

Anal. Found: N, 17.08. Calcd. for $C_8H_7N_3O_6$: N, 16.42.

C. Liquid Components Found in the Fraction Boiling Above 85°. 1. **Mesityl Oxide.**—This ketone was found mainly in the fraction that boiled at 125–135°. On redistillation a product was separated in a relatively pure form in the fraction that boiled at 128.5–130.5°, n_D^{20} 1.441–1.443. It formed a semicarbazone that melted at 164° and a 2,4-dinitrophenylhydrazone that melted at 201°. No depression in melting point was noticed with the respective derivatives of a known sample of mesityl oxide.

2. **Methyl Isobutyl Ketone.**—This ketone was present in a fraction that boiled at 110–122°. On redistillation a product was obtained that boiled at 115–119°, n_D^{20} 1.394–1.413, d_4^{20} 0.801, and corresponding to relatively pure methyl isobutyl ketone. It formed a semicarbazone which melted at 132° and which did not cause a depression in melting point when mixed with the corresponding derivative of a known sample of methyl isobutyl ketone.

3. **2,6-Dimethylheptenes.**—This hydrocarbon was separated from the fractions which boiled at 129–140°. After the removal of ketones and redistillation, a hydrocarbon was obtained which boiled at 132–135°, n_D^{20} 1.4369, d_4^{20} 0.761, M_D^{20} 43.39 (calcd. for C_9H_{11} , M_D 43.37). On catalytic hydrogenation a compound was obtained which distilled at 133–136°, n_D^{20} 1.4017; it corresponded to 2,6-dimethylheptane.

4. **Diisobutyl Ketone.**—Diisobutyl ketone was present in the fraction that boiled at 159–173°. On redistillation, a product was separated which boiled at 163–167°, n_D^{20} 1.412–1.414; it corresponded to diisobutyl ketone. The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone as well as the latter mixed with the authentic samples were 121–122° and 93–94°, respectively.

5. **Isophorone.**—Isophorone was separated on redistillation from the fractions which boiled at 170–190°. It distilled at 88° at 7 mm. It formed a semicarbazone which melted at 190–191° and decomposed at 193–195°.

Decomposition of Isopropyl Alcohol Containing Isophorone over Magnesia

A solution consisting of 80 mole per cent. of isopropyl

alcohol (117 g., 1.96 moles) and 20 mole per cent. of isophorone (69 g., 0.50 mole) was passed over 80 g. of magnesia at an hourly liquid space velocity of 0.9. The duration of the experiment was three hours and the temperature 493°.

The product of the reaction was analyzed by the usual method. Sixty-two per cent. of the isopropyl alcohol and 27% of the isophorone were recovered unchanged. On the basis of the reacted isopropyl alcohol the reaction product consisted of 75.5% of acetone. Fourteen and one-half grams (0.12 *M*) of liquid hydrocarbon was separated boiling at 130–132°, n_D^{20} 1.4672, and identified as 1,5,5-trimethyl-1,3-cyclohexadiene.

Summary

The decomposition of isopropyl alcohol over magnesia and magnesia which contained dehydrogenation and dehydration promoters at 490° has been studied.

Magnesia alone or in the presence of dehydrogenation promoters decomposes isopropyl alcohol to form propene, acetone, mesityl oxide, isophorone and liquid hydrocarbons. The latter consisted of 2-methylpentenes, 2-methylpentadienes and 1,5,5-trimethyl-1,3-cyclohexadiene.

The incorporation of molybdena in magnesia results in increased dehydration property of the catalyst as the content of the promoter is increased.

The introduction of alumina to magnesia results in the increase of propene formation. The liquid product consists of acetone, methyl isobutyl ketone, diisobutyl ketone, 2-methylpentene, 2-methylpentadienes and 2,6-dimethylheptenes.

EVANSTON, ILLINOIS

RECEIVED JANUARY 6, 1947

[CONTRIBUTION NUMBER 139 FROM THE GOODYEAR RESEARCH LABORATORY]

Effects of Cross-Linking and Branching on the Molecular Constitution of Diene Polymers¹

BY PAUL J. FLORY

The polymerization of dienes usually is accompanied by cross-linking reactions. While the percentage of the structural units which are cross-linked almost always is too small to be determined by chemical methods, frequently they are sufficient in number to seriously alter some of the physical properties of the polymerization products and to complicate their structural interpretation. Only a very small degree of cross-linking is sufficient to cause formation of a gel fraction which is insoluble in the usual solvents for the particular type of polymer and, hence, is not amenable to ordinary physico-chemical methods of characterization. Even if the number of cross linkages is insufficient to cause gelation, the molecular weight distribution may be severely distorted by them. The molecular weight distribution under these circum-

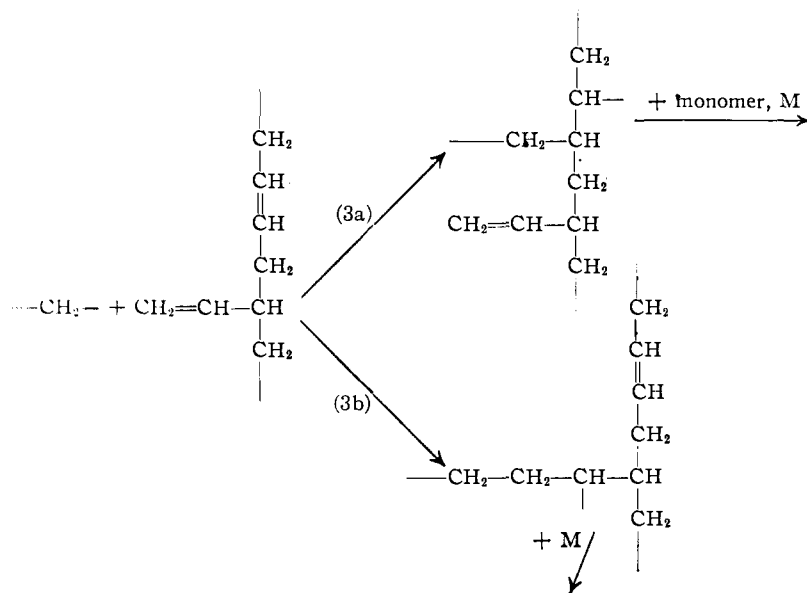
stances does not occupy its usual significance, either in reference to the physical characteristics of the product, or to the kinetic mechanism of the primary polymerization reaction.

In the present paper the probable origin of the cross linkages formed during the polymerization of dienes will be considered, and their effects on the polymer constitution and properties will be analyzed in the light of the statistical theory of three dimensional polymerizations.

I. Reaction Mechanisms

Cross-Linking.—The most likely mechanism for the formation of cross-linkages during polymerization (or copolymerization) of a 1,4-diene consists in the occasional addition of a growing free radical chain to an unsaturated carbon of a previously polymerized diene unit. The process, in the case of butadiene polymerizations, can be represented as follows

(1) Presented before the High Polymer Forum at the Atlantic City Meeting of the American Chemical Society, April, 1947.



where the long dashes indicate continuation of polymer chains. (The number "3" is assigned to these reactions, "1" being reserved in accordance with convention for initiation and "2" for normal propagation with monomer.) Chain growth may continue by successive addition of monomers proceeding from the free radical of one or the other of the above products. The net result of intervention of reaction (3a) or (3b) in the growth process is the introduction of a cross linkage between the polymer chain which is in the process of growth and another which was formed at an earlier stage of the conversion of monomer to polymer.

Often the view is expressed that diene polymer, or copolymer, molecules are highly ramified, irregular structures composed of relatively short chains joined together at numerous cross linkages and/or branch points. While this view possibly may be correct in some cases, it should be recognized that cross-linking reactions, such as the ones shown above, are incapable in themselves of producing very highly branched (finite) molecules. Before the degree of cross-linking proceeds to such an extent, gelation occurs with the result that the more complex molecular species are converted² preferentially to the insoluble gel fraction. Less than one cross linkage per two polymer chains is required to cause gelation^{2,3}; beyond the gel point the average degree of cross-linking in the remaining soluble molecules decreases^{2,4} with further addition of cross linkages. Hence, at no stage of a polymerization complicated by cross-linking is it correct to consider that more than a small fraction of the soluble polymer consists of highly cross-linked species.

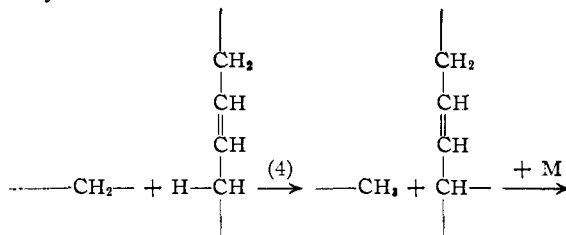
(2) P. J. Flory, *THIS JOURNAL*, **63**, 3083, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942).

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

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

Branching.—On the other hand, chain branching may occur during polymerization as a result of chain transfer between the free radical terminus of a growing chain and a previously formed polymer molecule⁵; as shown in formulas below. Subsequent growth from the substituted allyl radical⁶ of the polymer chain gives rise to a branch in the structural pattern of the molecule. Branching reactions of this sort cannot cause gelation without the assistance of other inter-linking processes. If transfer occurs readily and the reaction is carried to high conversions, highly branched molecules may be formed and the

molecular size distribution may be considerably distorted, but branching by transfer alone will not produce infinite networks.⁷ This branching mechanism may occur in the polymerization of vinyl monomers as well.



In the present paper we shall be primarily concerned with cross-linking processes, although a few remarks occurring toward the end of the Discussion pertain to the probable influence of branching on physical properties.

II. Kinetic Treatment of Cross-Linking Reactions

Dependence of Degree of Cross-Linking on Conversion.—The rate of conversion of monomer to polymer can be written in the usual form

$$d\alpha/dt = k_2[R^*](1 - \alpha) \quad (1)$$

(5) P. J. Flory, *ibid.*, **59**, 241 (1937).

(6) P. D. Bartlett and R. Altshul, *ibid.*, **67**, 812, 816 (1945), have shown that allyl radicals are relatively unreactive toward allyl acetate or allyl chloride. Instead of starting new chains, the allyl radicals disappear by combination in pairs. The diene monomers (M) are considerably more reactive than the allylic monomers and, further, the concentration of free radicals probably is much lower than in the polymerization of the allylic compounds. Hence, addition of diene monomers may supersede radical combination in the above scheme.

(7) If chain transfer to previously formed molecules occurs with ease so that in general each molecule is repeatedly re-activated by transfer, a condition is approached in which each initially formed polymer molecule undergoes further growth at a rate (or with a probability) proportional to its size. Very large polymer molecules could be formed in this manner. The kinetic treatment of this interesting situation has not been included here.

where α is the fractional extent of conversion of monomer to polymer, k_2 is the velocity constant for normal chain propagation, and $[R^*]$ represents the concentration of free radicals. The rate at which cross linkages are formed by propagation steps in which a previously polymerized unit is involved in accordance with reactions (3a) or (3b) is given by $k_3[R^*]\alpha$.⁸ It is convenient to consider that a diolefin monomer which eventually becomes cross-linked contributes two structural units, one to each of two "primary molecules." The term "primary molecule"^{4,9} has been applied to designate the linear molecules which would exist if all cross linkages were severed. The same meaning is intended here, although it is difficult to visualize severance of the cross linkage formed in reaction (3a) without also rupturing a primary molecule. For present purposes the primary molecules may be defined as the molecules which would exist if cross-linking additions (3a) and (3b) had been omitted from the growth processes. Throughout this paper it is assumed that no more than a very small fraction of the structural units become involved in cross linkages.

If ν is chosen to represent the proportion of cross-linked units (expressed as moles of cross-linked units per mole of monomer initially present), then in the light of the above definitions

$$d\nu/dt = 2k_3[R^*]\alpha \quad (2)$$

Dividing equation (2) by (1)

$$d\nu/d\alpha = 2K\alpha/(1 - \alpha) \quad (3)$$

where $K = k_3/k_2$ is the "reactivity ratio"¹⁰ of an unsaturated polymer unit as compared with a monomer molecule. Integrating equation (3) and dividing ν by α to obtain the "density" ρ of cross-linked units in the polymerized portion of the mixture

$$\rho = (\nu/\alpha) = -2K[1 + (1/\alpha) \ln(1 - \alpha)] \quad (4)$$

This function, plotted in Fig. 1, increases rapidly as α approaches unity. In other words, the density of cross linkages increases markedly at higher conversions. Suppression of gelation is known to become increasingly difficult with increase in conversion, as would be expected from the curve in Fig. 1 and the considerations leading to its derivation.

To illustrate more fully the significance of Fig. 1, suppose that in a given diene polymerization the relative reactivity ratio $K = k_3/k_2$ is equal to 5×10^{-4} . The ordinates in Fig. 1 correspond then to $\rho \times 10^3$. According to statistical theory,³ neglecting the effects of departure from randomness in the distribution of cross-linked units (*cf. seq.*), gelation will occur when ρ exceeds the reciprocal of

(8) The rate constant k_3 is the mean of k_{31} and k_{32} weighted according to the proportions of 1,2 and 1,4 units. Inasmuch as this proportion ordinarily does not vary with conversion, it is permissible to employ k_3 as a constant.

(9) P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).

(10) The quantity K corresponds to $1/\sigma$ in the copolymerization theory of Mayo and Lewis (*THIS JOURNAL*, **66**, 1594 (1944)), to α in the similar theory of Alfrey and Goldfinger, *J. Chem. Phys.*, **13**, 205 (1944), and to $1/r_1$ in the terminology adopted recently by Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

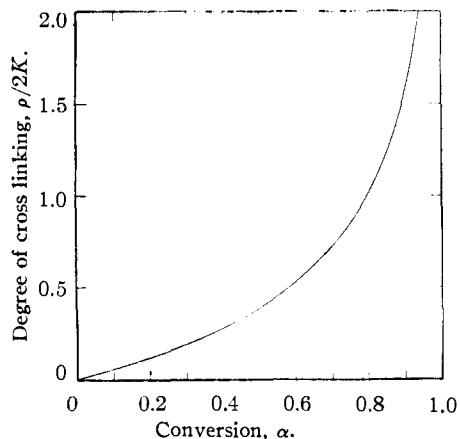


Fig. 1.—Degree of cross linking expressed in arbitrary units ($\rho/2K$) vs. conversion calculated from equation (4) based on the cross-linking mechanism shown in reactions (3a) and (3b).

the weight average degree of polymerization of the primary molecules, *i. e.*, the weight average degree of polymerization which would prevail if no cross linkages had been formed. If, for example, the weight average primary chain length is 5000 units, gelation should occur (see Fig. 1) at about 32% conversion¹¹; if it is 2000 units, the polymerization should proceed to 57% conversion before gel is formed; and for a weight average of 1000 units per primary molecule, gelation should occur at 80% conversion. The accelerated rise of the curve of Fig. 1 at higher conversions indicates that in order to further postpone gelation the average size of the primary molecules must be suppressed more drastically.

Conversely, the above calculations could be employed to compute the constant K from the percentage conversion at the gel point and the weight average degree of polymerization, \bar{y}_w , of the primary molecules. In the GR-S polymerization, for example, gelation occurs at about 70% conversion under conditions (modifier concentration) such that \bar{y}_w can be estimated to be of the order of 1000 to 2000 units. At 70% conversion $\rho/2K$ is about 0.7. Taking $\rho = 1/\bar{y}_w$ at the gel point, K is of the order of 5×10^{-4} .¹²

(11) Under conditions such that gelation occurs at lower conversions, calculation of the gel point in this manner is likely to be seriously in error, for reasons pointed out by Walling, *THIS JOURNAL*, **67**, 441 (1945). It is also assumed, as previously mentioned, that intramolecular connections may be neglected.

(12) T. Alfrey and J. G. Harrison, *THIS JOURNAL*, **68**, 299 (1946), in an investigation of the copolymerization of allyl chloride with styrene at 70°, found that the allylic monomer added at a rate only 3% of that for styrene. Reaction (3b), which probably is more rapid than (3a), is an analogous addition of a free radical to a substituted allyl radical. The reactivity ratio, K , governing the frequency of occurrence of the cross-linking addition reaction is much smaller than 0.03, but the hundred-fold difference probably can be attributed to two factors: the small proportion of 1,2-diene units (about 10 to 20%; see N. Rabjohn, C. E. Bryan, G. E. Inskeep, H. W. Johnston and J. K. Lawson, *THIS JOURNAL*, **69**, 314 (1947)) and the absence of an activating group or atom such as the chlorine in allyl chloride.

In making these calculations relating to the gel point the distribution in primary molecular sizes is unimportant provided the *weight average* is taken. If, for example, the average chain length of molecules formed at conversion α decreases with α (or if it increases with α owing to depletion of modifier), it is only necessary to compute the weight average size for all primary molecules. If cross-linking is excessively non-random (*cf. seq.*), this generalization will require modification.

The action of "regulators," or "modifiers" (*e. g.*, mercaptans),^{13,14,15} in postponing the occurrence of gelation to higher conversions is in harmony with the above treatment. Functioning as a chain transfer agent,^{5,16} the regulator merely reduces the average primary molecular weight. This suppression of gelation with attendant improvement in processibility is accomplished, however, only at the sacrifice of other desirable properties as will be pointed out in a later section of this paper. There is no reason to believe that the regulator, or any other added substance, actually suppresses cross-linking reactions, nor is there justification for the frequent assertion that the regulator gives rise to a more linear polymer, except in the sense that there are fewer cross-linkages *per molecule* owing merely to the smaller sizes of the molecules.

According to the above mechanism, cross-linking proceeds simultaneously with the polymerization at a relative rate dependent only on the relative concentrations of polymer and monomer, and on the characteristic relative reactivity ratio, K , for polymer units as compared with monomer. In general, K will depend on temperature, but will be independent of the catalyst, activators, etc., so long as the polymerization is propagated by free radicals.

Non-Randomness in the Distribution of Cross-Linked Units.—Theories of molecular weight distribution and gelation in three dimensional polymers invariably have employed the assumption that the cross-linkages occur at random, *i. e.*, that the probability that any given structural unit bears a cross linkage is independent of the status of other units in the same chain or molecule. This assumption is not strictly valid in polymers cross-linked during polymerization by a mechanism such as the one presented above. Proof for this statement can be set forth as follows.

Consider primary molecules growth of which occurred during a brief interval at the conversion α' . A fraction ρ_i of their structural units will have been formed by reactions (3a) or (3b) from members of previously polymerized molecules; *i. e.*, a fraction ρ_i of the units of the primary polymer

molecules formed at conversion α' will be cross-linked immediately on polymerization. As the conversion proceeds from α' to α , an additional fraction ρ_a of the structural units of these same primary molecules will become involved in cross linkages with subsequently formed primary molecules. The fraction of cross-linked units at conversion α in primary molecules which were formed at conversion α' is

$$\rho_{\alpha'} = \rho_i + \rho_a$$

Both ρ_i and ρ_a are assumed to be very small compared with unity.

The quantity ρ_i is simply equal to the ratio of the rate of generation of cross linkages ($dv/2dt$) to the rate of polymerization at conversion α' .

$$\rho_i = (dv/2d\alpha)_{\alpha'} = K\alpha'/(1 - \alpha') \quad (5)$$

The rate at which additional cross-linked units are acquired by these same primary molecules is

$$n_{\alpha'} d\rho_a/dt = k_2 n_{\alpha'} [R^*]$$

where $n_{\alpha'}$ is the number of structural units polymerized within an interval at α' . Dividing by equation (1)

$$d\rho_a/d\alpha = K/(1 - \alpha) \quad (6)$$

$$\rho_a = K \int_{\alpha'}^{\alpha} d\alpha/(1 - \alpha) = K \ln \left(\frac{1 - \alpha'}{1 - \alpha} \right) \quad (7)$$

Hence

$$\rho_{\alpha'} = K \left[\alpha'/(1 - \alpha') + \ln \left(\frac{1 - \alpha'}{1 - \alpha} \right) \right] \quad (8)$$

Equation (8) gives the degree of cross-linking occurring in primary molecules formed at conversion α' after the polymerization has been continued to conversion $\alpha > \alpha'$. According to equation (8) primary molecules formed at higher conversions carry a greater proportion of cross-linked units than those formed earlier. It is obvious that the number of cross-linked units at the instant of formation should be fewer at lower conversions, but it would not necessarily have been self evident that subsequent cross-linking of some of the units of these molecules fails to make up this deficiency.

Under these circumstances it is not permissible to assume that the probability that a given structural unit is cross-linked is entirely independent of the status of other units of the same primary molecule. Probabilities for the occurrence of cross-linked units differ for different primary molecules. If an abnormally large fraction of some of the units in a given primary molecule are found to be cross-linked, it is likely that this molecule was formed during the latter range of the conversion of monomer to polymer; hence, a higher than average probability ρ is likely to apply to other units in this molecule.

For the purpose of exploring the magnitude of this variation in ρ for polymer chains formed at different stages of the polymerization, it is instructive to examine the ratio of $\rho_{\alpha'}$, the degree of cross-linking in primary molecules formed at the final conversion α , to ρ_0 , the degree of cross-linking

(13) R. H. Ewart, private communication to the Office of Rubber Reserve, December, 1942.

(14) H. R. Snyder, J. M. Stewart, R. E. Allen and R. J. Dearborn, *THIS JOURNAL*, **68**, 1422 (1946); F. T. Wall, F. W. Banes and G. D. Sands, *ibid.*, **68**, 1429 (1946).

(15) W. V. Smith, *ibid.*, **68**, 2059, 2064, 2069 (1946).

(16) F. R. Mayo, *ibid.*, **65**, 2324 (1943).

in the co-existing primary molecules which were formed at the outset of the polymerization. Setting α' successively equal to α and to 0 in equation (8) and dividing

$$\rho\alpha/\rho_0 = \frac{-\alpha}{(1-\alpha)\ln(1-\alpha)} \quad (9)$$

In Fig. 2 this function is plotted against α . Only at high conversions does the spread between the average degrees of cross-linking become significantly large, as indicated by the ratio greater than unity. It is the extreme variation in average degrees of cross-linking which is indicated here, the mean deviation being considerably smaller. For ordinary purposes, disregard of the departure from random cross-linking probably can be ignored up to 60 or 70% conversion. At higher conversions the variation may be large enough to upset precise calculation of gel points, sol-to-gel conversion, etc.⁴ Gelation should occur at a somewhat lower degree of cross-linking than would be the case if the cross-linked units were distributed among the various primary molecules at random.

Change in Number of Polymer Molecules with Conversion.—Wall and Beste¹⁷ have deduced from osmotically determined molecular weights of samples of emulsion copolymers of butadiene and styrene (GR-S) removed at intervals that at high conversions approaching the point at which gel makes its appearance the total number of polymer molecules actually decreases with conversion. In other words, cross-linking reactions decrease the number of molecules faster than new ones are generated at higher conversions. It is of interest, therefore, to determine whether or not the mechanism of cross-linking employed here is consistent with this observation.

The number of cross linkages formed per unit polymerized is $d\nu/2d\alpha$ and the corresponding rate of generation of primary molecules ($dN/d\alpha$) is $1/\bar{y}_{n,\alpha}$ where $\bar{y}_{n,\alpha}$ is the number average number of units per primary molecule formed at conversion α . If intramolecular cross linkages are neglected (the present deductions being limited to conversions preceding gelation), then the rate of change in the total number of molecules is equal to the latter quantity minus the former. It is convenient to take the ratio of these two quantities

$$2dN/d\nu = (1/\bar{y}_{n,\alpha})(2d\alpha/d\nu) = (1-\alpha)/\alpha K \bar{y}_{n,\alpha} \quad (10)$$

as an index, which is less than unity when the total number of polymer molecules is decreasing with conversion.

For the purpose of illustrating the significance of equation (10), we may inquire under what conditions $2dN/d\nu$ becomes less than unity at conversions up to the gel point. According to the statistical theory of network formation,^{2,3,4} $\rho = 1/\bar{y}_w$ at the gel point, where \bar{y}_w is the *weight average* molecular weight of primary molecules

(17) F. T. Wall and L. F. Beste, *THIS JOURNAL*, **69**, 1761 (1947).

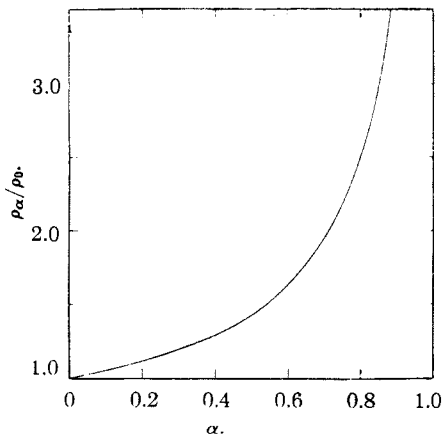


Fig. 2.—Non-random distribution of cross linkages vs. conversion. The ratio of cross-linked units in primary molecules formed, respectively, at conversions α and 0 vs. conversion α . Curve computed from equation (9).

(not merely those formed at conversion α), neglecting, of course, the minor effects of non-random distribution of cross linkages. Hence, according to equation (4)

$$1/2 K \bar{y}_w = -[1 + (1/\alpha_c) \ln(1 - \alpha_c)]$$

where α_c is the critical value of the conversion for incipient gelation. Employing this relationship to eliminate the parameter K from equation (10), there is obtained for the ratio of rate of formation of new chains to rate of combination with those formed previously

$$2dN/d\nu = -\{[(1 - \alpha_c)/\alpha_c][2 + (2/\alpha_c) \ln(1 - \alpha_c)]\} \bar{y}_w/\bar{y}_{n,\alpha} \quad (11)$$

The quantity in braces in equation (11) decreases from unity to zero as α_c goes from zero to unity; it reaches the value $1/2$ near $\alpha_c = 0.80$. If the ratio of chain transfer agent to monomer is constant throughout the polymerization, then $\bar{y}_{n,\alpha}$ will be independent of α and equal to the over-all \bar{y}_n . Under these circumstances \bar{y}_w will be twice \bar{y}_n . Hence, $2dN/d\nu$ will exceed unity up to the gel point provided gelation occurs at $\alpha < 0.80$; if gelation occurs at $\alpha > 0.80$ this ratio will be less than unity at the gel point, corresponding to a net decrease in the number of polymer molecules.

In the mercaptan-regulated copolymerization of butadiene and styrene, the regulator usually is consumed relatively more rapidly than the monomers.¹⁵ Hence, $\bar{y}_{n,\alpha}$ will exceed $\bar{y}_w/2$, and, consequently, $2dN/d\nu$ may fall below unity before gelation occurs at conversions somewhat less than 80%. Thus, the mechanism of cross-linking proposed here is consistent with the observations of Wall and Beste.

III. Physical Properties in Relation to Structure

Physical properties of high polymers necessarily are dependent on molecular weight and molecular weight distribution. In diene polymers and copolymers containing occasional cross linkages,

however, the actual connection between physical properties and molecular weight is especially elusive owing to disturbing variations in molecular pattern and to peculiarities of the molecular weight distribution caused by the cross linkages.

The molecular weight distribution, according to theory,^{2,3,4} is broadened by the introduction of cross linkages. This broadening becomes extreme as the gel point is approached. Experimental determination of the molecular weight distribution in partially cross-linked polymers is difficult.¹⁸ The usual fractionation methods based on solubility differences can be expected at best to be only of limited value inasmuch as two polymer molecules of the same molecular weight, one of them composed of several primary molecule chains and the other of a single linear chain, may differ significantly in solubility. Hence, separations will not take place explicitly according to molecular weight.

Even if the molecular weight distribution were accurately determinable, by fractionation or any other method, physical properties of the polymer generally could not be predicted unambiguously without also taking into account the concentration of cross linkages. Properties of vulcanized rubber-like diene polymers are of particular interest in this connection.

The structure of the vulcanized rubber is adequately described as a network composed of *primary* molecules of given molecular weight and molecular weight distribution randomly inter-linked by cross linkages (or inter-unit linkages of higher functionality in some cases). A small fraction of these cross linkages may have been formed prior to the vulcanization operation, but from the standpoint of vulcanizate structure (and properties) it is unimportant to differentiate between those formed prior to and those formed during vulcanization; only the total number of cross linkages is significant. Similarly, the molecular weight distribution prior to vulcanization is unsuitable as a basis of correlation when cross linkages are present and should be discarded in favor of the primary molecular weight distribution, *i. e.*, the molecular weight distribution in the total absence of cross linkages. It has been possible to account quantitatively in terms of structure for various physical properties of butyl rubber by proceeding from this point of view.¹⁹ Although unvulcanized butyl rubber is essentially free of cross linkages, there is no basic reason for doubt that

(18) I. Valyi, A. G. Janssen and H. Mark, *J. Phys. Chem.*, **49**, 461 (1945), fractionated copolymers of styrene with small percentages of divinylbenzene in an effort to observe effects of cross-linking on the molecular weight distribution. The solutions which they employed probably were too concentrated for efficient separations, and insufficient numbers of fractions were obtained from which to construct significant molecular weight distribution curves. Their application of molecular size distribution equations, derived for polymers composed of units of identical functionality, to such systems does not appear to be justified.

(19) P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).

this same scheme also can be applied successfully to other vulcanized rubbers.²⁰

The regulator, or modifier, by reducing the primary molecular weight prevents gelation, or suppresses it sufficiently, so that the resulting polymer retains thermoplasticity to the degree necessary for processing. This result is achieved, however, only at a sacrifice in the perfection of the network structure formed during vulcanization. As shown previously,^{9,19} each end of a primary molecule contributes a flaw to the vulcanizate structure. The number of these flaws, or "terminal chains" which are not subject to permanent orientation when the vulcanizate is deformed, is inversely proportional to the number average molecular weight of the primary molecules; consequently, the number of flaws in the vulcanizate network increases directly with the amount of modifier consumed during polymerization. Modulus, creep and tensile strength are influenced by the abundance of these flaws in the network structure.¹⁹ A deficiency in modulus may, of course, be compensated by increasing the degree of cross linking, but the loss in strength, and presumably in related physical properties as well, cannot be overcome in this manner. Thus, circumvention of the processing difficulties precipitated by cross-linking reactions through suppression of the primary molecular weight with a regulator can be expected to be accompanied to some extent by impairment of physical properties.

The determination of the primary molecular weight distribution, as required for interpretation of the properties of network structures produced by vulcanization, may be difficult in a polymer containing cross-linkages. It may be deduced, however, from detailed knowledge of the reaction kinetics. If, for example, the transfer constant¹⁶ for the regulator is known, the primary molecular weight distribution may be computed.

The number average primary molecular weight, without regard for the distribution, usually will suffice for characterizing the properties of a network structure. If a fragment of the transfer agent combines with each primary molecule, the number average primary molecular weight may be secured by analytical determination of this fragment. Alternatively, an approximate value may be obtained from osmotic measurements applied to the non-gelled polymer. According to theory,^{2,4} the number average molecular weight is altered relatively little by cross-linking up to the point at which gel appears. The number average primary molecular weight therefore will not differ seriously from the observed osmotic value for the cross-linked polymer.

(20) The relationship between tensile strength and network structure of the non-crystalline diene rubbers may differ from that for butyl rubber,¹⁹ since the strength of the latter is intimately associated with its ability to crystallize when stretched. Relationships between elastic properties, swelling and rate of relaxation under stress, on the other hand, should be similar to those which apply to butyl rubber.

Thus far the discussion has been concerned with the effects of cross-linking on linear polymer molecules. It has been suggested frequently that diene synthetic rubber molecules are highly branched, although no conclusive data bearing on this point are available. As already noted a preponderance of highly branched molecules cannot be produced by cross-linking reactions alone, owing to the intervention of gelation. However, branching reactions such as the one depicted in reaction (4) may conceivably result in highly branched polymer molecules. It may be of interest therefore to consider briefly some of the characteristics to be expected in network structures formed by cross-linking branched molecules.

For a given molecular weight distribution, the same number of cross linkages introduced at random gives rise to the same number of active network elements^{9,19} regardless of whether the molecules are linear or branched (or cross-linked). Hence, elastic modulus should not be affected very much by branching. On the other hand, a network formed from branched molecules will have many more terminal chains,^{9,19} consequently a larger proportion of the structure will not be oriented by stretching. On this basis a vulcanizate formed from branched molecules could be expected to exhibit lower strength than one formed from linear molecules of the same molecular weight. It is important, therefore, to distinguish branching from cross-linking reactions.

Summary

Reaction mechanisms whereby cross-linked and

branched polymer structures may be formed during the polymerization of dienes are discussed. A kinetic treatment of the formation of cross linkages via the occasional addition of a free radical to the unsaturated carbon of a structural unit of a previously polymerized molecule is presented. It is pointed out that the rate of this addition step relative to monomer addition can be deduced from the average chain length and the conversion at which gelation occurs.

Cross linkages introduced by the mechanism under consideration are not distributed at random, but the deviations from a random distribution are unimportant except at high conversions. Conditions are examined under which the cross-linking reaction decreases the total number of molecules more rapidly than they are formed.

Physical properties of polymers (with particular emphasis on vulcanized rubbers) are most conveniently interpreted in terms of (1) the primary molecular weight (*i. e.*, molecular weight in the absence of cross linkages) and its distribution, and (2) the concentration of cross linkages. The actual molecular weight distribution, which may be severely distorted by the presence of cross linkages, is inappropriate for direct correlation with the more important physical properties. The modifiers, or regulators, commonly employed in diene polymerizations suppress gel formation by reducing the primary molecular weight; they do not actually reduce cross-linking. This reduction in molecular weight is not without other undesired consequences, however.

AKRON, OHIO

RECEIVED FEBRUARY 24, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

Perbenzoic Acid Oxidation of 20-Ketopregnanes

BY LEWIS HASTINGS SARETT

The transformation of 20-ketopregnane derivatives to the corresponding 17-acetoxyetiocholanes by the use of Caro's acid has been described.^{1,2} With allopregnane-20-one, 60-70% of a mixture containing equal parts of allopregnane-21-ol-20-one acetate and androstane-17(α)-ol acetate was obtained. Similar results were found with Δ^5 -pregnene-3(β)-ol-20-one dibromide, allopregnane-3(β)-ol-20-one, and pregnane-3(α)-ol-20-one.

It has also shown³ that perbenzoic acid reacts readily with unsubstituted 3-ketosteroids to give lactones. However, the oxidation of allopregnane-3(β)-ol-20-one acetate with this reagent gave only a few per cent. of androstanediol.

In the course of an investigation in this Labora-

tory on methods of degradation of pregnanes to etiocholanes, the effect of perbenzoic acid on 20-ketopregnanes as a possible preparative method was tested. It was found that in the best case 85% of the 17(α)-acetoxyetiocholane was obtained, but that the yields varied with the 20-ketopregnane used. Neither the 17(β)-acetoxy isomer nor products resulting from oxidation of the C-21 methyl group could be isolated. It was also determined that, as might be anticipated, the rate of oxidation was considerably slower than that reported³ for 3-ketosteroids. After sixteen hours at 16°, the latter reaction was complete, whereas seven to ten days at 25-30° in very concentrated solution was required for the completion of the side chain cleavage.

Four compounds were subjected to the perbenzoic acid oxidation: pregnane-3(α)-ol-11,20-dione acetate (I), pregnane-3(α)-ol-11,20-dione ben-

(1) Marker, *THIS JOURNAL*, **62**, 650 (1940).

(2) Marker, Rohrmann, Wittle, Crooks and Jones, *ibid.*, **62**, 2543 (1940).

(3) Burckhardt and Reichstein, *Helv. Chim. Acta*, **25**, 821, 1434 (1942).