Network Structure in Terms of Prepolymer and Curative Parameters

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SUMMARY

The structure of polymer networks is considered. The networks are assumed to be formed from the reaction of functional groups on low molecular weight telechelic polymers with a cross-linking agent. Relationships are derived between cross-link density and properties of the prepolymer mix such as functional group equivalent weight, functionality, and including the maximum or final extent of reaction of the functional groups and the gel content of the cured stock.

At an equivalent reactant ratio of 1.0 to 1.0 and with the branch points uniting no more than three chain ends, the cross-link density in the gel was found to be proportional to the product of a concentration term, q, and a geometrical term, $(1 - 1/f_a - 1/f_p)$, which is called the branching function. The absolute value of the network cross-link density in moles/g was found to be

$$2q(1 - 1/f_a - 1/f_p)(CDF)W_g$$

where q = equivalents of prepolymer functional groups per gram, f_p = functionality of prepolymer, f_a = functionality of cross-linking agent, CDF = cross-link decrease factor, a constant having a value between 0.42 and 0.66, and W_g = weight fraction of gel.

The CDF term is the factor by which the cross-link density in the gel is decreased because of failure of the reaction to go to completion at the maximum degree of cure. At a reactant ratio of 1.0 this term was found to have the form

$$\frac{1 - \dfrac{1 - e}{1 - e_c}}{1 - \dfrac{1 - e}{3(1 - 1/f_a - 1/f_p)}}$$

where e is the maximum or final extent of the curing reaction in the gel, and e_c is the extent of reaction at the gel point. At a reactant ratio of 1.0 the CDF term was constant over a wide range of functionalities. The extent of reaction in the gel was determined from a previously published equation of the form $e^2 = (1 - k)e_c^2 + k$. The value of the constant k was estimated to be 0.3 ± 0.1.

INTRODUCTION

Materials containing polymer networks formed from the reaction of low molecular weight cross-linking agents with functional groups on prepolymers of intermediate molecular weight are finding ever wider use in the adhesives, coatings, sealants, and propellants industries. The chemist formulating these resins can usually vary the curative functionality and equivalent weight by using different curatives and can also vary the ratio of the curative to the prepolymer. In some cases he may have available a series of prepolymers of different functionality and equivalent weight. Although polymer network structure has been well understood for some time [1], it is noteworthy that a description of such structures has not been available in terms of the parameters of the building blocks from which the networks are derived [14].

One reason for the dearth of information on this subject may be the lack of knowledge about the maximum or final extent of reaction of the functional groups during cure. No valid conclusions can be drawn without such information. Recently, R. A. H. Strecker of this laboratory devised a method of following the curing reaction of certain prepolymers after the gel point [2]. In a later paper [3] it was shown that the final extent of reaction during cross-linking of prepolymers is geometrically determined and related to the functionality of the prepolymer and curative by simple

equations (see Eq. 22 and 23 below). As a result, a coordinated discussion of cross-linked prepolymer structure becomes possible.

The aim of the present work is to derive relationships between polymer network cross-link density and properties of the prepolymer mix such as functional group equivalent weight, functionality, and reactant ratio, and including the maximum extent of reaction of the functional groups and gel content. It will be assumed that the prepolymer contains no branch points with more than three chains united at the branch points. Very simple mathematics will be used but the complexity of the subject requires rather close thinking.

Definition of Symbols

n_p = moles of prepolymer

n'_p = product of n_p and the weight fraction of gel.

f_p = functionality of prepolymer, average number of reactive groups per molecule. The word functionality as used here does not refer to the number of chain ends united at branch points in polymer networks.

q = equivalents of prepolymer reactive groups per gram

W_p = equivalent weight of prepolymer = $1/q$

M_p = molecular weight of prepolymer

n_a = moles of cross-linking agent

f_a = functionality of cross-linking agent

W_a = equivalent weight of cross-linking agent

M_a = molecular weight of cross-linking agent

w = weight

X = moles of branch points in the polymer network

X_d = moles of branch points/gram, cross-link density

S = moles of chain segments/gram (a segment is that portion of a polymer network between branch points or that portion of a prepolymer molecule between a branch point and a reactive group)

M_c = molecular weight between cross-links

r = ratio of number of cross-linking groups to prepolymer reactive groups

e or e_a = extent of reaction of the prepolymer in terms of 1 for complete reaction

e_c = extent of reaction of the prepolymer at the gel point

e_a = average extent of reaction of the whole prepolymer

e_g = extent of prepolymer reaction in the gel

e_s = extent of prepolymer reaction in the sol

W_g = weight fraction of gel

W_s = weight fraction of sol

m = ratio of network segments which do not form to the number of functional groups which fail to react in the network in an incomplete reaction

CDF = cross-link decrease factor; the factor by which the cross-link density is decreased because of failure of the curing reaction to go to completion.

Some Relationships

$$M_p = f_p W_p \tag{1}$$

$$M_a = f_a W_a \tag{2}$$

$$X_d = X/w \tag{3}$$

$$X_d = \frac{2}{3}S \tag{4}$$

$$M_c = \frac{M_p}{\text{mole segments per mole}} = 1/S = 2/3X_d \tag{5}$$

$$r = n_a f_a / n_p f_p \tag{6}$$

$$w = n_p M_p + n_a M_a \tag{7}$$

These relationships follow from definitions except in the case of Eqs. (4) and (5). These latter depend on the fact that the number of branch points in a polymer network is equal to twice the number of chain segments divided by the number of chain ends united at the branch points - three in this case, since we are restricting the cross-linking agent to a maximum functionality of three [4]. If branch points unite more than three chain ends, appropriate corrections must be made to Eqs. (4) and (5) which will change the course of the following treatment.

It should be noted that restriction of the number of chain ends united at the branch points to three in the polymer network does not restrict the number of reactive groups on the monomer molecules as long as the branch points in the monomer unite no more than three chain ends. A monomer containing a carbon chain with more than three reactive groups situated along the chain would be such a case.

DISCUSSION

Variation of Cross-link Density with Functionality

In this discussion we will consider the reaction of a prepolymer whose chain ends are terminated by reactive groups with a cross-linking agent capable of reacting with the prepolymer functional groups. No restriction will be placed on the number of reactive groups per molecule (which will be termed the functionality) in the case of the prepolymer as long as no branch point unites more than three chains, but the functionality of the cross-linking agent will be assumed to be no greater than three. It will be further assumed that the molecular weight of the cross-linking agent can be ignored in comparison with that of the prepolymer.

Now since a single chemical bond in itself does not constitute a branch point, it follows that the branch points in a polymer network formed as above will be the sum of the branch points originally present in each of the constituents of the network assuming complete reaction of all groups [5].

$$X = (f_p - 2)n_p + (f_a - 2)n_a \qquad (8)$$

$$X_d = \frac{(f_p - 2)n_p + (f_a - 2)n_a}{w} \qquad \text{(from Eq. 3)}$$

$$= \frac{(f_p - 2)n_p + (f_a - 2)\dfrac{rn_p f_p}{f_a}}{f_p W_p n_p + f_a \dfrac{W_a rn_p f_p}{f_a}} \qquad \text{(from Eqs. 7, 1, 2, and 6)}$$

However, complete reaction of all functional groups has been assumed. It follows that the relationship holds only when the reactant ratio, r, is 1. Hence

$$X_d = \frac{f_a(f_p - 2) + f_p(f_a - 2)}{f_a f_p(W_p + W_a)} \qquad (9)$$

If $W_a \ll W_p$

$$X_d = \frac{2(1 - 1/f_a - 1/f_p)}{W_p}$$

$$= 2q(1 - 1/f_a - 1/f_p) \tag{10}$$

Utilizing Eq. (5)

$$M_c = \frac{f_p W_p}{3f_p(1 - 1/f_a - 1/f_p)} \tag{11}$$

If $f_a = 3$

$$M_c = \frac{f_p W_p}{2f_p - 3} \tag{12}$$

It will be noted that the numerator of Eq. (11) is the molecular weight of the prepolymer. It follows from the definition of M_c that the denominator is the moles of chain segments per mole of prepolymer (or SM_p).

Equation (12) can also be deduced by considering the form of the relation between f_p and the number of network segments when $f_a = 3$. This relation will have the form $af_p - b$, where a and b are constants. By introducing two boundary conditions, a and b can be shown to have the values 2 and 3, respectively.

The above treatment holds only when all the functional groups have reacted, which requires that the reactant ratio have the value of 1. Although the reactant ratio, r, was used, it entered the discussion only in order to present n_a in terms of n_p. Variation in reactant ratio can be considered in terms of its effect on the effective values of f_a and f_p. However, we will consider r to have the value of 1.

Variation With Extent of Reaction in the Gel

The purpose of this work is to derive a relationship between parameters of monomers and the cross-link or branch point density of the cured polymer which contributes to physical properties. The soluble or sol portion of a stock contains branch points and segments between branch points which have arisen during the polymerization reaction but they do not contribute to properties and we are not interested in them. Consequently, we take as the initial point for the development of cross-links the critical stage where the polymer network first fills the container, the gel point.

If we consider the gel phase only, there can be no gel cross-links before

the gel point and we can equate the cross-link density of the gel to 0 at this critical point. In a sense such a relation means that we are defining cross-link density in terms of a physical property such as modulus of elasticity whose value is 0 at the gel point. In other words, at the gel point the breaking of a single bond of the gel would produce two sol molecules which we will define as having no cross-links.

Within the gel the moles of prepolymer in the network will be n_pW_g, where W_g is the weight fraction of gel. This quantity, n_pW_g, will be designated n'_p. The cross-link density will be considered as 2/3 of the number of polymer segments within the network divided by the effective molecular weight (Eq. 4). The unreacted groups in the gel are at the ends of dangling segments which are not to be considered as part of the network. The effective number of segments then will be the total number at 100% reaction, $3n'_pf_p(1 - 1/f_a - 1/f_p)$ from Eq. (11), less the number of segments associated with the unreacted groups, while the effective molecular weight will be the total molecular weight, $n'_pf_pW_p$, minus the molecular weight associated with the unreacted groups. If

$$e = \text{extent of reaction} = \frac{\text{reacted prepolymer groups}}{\text{total prepolymer groups}}$$

$$\text{reacted groups} = en'_pf_p \qquad (13)$$

$$\text{unreacted groups} = (1 - e)n'_pf_p \qquad (14)$$

The molecular weight associated with the unreacted prepolymer groups is the number of unreacted groups times the average molecular weight associated with each group's prepolymer segment. The molecular weight associated with each group's segment will be M_c at 100% reaction as given by Eq. (11). The molecular weight associated with unreacted groups will be

$$(1 - e)n'_p \frac{f_pf_pW_p}{3f_p(1 - 1/f_a - 1/f_p)}$$

The remaining molecular weight will be $n'_pf_pW_p$ minus the above expression, or

$$n'_p f_p W_p \left[1 - \frac{(1 - e)}{3(1 - 1/f_a - 1/f_p)} \right] \tag{15}$$

The number of network segments formed in an incomplete reaction is a more complicated matter. Loss of one segment in a network can in reality mean the loss of two or three segments instead of one. In this illustration five segments are reduced to two by the loss of one segment.

It is necessary to introduce another quantity, m, which is the factor relating the number of unreacted groups, $(1 - e)n'_p f_p$, to the number of segments of the infinite network which do not form when a group fails to react. That is, the number of segments which do not form when a group fails to react will be

$$m(1 - e)n'_p f_p$$

The number of segments which do form will be the total number at 100% reaction as given by the denominator of Expression (11) minus the above quantity

$$n'_p \left[3f_p(1 - 1/f_a - 1/f_p) \right] - m(1 - e)n'_p f_p$$

or

$$n' \left\{ \left[\frac{3(f_a - 1)}{f_a} - m(1 - e) \right] f_p - 3 \right\} \tag{16}$$

The cross-link density is then 2/3 of Expression (16) divided by Expression (15)

$$X_d = \frac{2\left\{\left[(\frac{f_a - 1}{f_a}) - \frac{m(1 - e)}{3}\right]f_p - 1\right\}}{f_p W_p \left[1 - \frac{1 - e}{3(1 - 1/f_a - 1/f_p)}\right]} \tag{17}$$

The denominator of this expression is the effective molecular weight per pre-polymer unit, with the ratio in parenthesis being the fraction by which the molecular weight is reduced because of failure of the reaction to go to completion (dangling chain ends). The numerator is 2/3 of the moles of chain segments per effective mole of prepolymer.

We should note that n'_p which includes the fraction of gel has cancelled from the numerator and denominator. If the reaction could be reversed, n'_p would decrease to 0 at the gel point but the limit of n'_p/n'_p would still be 1. If the cross-link density at the gel point is 0 as discussed above, then the numerator of Eq. (17) must be 0 at the gel point since the denominator cannot become infinity. Thus

$$\left[\frac{f_a - 1}{f_a} - \frac{m(1 - e_c)}{3}\right]f_p - 1 = 0 \tag{18}$$

where e_c is the extent of reaction at the gel point. Solution of Eq. (18) for m yields

$$m = \frac{3(1 - \frac{1}{f_a} - \frac{1}{f_p})}{(1 - e_c)} \tag{19}$$

Values of e_c for any set of values of f_a and f_p may be obtained from Stockmayer's [6] and Kahn's [7] gel-point relationship

$$e_c{}^2 = \frac{r}{(f_a - 1)(f_p - 1)} \tag{20}$$

Equation (20) as derived by Stockmayer and by Kahn employed weight-average functionalities rather than the number-average functionalities used above. This should not disturb us since the functionality values used in this equation (and in applying the related Eq. 25 below) are not used directly here. As long as calculated values of e_c (and the maximum extent of re-

action) are in accordance with experiment, we may employ weight-average functionalities in Eq. (20). It must be kept in mind, however, if one is working with an actual prepolymer system, that two types of functionality averages have been used in Eq. 20 as opposed to Eq. 17 and those equations derived from it.

By substitution of Eq. 19 for m and of q, the prepolymer reactive group concentration, for $1/W_p$, Eq. (17) may be rearranged to the form

$$X_d = 2q \left(1 - 1/f_a - 1/f_p\right) \left[\frac{1 - \dfrac{1 - e}{1 - e_c}}{1 - \dfrac{1 - e}{3(1 - 1/f_a - 1/f_p)}} \right] \qquad (21)$$

where X_d is the cross-link density in moles/gram and q is the prepolymer reactive group concentration in equivalent/gram. The final term in brackets reduces to 1 if e becomes 1 and is the factor by which the cross-link density is decreased because of failure of the reaction to go to completion. This term, which will be called the CDF term, cross-link decrease factor, must be evaluated in order to use Eq. (21).

Calculation of Cross-link Density

For any values of f_a and f_p, e_c may be evaluated from Eq. (20). The maximum extent of reaction, e, has been found to be determined by the following relation [3];

$$e^2 = 0.88e_c{}^2 + 0.10r \qquad (22)$$

or with sufficient exactitude

$$e^2 = (1 - k)e_c{}^2 + kr \qquad (23)$$

where k = 0.10.

It would seem that the CDF term could now be calculated. However, the extent of reaction used in determining the constants in Eq. (22) was the average extent of reaction of the whole system including sol and gel whereas the treatment here has been concerned only with a complete polymer network. Soluble materials were assumed absent. Unfortunately, the extents of reaction in sol and gel are different and not equal to the average extent of reaction except at the gel point and at 100% reaction. The extent of

reaction in the gel is greater, and in the sol is less, than the average. In any stock some sol will be present.

Further treatment will assume that the extent of reaction in the gel is determined at least approximately by an equation of the form of Eq. (23). The problem of calculating e, therefore, reduces to the question of the proper value of k to use in Eq. (23) to obtain the final extent of reaction in the gel. The variation of gel and sol content with extent of reaction has been discussed in various sources (Ref. 1a, pp. 347-397, and Refs. 9-12), but not in a form useful in the present discussion.

Arguments may be advanced to place limits on possible values of k. However, it will be shown below that the exact value of k is probably of minor importance. It will suffice that limits between 0.10 and 0.37 were deduced as illustrated in Fig. 1 by making use of a maximum possible value of the final extent of reaction in the gel for a particular stock. Sol-gel determinations were made on a number of stocks [13] and the proportion of gel was found for the stock whose functionalities satsified the relation

$$(f_a - 1)^{-1}(f_p - 1)^{-1} = 0.5$$

Then using the equation

$$e_a = W_s e_s + W_g e_g \tag{24}$$

where e_a = average extent of reaction, e_s = extent of reaction in the sol, W_s = weight fraction of sol, e_g = extent of reaction in the gel, W_g = weight fraction of gel, and $W_s + W_g = 1$, the maximum possible value of e_g was calculated by letting $e_s = 0$ and substituting the experimental value of W_g.

Determination of the intercept on the abscissa of Fig. 1 gave a maximum possible value of k of 0.37. The most probable value of k will have to be closer to 0.37 than to 0.10. It will suffice to use 0.3 ± 0.1 to cover the consequences of the uncertainty in the value of k.

Using these values of k it is possible to calculate (1 - e) for various values of f_a and f_p from Eqs. (20) and (23). Tables and curves can be constructed showing the variation of (1 - e_c), (1 - $1/f_a$ - $1/f_p$), and $2f_a f_p/(f_a + f_p)$ with f_a and f_p. The last function is the average functionality of f_a and f_p at r = 1.

Calculation of the CDF term yields the result shown in Fig. 2. From an average functionality of the system of 2.05 to 3.0 the CDF is constant regardless of the value of k employed in the calculation. As a consequence one may take the cross-link density as varying with $q(1 - 1/f_a - 1/f_p)$ and neglect the variation with CDF in Eq. (21). Equation (21) may then be
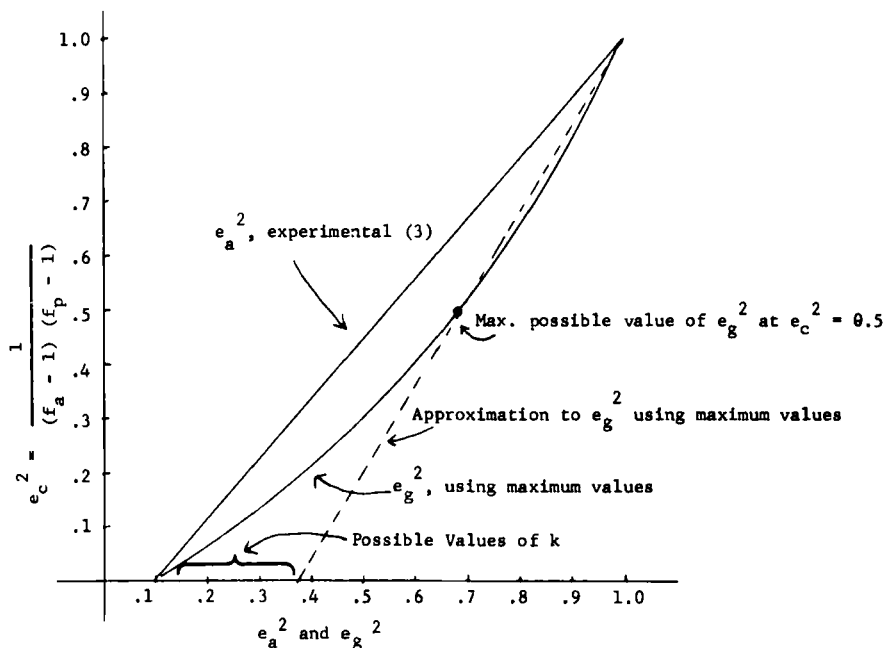
Fig. 1. Limiting values of k in $e_g^2 = (1 - k) e_c^2 + k$.

stated as

$$X_d = 2q(1 - 1/f_a - 1/f_p)(CDF) \qquad (25)$$

where CDF is a constant having a value between 0.42 and 0.66.

Table 1 shows numerical values of $(1 - 1/f_a - 1/f_p)$, CDF, and the cross-link density per equivalent of reactant, X_d/q, obtained using Eq. (21) and three values of k. Figure 3 shows graphically the linearity of $(1 - 1/f_a - 1/f_p)$, which will be called the "branching function," with the calculated values of the cross-link density per reactant equivalent, $X_d/q = (1 - 1/f_a - 1/f_p)(2CDF)$.

It must be emphasized that the constancy of the CDF term is known to be true only when reactant ratio is 1.0 and that the cross-link density values in Table 1 are those of the gel phase only.

It was shown logically that the CDF term had to be nearly constant over low values of f_a and f_p. However, efforts to prove that the term was mathematically constant were not successful. It was found that the CDF term
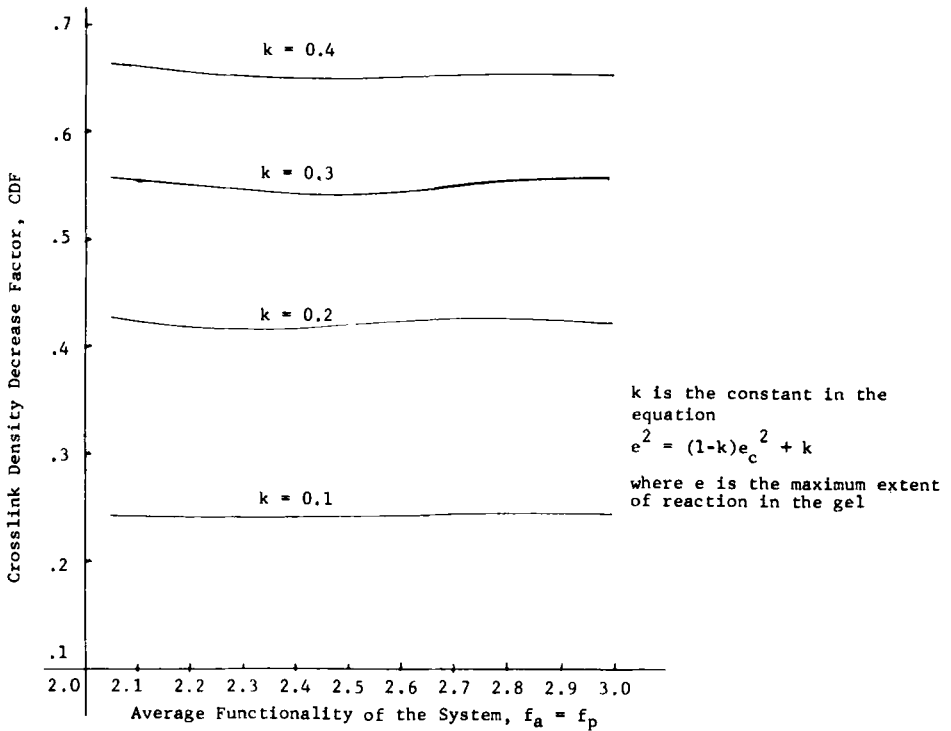
Fig. 2. Constancy of the cross-link decrease factor.

was approximately equal to the square root of k in Eq. (23).

Effect of Sol and Inert Diluent

Most practical prepolymer stocks contain plasticizers or fillers. The fillers, being insoluble, are not part of the prepolymer phase. They are partly or completely bonded to the cured prepolymer and effectively raise the cross-link density in a manner which is outside the scope of this discussion. A plasticizer or modifying resin, on the other hand, is part of the prepolymer phase and its effect must be considered as must also the effect of the pre-polymer not bound to the network after reaction.

The soluble inert diluent, being nonreactive, does not become part of the polymer network. It does, however, spacially separate the prepolymer mol-ecules and so fewer cross-links result per unit volume of material. The equiv-alent weight of the functional groups as measured in the prepolymer phase

Table 1. Cross-link Density Functions

f_p or f_a	2.0	2.05	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
f_a or f_p	2.0	2.05	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
Cross-link decrease factor, $k = 0.2$[a]		.43	.42	.414	.416	.417	.419	.420	.423	.422	.421	.420
$k = 0.3$		.56	.55	.548	.540	.537	.535	.545	.555	.557	.552	.550
$k = 0.4$		.66	.66	.652	.648	.645	.640	.645	.647	.647	.649	.650
$(1 - 1/f_a - 1/f_p)$	0	.024	.046	.093	.130	.167	.200	.230	.258	.284	.310	.333
Cross-link density per reactant equivalent[b] $k = 0.2$	0	.021	.039	.077	.108	.139	.163	.193	.218	.240	.261	.280
$k = 0.3$	0	.027	.051	.102	.140	.179	.214	.251	.286	.317	.342	.366
$k = 0.4$	0	.032	.061	.121	.168	.215	.256	.296	.334	.368	.402	.433

f_p or f_a	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
f_a or f_p	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	4.0
Cross-link decrease factor, $k = 0.3$		.57	.56	.55	.54	.55	.56	.55	.54	.54	.55	.56
$(1 - 1/f_a - 1/f_p)$	0	.023	.049	.065	.083	.100	.115	.130	.143	.155	.167	.250

f_p or f_a	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
f_a or f_p	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	4.0
Cross-link decrease factor, $k = 0.3$	.58	.58	.56	.55	.55	.55	.54	.55	.56	.56	.56	.56	.55	.55	.55	.55	.56
$(1 - 1/f_a - 1/f_p)$	.042	.079	.111	.140	.167	.191	.212	.232	.250	.267	.282	.297	.310	.322	.333		.417

[a] The constant in $e_g^2 = (1 - k)e_c^2 + kr$, $e_c^2 = r(f_a - 1)^{-1}(f_p - 1)^{-1}$, and $r = 1$.

[b] $2(1 - 1/f_a - 1/f_p) \times$ cross-link decrease factor, $r = 1$, and does not consider the sol content.
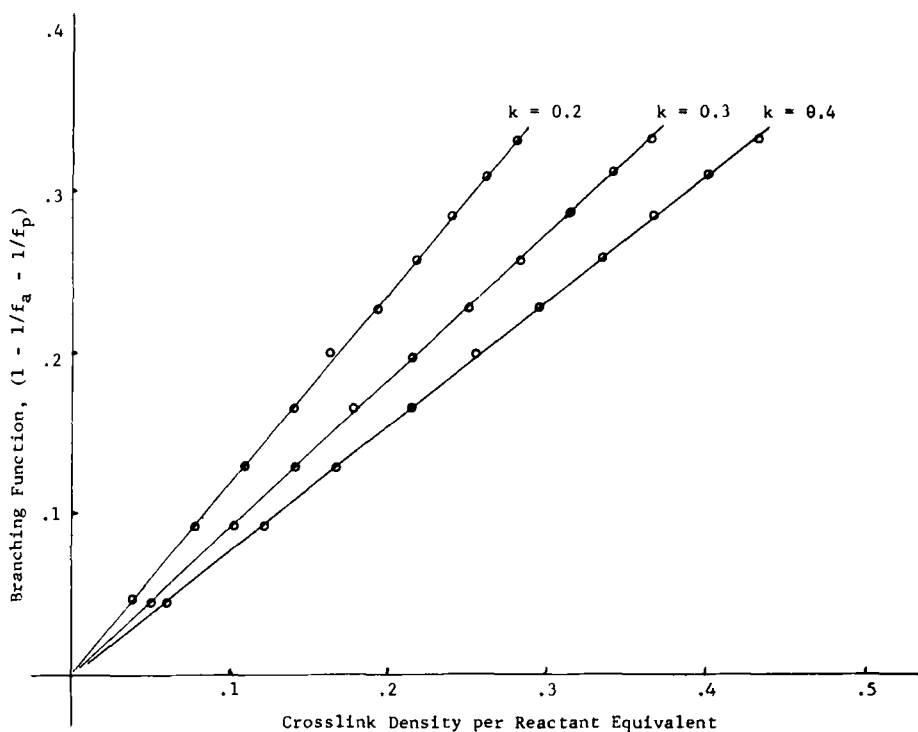
Fig. 3. Linearity of branching function with calculated cross-link density in gel at $r = 1$.

before cure is greater and so is the sol content on extraction of the cured product.

Since the treatment in the previous section was concerned only with a complete polymer network, every part of which was connected to every other part, soluble materials were assumed absent and Eq. (25) can be valid only in the case of 100% gel. Material in the cured stock which is neither gel nor filler can be divided into soluble polymer not connected to the gel and inert soluble diluent introduced into the mixture before cure. In this section we will restrict the term "sol" to the former and use the words "soluble diluent" for the latter division. We can conceive of stocks containing sol and no soluble diluent, soluble diluent and no sol, and both sol and soluble diluent. In actuality all stocks contain some sol and the second case is hypothetical.

In the hypothetical case of stocks containing soluble diluent and no sol, correction of cross-link density for the presence of the diluent could be accomplished by using the functional group equivalent weight or reactive group content, q, as determined on the whole mixed sample. This procedure is the same as multiplying the cross-link density as determined from Eq. (25) by the fraction of gel, W_g, since in the absence of sol as defined above

$$W_g = (1 - \text{fraction soluble ingredients})$$

and

$$q \text{ diluted} = q(1 - \text{fraction soluble ingredients})$$

If there is no soluble diluent, there will still be some sol, and correction of cross-link density can be made by multiplying the cross-link density from Eq. (25) by W_g.

If there is both sol and soluble diluent, correction can be made by multiplying the cross-link density from Eq. (25) by W_g, using a functional group content, q, based on the undiluted sample, or by multiplying the cross-link density by (W_g + fraction soluble diluent) and using a functional group content, q, based on the diluted sample.

Thus for the general case Eq. (25) becomes

$$X_d = 2q(1 - 1/f_a - 1/f_p)(CDF)W_g \tag{26}$$

where q is on the undiluted sample. The functionalities are those of the re-active moles only. The means for measuring functionality should therefore not be the molecular weight-equivalent weight method but should be independent of inert diluent as in a gel point method [8]. Some experimental work was carried out to determine the variation of W_g with f_a and f_p [13]. There was considerable scatter in the data. Very approximately, the weight fraction of sol was found to be $0.010/(1 - 1/f_a - 1/f_p) + 0.05$.

Variation with Reactant Ratio

The formulator of prepolymer stocks frequently varies the reactant ratio, r, and it would be desirable to know the effect of this variation on the form of Eq. (26). Reviewing the derivation of this equation, it is found that Eq. (10) was derived on the basis that all functional groups were reacted, which requires that r = 1. The expressions in Eq. (10) were then used as integral

parts of relations leading to Eq. (26). The opinion is advanced that Eq. (26) should not employ the reactant ratio except as the reactant ratio changes the effective functionality of the two reactants and except as it changes the extent of reaction as shown in Eqs. (20) and (23).

When r is greater than 1, we have a deficiency of prepolymer and an excess of cross-linking agent. The number of groups on the cross-linking agent which will be capable of reaction will be equal to the number of reactive groups on the prepolymer, $n_p f_p$. Hence the effective functionality of the cross-linking agent will be $n_p f_p / n_a$. But $n_p f_p = n_a f_a / r$, or the effective functionality of the cross-linking agent will be f_a / r.

When r is less than 1, we have an excess of prepolymer and a deficiency of cross-linking agent. The number of groups on the prepolymer which will be capable of reaction will be equal to the number of reactive groups on the cross-linking agent, $n_a f_a$. The effective functionality of the prepolymer will be $n_a f_a / n_p = r f_p$. Similarly, the effective equivalent weight of the prepolymer will be W_p / r. Hence, $f_p W_p$ remains unchanged.

Although it is possible by using the above ideas to write expressions giving the variation in cross-link density with variable reactant ratio, presenting such expressions does not seem advisable in view of doubt of the correctness of these ideas.

CONCLUSION

The usefulness of the conclusions reached here resides chiefly in the finding that the cross-link density in networks formed from telechelic prepolymers is proportional to the product of a concentration term, q, and a geometrical term, the branching factor, $(1 - 1/f_a - 1/f_p)$, when the equivalent reactant ratio is 1.0. The quantities q, f_a, and f_p will generally be known or can be measured. The absolute value of the cross-link density will be proportional also to the weight fraction of gel and to twice the cross-link decrease factor (CDF). Although the CDF term is constant at a reactant ratio of 1.0, its value cannot be assigned at present to closer than the limits 0.42 to 0.66 because of ignorance of the final extent of reaction in the gel phase. It may be of significance that twice the CDF term is reasonably close to 1.0, being within the range 1.08 ± 0.24.

It is hoped that this discussion is free of errors of logic and that it will be of use to chemists who deal with the confusing variables of polymer network structure. Experimental investigation of some of the ideas discussed its certainty needed. It is planned to present such data in future communications.

ACKNOWLEDGMENTS

REFERENCES AND COMMENTS

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