. This would, of course, result in only a slight increase in L_i. However, at higher degrees of cross-linking, because of the fact that a substantial amount of chain orientation is present, this reversal of chain directions should be decreased. Hence, the number of chain vectors intersecting a given transverse plane should tend to remain constant and one would expect the dependence of L_i on $\rho^{1/2}$ that is observed. The fact that this straight line extrapolates to the origin

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would appear to indicate that these conditions hold after about 1% of the chain units are cross-linked.

Isotropic Melting Temperature.—When a homopolymer of sufficiently regular structure as natural rubber is brought to an appropriate temperature, crystallization will ensue without the application of any external stress. X-Ray diffraction studies indicate that when the crystallization is induced solely by cooling, the crystallites will be randomly arranged relatively to one another. When adequate care is taken during the subsequent fusion process to ensure that conditions close to equilibrium are maintained, the melting of a homopolymer is very sharp. The melting process under these circumstances can be considered to be thermodynamically reversible, and the last traces of crystallinity disappear at a well defined and reproducible temperature.

On the other hand, if the crystallites in a polymer system are oriented without the maintenance of an equilibrium stress, though at a given temperature a crystal-to-liquid transformation occurs, this temperature is not necessarily one of thermodynamic equilibrium. The non-equilibrium aspects of the fusion of oriented systems (when as equilibrium external force is not applied) was first discussed with respect to the problem of melting of stark rubber[30] and more recently with regard to the shrinkage of racked rubber[31] and the hydrothermal shrinkage of native collagen.[32] Though there are restrictions as to when equilibrium considerations can be applied to the fusion of polymers, it is a legitimate procedure to employ when the crystallization is induced from the melt solely by cooling. It is thus a matter of interest to see how the melting temperature of a network crystallized solely by cooling will depend on the mode of network formation and the concentration of cross-linkages.

As a consequence of the heating rate employed T_{m} for the non-cross-linked rubber was found to be between 9 and 10°, which is appreciably lower than the expected equilibrium melting temperature of 28–30°.[10,33] The experimentally observed melting temperatures of the two different types of networks are illustrated in Fig. 3. The upper curve in this plot represents the results for the networks formed from originally oriented chains while the lower curve is for the usual type of network. For both types of networks an appreciable depression of the melting point occurs as the fraction of units cross-linked is increased. This effect is similar in magnitude to that which has been reported previously[34] for the melting of natural rubber networks formed from unoriented chains by chemical methods. For the latter cases the melting temperatures were determined under conditions which should yield the equilibrium melting temperatures. This unexpected result appears to be due solely to the introduction of cross-links and is independent of the mode of cross-linking. Despite this fact, the data clearly indicate that at all levels of cross-linking the values of $T_{\mathrm{m}}^{\mathrm{i}}$ for the usual type of network is less than the corresponding value for networks formed from oriented chains. These differences range from 1–3° at the smaller values of cross-linking to 9–10° when ρ equal to 15×10^{-3} and appear to be diverging further at still higher levels of cross-linking. It is significant to note that for the usual type networks having cross-linking values in the range of ρ equal to $2\text{–}3 \times 10^{-2}$, no crystallization is detected when these samples are held at $-36°$ for an extended period of time while crystallization ensues relatively rapidly for comparable networks formed from oriented chains. Thus we conclude that the value of $T_{\mathrm{m}}^{\mathrm{i}}$ depends not only on the fraction of the units cross-linked but also in a significant manner on the arrangement of the chains prior to network formation.

For a network formed from chain units randomly arranged, it might be supposed that the units involved in the cross-linkages will not participate in the crystallization. The melting temperature would then be expected to be depressed in a manner similar to that which occurs on the random introduction of non-crystallizing copolymeric units to a homopolymer. If this fact were the sole consideration, then for the usual range of cross-linking encountered, melting temperature depressions of only two or three degrees would be expected.[33,34] The experimental results indicate that this is obviously not the case. Though the rather large melting point depression observed on cross-linking has not as yet received a quantitative theoretical explanation, a qualitative hypothesis can be advanced. The relations derived for the melting temperature of random copolymers are based in part on the assumption that since the polymer chains are not tied together in any permanent manner, there are no restrictions applied to the lateral growth of the crystallites which are formed.[35–37] Under equilibrium conditions the longitudinal size of the crystallites would be restricted however by the requirements of the copolymer composition. In a network, however, the points of cross-linkage will not only restrict the longitudinal growth, but since portions of chains are permanently tied together unrestricted lateral growth of a crystallite cannot occur. This would appear to be the major difference between the equilibrium crystallization and melting of a network and a random copolymer. For the same composition of extraneous ingredients, *i.e.*, cross-linkages or non-crystallizing copolymeric units, crystallites in a network would be expected to melt at a lower temperature than the corresponding copolymer under equilibrium conditions. The melting point depression would then depend primarily on the fraction of the units cross-linked and only to a lesser extent on the nature of the cross-linking process. This effect should be solely the result of the introduction of cross-links and should not depend on the relative disposition of the chains prior to cross-linking.

When polymer molecules in the random state

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are cross-linked no change occurs in the configurational entropy of the individual chains since the units which are paired together are selected at random. Thus the contribution of the configurational entropy in the liquid state to the total entropy of fusion will remain unaltered. However, as Flory[3] has pointed out, the situation is quite different when axially oriented chains are cross-linked. In this case a cross-link must join two adjacent molecules together. Thus if a unit of a given molecule is to be cross-linked to another unit, this latter unit must be in an adjacent position on a neighboring molecule. Even though the cross-links are distributed at random in space, the cross-linking process does not involve the random selection of pairs of units. The specification of adjacent units of neighboring molecules imposes an order on the system, which will persist in the liquid state because of the permanence of the cross-links. The configurational entropy of the chains in the liquid state is decreased by this process, and the entropy of fusion will be altered in a corresponding manner. The melting temperature of this type network would then be expected to be larger than that for the non-cross-linked system from which it is formed and also should be greater than the corresponding network formed from random chains. However, this expected increase in $T_m{}^i$ on cross-linking oriented chains may be offset by the non-configurational effects of the cross-links which cause a major depression of the melting point. These considerations are in accord with the observed values of $T_m{}^i$ for both types of networks.

An exact quantitative comparison between experiment and theory must await a more detailed explanation of the large melting point depression caused by the cross-linking of the random chains as well as the determination of melting temperatures under conditions more closely approaching those of equilibrium. Preliminary calculations utilizing the data of Fig. 3 indicate very good accord between the difference in melting temperature of the two types of networks and the theoretical equations.[3]

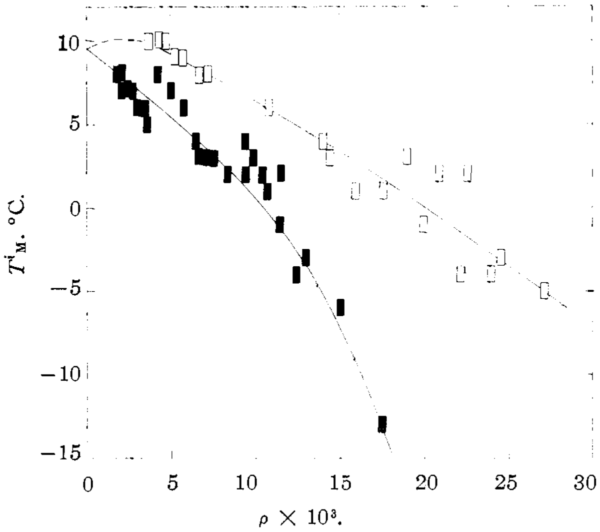

Fig. 3.—Isotropic melting temperature, T^i_M, *versus* fraction of units cross-linked, ρ: results for networks formed from random chains, ■; results for networks formed from oriented chains, □.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Thermodynamics of Shrinkage of Fibrous (Racked) Rubber[1]

BY J. F. M. OTH[2] AND P. J. FLORY

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Highly oriented natural rubber samples of Roberts and Mandelkern, prepared by racking and subsequently cross-linked using γ-radiation, undergo a spontaneous shrinkage upon melting which closely resembles the shrinkage of collagen. If the transformation is arrested by application of a tensile force, a state of equilibrium may be established between two distinct zones, or phases, one being totally amorphous (shrunken) and the other unchanged (*i.e.*, racked). Determination of the stress τ_{eq} required for phase equilibrium at various temperatures is described. Extrapolation to $\tau_{eq} = 0$ gives equilibrium melting temperatures $T_m{}^i$, which are about 8° below the temperatures $T_s{}^i$ for spontaneous shrinkage. The heat of transformation of racked to amorphous rubber calculated from the dependence of τ_{eq} on T is 4.5 cal. g.$^{-1}$. Since the degree of crystallinity is only 0.24, the heat of fusion calculated for 1 g. of crystalline rubber is *ca.* 19 cal., which agrees satisfactorily with the value 15.3 cal., deduced by Roberts and Mandelkern through use of the melting point depression method. The shrinkage of racked rubber displays all of the important features associated with the similar contraction of fibrous proteins.

Highly oriented, crystalline fibrous proteins display marked contractions when subjected to conditions which induce melting. The dimensional change is particularly striking in the case of native collagen fibers which melt with reduction in length by a factor of about one-fifth. Moreover, the transformation is macroscopically discontinuous, a partially shrunken fiber comprising two distinct regions meeting at a rather well-defined boundary transverse to the fiber axis.[3] One of these regions consists of native fiber, highly birefringent and relatively inextensible under tension; the other

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