

tion for gas imperfection is more accurate than the use of available equations of state.

C_p^0 for the two compounds studied may be represented by the following empirical equations with a mean deviation of less than 0.1%

$$n\text{-Heptane } C_p^0 = -0.236 + 0.14864T - 0.000055583T^2$$

$$2,2,3\text{-Trimethylbutane: } C_p^0 = 1.800 + 0.15320T - 0.000053907T^2$$

The method of measurement also yields precise heats of vaporization. For *n*-heptane the heats of vaporization reported at 90.48, 77.33 and 58.00° are 7,715, 7,938 and 8,244 cal./mole respectively while for 2,2,3-trimethylbutane the values at 80.80 and 40.68° are 6,918 and 7,461 cal./mole.

BARTLESVILLE, OKLAHOMA RECEIVED AUGUST 8, 1946

[CONTRIBUTION NO. 134 FROM THE GOODYEAR RESEARCH LABORATORY]

Molecular Size Distribution in Three Dimensional Polymers. V. Post-gelation Relationships

BY PAUL J. FLORY

In previous papers¹⁻⁴ of this series statistical methods were applied to the structural interpretation of three dimensional polymers, *i.e.*, polymers some of the structural units of which are polyfunctional in the sense that they connect with more than two other neighboring units of the polymer. Critical conditions for the occurrence of gelation were explored, and methods were set forth for computing the extent of reaction at the gel points in condensation processes involving polyfunctional units¹ or in addition polymerizations accompanied (or followed) by cross-linking reactions.^{3,4} The theory of gelation resulting from cross-linking was extended by Stockmayer⁵ and by Walling.⁶

Gelation occurs in three dimensional condensation polymerizations at somewhat higher extents of reaction than predicted by theory owing to intramolecular condensations^{1,7} which are not taken into account by the theory.⁸ The discrepancy generally is small, and the essential correctness of the statistical theory is adequately confirmed by the correlation between observed and calculated gel points.

The writer applied the statistically derived molecular size distribution relationships beyond the gel point as well as to polymers which had not been carried to gelation. By appropriately summing over the distribution functions for all *finite* species, it was possible to derive the weight fraction of sol, average molecular weights of the sol, and the concentration of cross linkages in the

sol; gel properties were obtained by difference. Stockmayer⁹ generalized and extended the size distribution relationships, but was hesitant to apply them beyond the gel point. His criticisms of the writer's efforts in this direction centered upon the approximation^{2,3} according to which intramolecular ("cyclic") connections in finite (sol) molecules are neglected while acknowledging that they must be present in the infinite network (gel) structures. On the other hand, the derivation of the size distribution equations applies equally to the sol existing beyond the gel point, or to the polymer preceding gelation.¹⁰ The distribution equations are oblivious of the gel (except by omission), hence the frequent occurrence of intramolecular connections in the gel does not constitute a violation of the basic approximation.

While the logic of this procedure appears to be satisfactory, it must be admitted that derivation of gel properties by difference is not as straightforward as might be desired. In this paper polymers *randomly* cross-linked to the extent that they contain a gel fraction will be treated by a more general procedure applicable to *any* distribution of chain lengths. The method here employed is independent of size of complexity distribution equations (except in calculating weight average molecular weight); it is more direct and simpler than the procedures previously applied to the problem of post-gelation constitution. The results obtained confirm and extend previous conclusions.

Theoretical Treatment

Molecular size distribution functions^{2,3,9} for three dimensional polymers may show a single maximum at relatively low molecular weight, but beyond this maximum they decrease monotonically toward zero. This is true after as well as before gelation. It is evident, therefore that an intermediate fraction between finite sol molecules

(1) P. J. Flory, *THIS JOURNAL*, **63**, 3083 (1941).

(2) P. J. Flory, *ibid.*, **63**, 3091 (1941).

(3) P. J. Flory, *ibid.*, **63**, 3096 (1941).

(4) P. J. Flory, *J. Phys. Chem.*, **46**, 132 (1942).

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

(6) C. Walling, *THIS JOURNAL*, **67**, 441 (1945).

(7) W. H. Stockmayer and L. L. Weil, unpublished. See "Advancing Fronts in Chemistry," Reinhold Publishing Corp., New York, N. Y., Chapter 6 by W. H. Stockmayer.

(8) A theory which will take into account intramolecular connections obviously is needed but, as Stockmayer has pointed out (paper given before the Division of High Polymer Physics of the American Physical Society, January, 1946), the mathematical difficulties appear to be insuperable.

(9) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).

(10) P. J. Flory, *Chem. Rev.*, **39**, 137 (1946).

and what we have termed "infinite" networks,¹¹ or gel, will be infinitesimal in amount. In other words, there should exist a sharp demarcation between sol and gel,⁴ the distinction being real rather than arbitrary. This prediction of previous theories, which is confirmed by various experiments, is a premise of the treatment presented below.

Consider a system of primary molecules (*i.e.*, molecules in the absence of cross-linkages) having the size distribution given by $w_y = f(y)$, where w_y is the weight fraction of species composed of y units. Cross linkages are then introduced between various structural units at random for a total of $\rho/2$ cross linkages per structural unit; in other words, a fraction ρ of the units became involved in cross-linkages. In accordance with previous procedures, intramolecular connections within finite molecules will be neglected.

Partition of Chains between Sol and Gel.—Let a quantity φ_s be defined as the probability that a non-cross-linked structural unit selected at random is part of the sol fraction. A given cross linkage will occur in the sol fraction only in the event that both of the subjoined units would belong to the sol in the absence of this particular cross linkage. The probability that an arbitrarily selected cross-linkage belongs to the sol is φ_s^2 , therefore. The probability that a cross-linked unit selected at random is a part of the sol is likewise φ_s^2 . Hence, the weight fraction of sol is given by

$$W_s = (1 - \rho)\varphi_s + \rho\varphi_s^2 \quad (1)$$

or

$$W_s/\varphi_s = 1 - \rho(1 - \varphi_s) \quad (2)$$

Solving (1) for φ_s and expanding in series

$$\varphi_s = W_s[1 + \rho(1 - W_s) + \rho^2(1 - W_s)(1 - 2W_s) + \dots] \quad (3)$$

When the primary molecules average many units in length, ρ will be much smaller than unity in the region of interest. Under these conditions, φ_s is approximately equal to W_s and Equation (2) may be written

$$W_s/\varphi_s \cong 1 - \rho(1 - W_s) \quad (2')$$

to a usually satisfactory approximation.

The probability that a y -mer primary molecule selected at random is a part of the sol will be

$$s_y = \sum_{i=0}^y P_y(i)\varphi_s^i \quad (4)$$

where $P_y(i)$ is the probability that there are i cross-linked units in the y -mer. If the structural units are cross-linked at random

$$P_y(i) = [y!/(y-i)!i!]\rho^i(1-\rho)^{y-i} \quad (5)$$

(11) Actually the gel molecular weight cannot be infinite since we are dealing with a finite amount of material. Any attempt to express its size on the molecular weight scale would give a figure dependent on the size of the sample and so large as to warrant the term "infinite."

Substituting equation (5) in (4) and evaluating the summation

$$s_y = [1 - \rho + \rho\varphi_s]^y = (W_s/\varphi_s)^y \quad (6)$$

from which the partition of y -mer primary molecules between sol and gel can be computed, given the value of W_s/φ_s .

The Weight Fraction of Sol.—The partition factors s_y are related to the weight fraction of sol according to the relationship

$$\begin{aligned} W_s &= \sum_{y=1}^{\infty} w_y s_y \\ &= \sum_{y=1}^{\infty} w_y (W_s/\varphi_s)^y \end{aligned} \quad (7)$$

$$\cong \sum_{y=1}^{\infty} w_y [1 - \rho(1 - W_s)]^y \quad (7')$$

If ρ and the y -distribution (*i.e.*, the w_y 's) are known, W_s may be found by simultaneous solution of equations (2) and (7). The solution is simplified somewhat if ρ is small so as to permit the use of equation (7') for this purpose. Even this latter equation is not explicitly soluble for W_s . However, the summation can be performed graphically using trial values of W_s , or by integration if the w_y 's can be expressed in suitable analytical form. The value of W_s for which the summation equals W_s can then be deduced by graphical methods or by successive approximations. Conversely, if W_s has been determined experimentally and the y -distribution is known, ρ can be deduced by similar procedures.¹²

When the polymer is homogeneous

$$\begin{aligned} W_s &= (W_s/\varphi_s)^y \\ \ln W_s &= y \ln (W_s/\varphi_s) \end{aligned}$$

If ρ is small

$$\ln W_s \cong -y\rho(1 - W_s)$$

or

$$(-\ln W_s)/(1 - W_s) \cong \rho y = \gamma \quad (8)$$

where γ is the "cross-linking index"¹³ or average number of cross-linked units per primary molecule. This is the equation previously derived^{4,13} by other methods.

Partition of Cross Linkages between Sol and Gel.—Since the fraction of the cross linkages which occur in the sol equals φ_s^2 , we can write

$$\varphi_s^2 = \rho' W_s/\rho$$

where ρ' is the fraction of the units of the sol which are cross-linked. The above equation defines ρ' .

$$\rho' = \rho\varphi_s^2/W_s \quad (9)$$

(12) The inconvenience arising from the failure of these equations to be explicitly soluble for the dependent variables seems to be inherent in the problem rather than in the present procedure. Application of the previous summation procedure² to certain of Stockmayer's⁹ distribution functions leads to equations the solutions of which present similar difficulties. Equivalent results are obtained by this procedure.

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

Substituting from equation (2') for W_s/φ_s^2

$$\begin{aligned}\rho' &\cong \rho W_s [1 - \rho(1 - W_s)]^{-2} \\ &\cong \rho W_s [1 + 2\rho(1 - W_s)]\end{aligned}\quad (9')$$

or to a further approximation

$$\rho' \cong \rho W_s \quad (9'')$$

Similarly the fraction ρ'' of the units in the gel which are cross-linked is

$$\rho'' = \rho(1 - \varphi_s^2)/(1 - W_s) \quad (10)$$

which on introducing approximations corresponding to those used in the preceding paragraph, reduces to

$$\rho'' \cong \rho(1 + W_s - 2\rho W_s^2) \quad (10')$$

For long chains, and hence for small values of ρ in the significant range

$$\rho'' \cong \rho(1 + W_s) \quad (10'')$$

These equations show that the partition of the cross linkages between sol and gel depends almost entirely on the weight fraction of sol. The concentration of cross linkages in the gel first formed just beyond the gel point is always approximately twice that in the sol, *i.e.*, when $W_g = 1 - W_s$ is very small

$$\rho'' \cong 2\rho \cong 2\rho'$$

Distribution of Cross Linkages in the Sol Fraction.—Let $P'_y(i)$ represent the probability that a given y -mer primary molecule, known to be a part of the sol, contains i cross-linked units. It will be shown that $P'_y(i)$ is of the form of equation (5) and, hence, that the distribution of cross-linked units within the sol is random.

By definition

$$s_y P_y(i) = P_y(i) \varphi_s^i$$

Substituting for $P_y(i)$ from equation (5) and for s_y from equation (6)

$$P'_y(i) = [\rho \varphi_s^2 / W_s]^i [(1 - \rho) \varphi_s / W_s]^{y-i} y! / i! (y - i)!$$

Substituting from equation (1) for the second quantity in brackets, and recalling equation (9)

$$P'_y(i) = (\rho')^i (1 - \rho')^{y-i} y! / i! (y - i)! \quad (11)$$

Equation (11) is identical with (5) except that ρ has been replaced with ρ' . The distribution of cross linkages in the sol fraction is the same as would have been obtained if a linear polymer having the same distribution as the y distribution of the sol, were randomly cross-linked directly to the extent ρ' no gel being formed.

Primary Molecule Distribution within the Sol Fraction.—The weight fraction of the sol which is composed of y -mer primary molecules is given by

$$\begin{aligned}w'_y &= w_y s_y / \sum_{y=1}^{\infty} w_y s_y \\ &= w_y s_y / W_s \\ &= w_y (W_s / \varphi_s)^y / W_s \\ &\cong w_y [1 - \rho(1 - W_s)]^y / W_s\end{aligned}\quad (12)$$

The number average value of y in the sol, *i.e.*, the number average molecular weight of the

primary molecules occurring in the sol fraction (not to be confused with the number average molecular weight of the sol, *cf. seq.*), which will be designated by \bar{y}'_n , can be computed as follows

$$\begin{aligned}\bar{y}'_n &= \Sigma w'_y / \Sigma w'_y / y \\ &= W_s / \Sigma (w_y / y) (W_s / \varphi_s)^y\end{aligned}\quad (13)$$

The weight average value of y in the sol is

$$\begin{aligned}\bar{y}'_w &= \Sigma y w'_y \\ &= (1 / W_s) \Sigma y w_y (W_s / \varphi_s)^y\end{aligned}\quad (14)$$

Average Molecular Weights of the Sol Fraction.—Neglecting intramolecular cross-linking in the sol, the number of sol molecules will equal the number N' of primary molecules minus the number $\rho'/2$ of cross-linkages. Hence, the number average degree of polymerization of the sol will be given by

$$\bar{x}'_n = 1 / (N' - \rho'/2)$$

where N' and ρ' are expressed in moles per gram equivalent of structural units.

$$\bar{x}_n = W_s / \{ \Sigma (w_y / y) (W_s / \varphi_s)^y - \rho \varphi_s^2 / 2 \} \quad (15)$$

The weight average degree of polymerization in the sol can be calculated by employing Stockmayer's⁵ equation, since the distribution of cross-linked units is random throughout the sol. In the terminology of the present paper this equation becomes

$$\bar{x}'_w = \bar{y}'_w (1 + \rho') / [1 - \rho'(\bar{y}'_w - 1)] \quad (16)$$

(See equation (23) of reference.⁵)

Discussion

If the size distribution of the primary molecules (*i.e.*, the size distribution before cross-linking) is known and either the degree of cross-linking ρ or the weight fraction of sol has been determined, the constitution of the resulting polymer can be characterized with the aid of the relationships derived above. Three summations must be evaluated for this purpose

$$\begin{aligned}I_1 &= \Sigma (w_y / y) (W_s / \varphi_s)^y \\ I_2 &= W_s = \Sigma w_y (W_s / \varphi_s)^y \\ I_3 &= \Sigma y w_y (W_s / \varphi_s)^y\end{aligned}\quad (7)$$

Regardless of whether ρ or W_s is given, the first and most difficult problem is to find a value of (W_s / φ_s) consistent with equations (2) and (7), or with equation (7') if this approximation is employed. The unknown one of these two quantities then is readily found, and the other summations are amenable to evaluation by straightforward methods. I_1 is required for the calculation of \bar{y}'_n and \bar{x}'_n , and I_3 for \bar{y}'_w and \bar{x}'_w .

In the following paragraphs we shall consider the application of these methods to cross-linked primary molecules of arbitrarily selected distributions.

Application to the "Most Probable Distribution."—The familiar distribution represented by

$$w_y = y(1 - p)^2 p^{y-1} \quad (17)$$

where the parameter p (which may approach, but

never reach unity) equals the extent of reaction or degree of coupling of the bifunctional units, has been referred to¹⁴ as the most probable distribution for linear polymers.¹⁵ Many synthetic linear polymers approximate this distribution; a few are believed to be more homogeneous, and many possess broader distributions.

Substituting (17) into the above summations, the following expressions are found for I_1 , I_2 and I_3 .

$$\begin{aligned} I_1 &= (W_s/\varphi_s)(1-p)^2/(1-pW_s/\varphi_s) \\ I_2 &= W_s = (W_s/\varphi_s)(1-p)^2/(1-pW_s/\varphi_s)^2 \\ I_3 &= (W_s/\varphi_s)(1-p)^2(1+pW_s/\varphi_s)/(1-pW_s/\varphi_s)^3 \end{aligned}$$

For purposes of illustration, p has been taken equal to 0.996, corresponding to number and weight average degrees of polymerization prior to cross-linking as follows¹⁶

$$\bar{y}_n = 250 \quad \bar{y}_w = 499$$

Arbitrary values of W_s/φ_s ranging from 0.9998 to 0.98 were substituted in the above equations for I_1 , $I_2 (= W_s)$, and I_3 . Having found corresponding values for W_s , the "density" ρ of cross-linked units was obtained from equation (2') to an entirely adequate approximation. Similarly, the densities of cross-linked units in the sol (ρ') and gel (ρ'') were computed from equations (9') and (10'), respectively. The number average degree of polymerization, \bar{x}'_n , of the sol was computed from I_1 substituted into (15), *i.e.*

$$\bar{x}'_n = W_s/(I_1 - \rho\varphi_s^2/2)$$

According to equation (14), $\bar{y}'_w = I_3/W_s$, which when substituted into (16) gives the weight average degree of polymerization of the sol. Number and weight averages prior to gelation have been calculated from the same formulas, with $W_s/\varphi_s = 1$ and $W_s = 1$, and with ρ' in equation (16) replaced by ρ .

Results of these calculations are shown in Figs. 1 and 2. The weight fraction of gel, $W_g = 1 - W_s$ rises abruptly as the density of cross-linked units is increased beyond the gel point, the approach to 100% being gradual for larger values of ρ . As already noted, the density of cross-linkages in the gel first formed is twice that of the co-existing sol. With the addition of more cross linkages, ρ'' increases while ρ' decreases. In other words, a lower proportion of the units of the co-existing sol are cross-linked the greater the concentration of cross-linkages in the aggregate of sol and gel. This can be looked upon as a consequence of the preferential conversion of the larger (and hence on the average more highly cross-linked) species to gel.^{2,3,4} It is also to be noted

(14) P. J. Flory, THIS JOURNAL, 64, 2205 (1942); J. Chem. Phys., 12, 425 (1944).

(15) The cross-linking problem in this particular case can be handled through the use of Stockmayer's equations for polymers formed by random co-reaction of bifunctional units with a small proportion of tetrafunctional units (see equation (41) of ref. (9)). The distribution obtained by random co-reaction of bi- and tetrafunctional units is the same as that resulting from random cross-linking of chains of random length.

(16) P. J. Flory, THIS JOURNAL, 58, 1877 (1936).

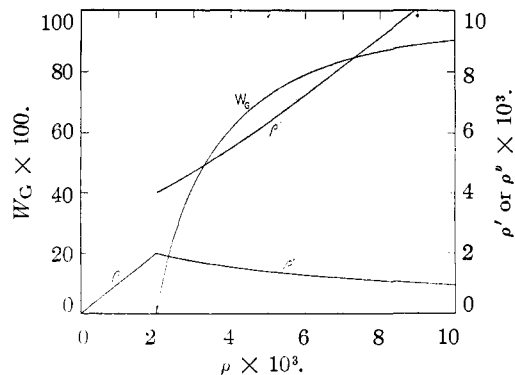


Fig. 1.—Weight fraction (W_g) of gel and concentrations of cross-linked units in sol (ρ') and in gel (ρ'') vs. the degree of cross-linking (ρ) for the "most probable" primary molecular weight distribution as given by equation (17) with $p = 0.996$.

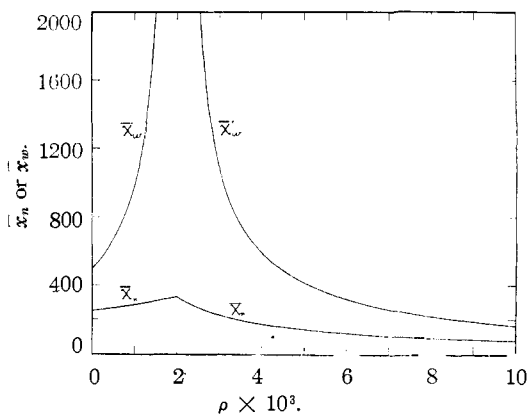


Fig. 2.—Number and weight average degrees of polymerization prior to gelation and for the sol after gelation vs. degree of cross-linking (ρ) for the "most probable" primary molecular weight distribution with $p = 0.996$.

that ρ'' approaches ρ for values of ρ far beyond its value at the gel point.

As pointed out in previous publications,^{2,3} the weight average molecular weight increases to infinity at the gel point (see Fig. 2). The weight average for the sol decreases as the degree of cross-linking is further increased. The number average increases only slightly up to the gel point, then \bar{x}'_n for the sol falls off rather rapidly.

The partition of the primary molecules between sol and gel does not, in this case, modify the form of the y -distribution within the sol, as can be seen by reference to equations (6) and (12), from which there is obtained

$$w'_y = [(1-p)^2/\varphi_s]y(pW_s/\varphi_s)^{y-1}$$

As ρ increases W_s/φ_s decreases, but the form of the distribution is preserved. The sol is of the same constitution as would have been obtained from a lower polymer having a size distribution given also by equation (17), but with p replaced by pW_s/φ_s , this polymer being cross-linked to the extent ρ' .

Application to a "Rectangular" Distribution.—

To illustrate the application of the above relationships to a broader primary molecular weight distribution, consider a polymer in which the weight fraction of every species composed of from 1 to 1000 units is the same, *i.e.*, $w_y = 0.001$ for $y = 1$ to 1000 and for $y > 1000$, $w_y = 0$. For such a distribution $\bar{y}_w = 500$, and, hence, gelation will set in when ρ exceeds 0.002;⁵ *i.e.*, the weight average and gel point are the same as for the distribution previously considered.

Designating the constant value of w_y by $1/Y$, and replacing summations by integrals

$$I_1 \cong (1/Y) \int_1^Y (W_s/\varphi_s)^y d \ln y$$

which can be evaluated graphically, and

$$\begin{aligned} I_2 &\equiv W_s \cong (1/Y) \int_0^Y (W_s/\varphi_s)^y dy \\ &\cong [1 - (W_s/\varphi_s)^Y] / [-Y \ln (W_s/\varphi_s)] \\ I_3 &\cong (1/Y) \int_0^Y (W_s/\varphi_s)^y y dy \\ &\cong \frac{(W_s/\varphi_s)^Y [Y \ln (W_s/\varphi_s) - 1] + 1}{Y [\ln (W_s/\varphi_s)]^2} \end{aligned}$$

Taking $Y = 1000$, these equations were solved for trial values of W_s/φ_s , and the various quantities were deduced as in the preceding example. In addition, partition factors s_y have been calculated for various values of W_s/φ_s using Equation (6). These are plotted in Fig. 3 against y for the several values of ρ indicated, which correspond to values of W_s/φ_s from 0.9995 to 0.993. The preferential transfer of the longer primary molecules to the gel is evident, but it is also clear that the separation is not highly selective.

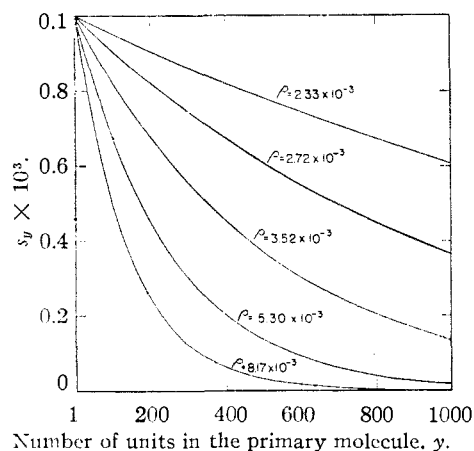


Fig. 3.—Partition of primary molecules between sol and gel for the "rectangular" primary molecular weight distribution at the degrees of cross-linking shown. Fraction s_y retained by the sol *vs.* number of units y in the primary molecule.

Figures 4 and 5 correspond to Fig. 1 and 2 of the preceding example. The curve representing the weight fraction of sol *vs.* ρ happens to be almost

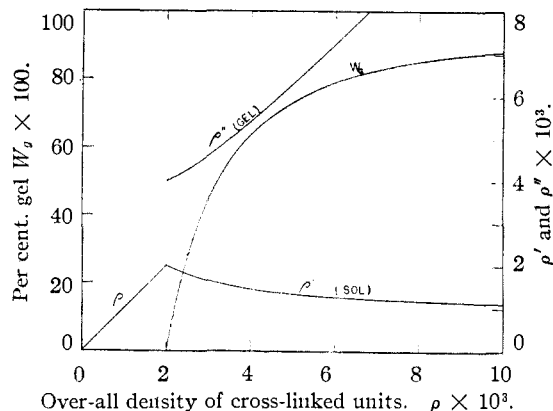


Fig. 4.—Weight fraction (W_g) of gel and concentrations of cross-linked units in sol (ρ') and in gel (ρ'') *vs.* the degree of cross-linking (ρ) for the "rectangular" primary molecular weight distribution.

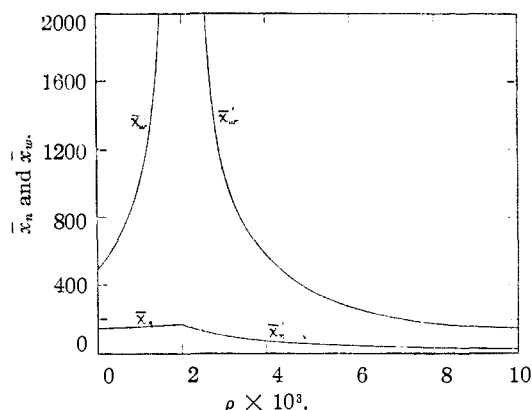


Fig. 5.—Number and weight average degrees of polymerization prior to gelation and for the sol after gelation *vs.* degree of cross-linking (ρ) for the "rectangular" primary molecular weight distribution.

the same as the one for the most probable distribution. The corresponding curve for a homogeneous polymer, calculated from equation (8),^{4,13} rises more rapidly toward 100% with increase in ρ . Other curves are similar to those for the most probable distribution; \bar{x}_n increases less as ρ increases from zero to the gel point, and thereafter both \bar{x}_n' and \bar{x}_w' decrease more rapidly with further increase in ρ .

The above treatment rests on two basic postulates, namely, that intramolecular connections within sol molecules can be neglected and that cross-linking occurs at random. Regarding the first of these, it should be pointed out that intramolecular connections will be most abundant in the highly cross-linked species. There will be more of these species the greater the concentration ρ' of cross-linkages in the sol.^{2,3} The maximum value of ρ occurs at the gel point; proceeding in either direction from the gel point, the concentration of cross linkages in the soluble portion decreases. Hence, the greatest error from the

neglect of intramolecular cross-linking can be expected to occur at the gel point, this error diminishing with increasing displacement in either direction from the gel point. This conclusion, which is particularly well demonstrated by the above calculations based on the present treatment, also can be deduced from molecular size distribution equations, which display a diminution in the abundance of highly complex finite species with increasing cross-linking beyond the gel point. The physical reasons for this course of affairs beyond the gel point are evident apart from statistical theory.

According to this analysis, statistical calculations beyond the gel point are vitiated less by the disregard of intramolecular connections than is the calculation of the gel point under the same approximation.^{1,5} The discrepancies between calculated and observed gel points^{1,7} furnish an indication of the magnitude of the error introduced. Presumably its correction would require a distortion of the ρ scales in Figs. 1, 2, 4 and 5, the gel points occurring at somewhat higher values of ρ and the magnitude of the distortion factor diminishing in either direction from the gel point.

The assumption that the units are cross-linked at random should apply satisfactorily to cases where the cross-linkages are introduced by a reaction which occurs subsequent to and independent of the process of polymerization of the chains (*e.g.*, a vulcanization reaction). In the polymerization of dienes, or in the copolymerization of vinyl and divinyl compounds, cross-linkages are formed simultaneously with the main chain polymerization process. Here, according to the most plausible mechanisms for such processes, it can be shown that the distribution of cross-linked units may not be precisely random; the

probability that a given structural unit is cross-linked is not entirely independent of the number of other cross-linked units in the same polymer chain.¹⁷ The departure from random cross-linking appears not to be serious, so far as application of the above theory is concerned, unless the polymerization is carried to high conversion.¹⁷

Whether or not the cross-linking reaction is such as to permit a given unit to enter into more than one cross linkage is of no particular concern provided the degree of cross linking ρ is small.

Polymers in which the cross linkages are formed by a reversible process also may be treated by the present theory. Whether the abundance and disposition of cross linkages is governed by equilibrium, kinetic or stoichiometric factors is irrelevant, so long as they occur at random, or approximately so.

Summary

The constitution of randomly cross-linked polymers containing a sufficient concentration of cross linkages to produce a gel fraction has been treated statistically by a method which avoids the use of molecular size distribution equations. The treatment is sufficiently general to cover any distribution of "primary" polymer chain lengths.

The new theory has been applied, for purposes of illustration, to two arbitrarily selected primary chain length distributions. Results are similar to those previously deduced in a less direct manner from size distribution equations. Limitations imposed by the basic assumptions relating to the absence of intramolecular cross-linking in finite molecular species (sol) and to the random occurrence of cross-linked units are discussed.

(17) Unpublished work.

AKRON, OHIO

RECEIVED SEPTEMBER 6, 1946

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, SINCLAIR REFINING COMPANY]

Adsorption-Desorption Isotherm Studies of Catalysts. II. A Comparison of Low Temperature Isotherms of Ammonia and Nitrogen¹

BY HERMAN E. RIES, JR., ROBERT A. VAN NORDSTRAND AND WILLIAM E. KREGER

As part of a program for the study of adsorption-desorption isotherms of gases on catalysts experiments have been performed with ammonia as the adsorbate. A comparison of the complete isotherms of ammonia with those of nitrogen, which is generally used, is of interest with respect to surface area values, pore volumes, pore radii and general hysteresis effects since the two adsorbates are quite different. The boiling point of ammonia is considerably higher than that of nitrogen, its surface tension is much greater and its molecule is smaller and of higher dipole moment.

(1) Presented before the Petroleum Division of the American Chemical Society, Atlantic City, April, 1946.

Earlier work in these laboratories has demonstrated that nitrogen adsorption-desorption hysteresis effects are remarkably similar for both the pellet and powder forms of two supported cobalt catalysts, H-G and H-A, which are alike in chemical composition but considerably different in area.^{1a} The pelleted form of the catalyst of greater area, H-G, was selected for the present ammonia study.

I. Experimental

Apparatus and Materials.—General methods for the study of adsorption isotherms have been described by Em-

(1a) Ries, Van Nordstrand, Johnson and Bauermeister, *THIS JOURNAL*, **67**, 1242 (1945).