Determination of crosslink density by end group analysis after partial degradation:
1. Theory

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A method is derived for estimating the intermolecular crosslink density of any polymeric gel, provided it can be partially solubilized by main-chain degradative procedures to yield a soluble fraction that can be analysed for end groups. Predicted end group concentration for a given solubilization is derived from a model that assumes uniform initial chain lengths before crosslinking, random crosslink sites, and random attack on main chain bonds. Results are almost invariant with respect to chain length, so that simpler expressions can be used that are derived for infinite chain length, and which have the advantage of being applicable to gels in which the initial chain molecular weight or its distribution is unknown.

INTRODUCTION

Breakage of some of the crosslinks or main chain bonds of an otherwise insoluble crosslinked polymer frees a portion that can be removed from the remaining gel by an appropriate swelling solvent. The amount dissolved depends on the initial intermolecular crosslink density, the fraction of crosslinks broken, the initial molecular weight distribution of the main chains (considered as though they were not crosslinked), and the fraction of main chain bonds broken. Knowledge of the mathematical relationships among these variables would enable calculation of one from the others, but the procedure would be extremely complex. An alternative approach is to use a simplified model, for which analytic solutions can be obtained without undue sacrifice of the major physical features of the crosslinked system.

In a previous publication[1], an exact closed form expression was derived for the extent of solubilization of a randomly crosslinked polymer gel with an initially uniform molecular weight distribution, following random breakage of arbitrary numbers of crosslinks, main chain bonds, or both, simultaneously. In this paper the theory will be extended to develope a method for estimating the extent of intermolecular crosslinking of a polymer by observation of the fraction solubilized after cleavage of a portion of the main chain bonds, and subsequent determination of the number of chain ends appearing in the soluble fraction. Application of the method to a polymer gel formed by crosslinking of heterodisperse polymer molecules is facilitated by the fortunate circumstance that the correlation between the above measurable quantities depends strongly on the crosslink density, and is nearly independent of molecular weight or molecular weight distribution.

Although this approach was originally developed for application to densely crosslinked keratins, for which end group determinations for the cleaved protein chains are particularly simple, any other crosslinked polymer could be similarly investigated as long as it can be solubilized by primarily main chain breakage to yield analysable end groups.

THEORY

The starting model polymer studied in a previous work[1] was produced by hypothetically crosslinking initially monodisperse chains randomly. It was assumed that the state reached after partial degradation of this model polymer, namely a distribution of molecular chains with varying amounts of crosslinking, could also be reached by taking the same final distribution and randomly introducing the necessary number of crosslinks. Cleavage of main chain bonds or crosslinks, and the formation of new crosslinks, were assumed to proceed randomly. This assumption permits the theoretical calculations to take a much simpler course in defining the final state of the degraded polymer than would be possible if the actual kinetic details were followed. In applications studied so far, there is no evidence that this assumption of randomness is in any way limiting.

Initially, the model polymer is taken to be a collection of A_0 non-crosslinked molecules, each with a uniform degree of polymerization U. The total number of monomer units is $A_1 = U A_0$. Random severing of a fraction P of the total number of monomer–monomer bonds produces a variety of chain lengths. Montroll and Simha[2] derived the following number distributions of molecules with degree of polymerization u that result from random scission of initially uniform chains:

$$N(u<U) = A_0 P(1-P)^{u-1}[2+(U-1-u)P] \quad (1)$$

and

$$N(U) = A_0(1-P)^{U-1} \quad (2)$$

The heterogeneous broken chains are engaged in random crosslinking until a fraction Q of their monomer units is intermolecularly linked. The method of Charlesby[3] is used to calculate the relative proportion of soluble and gel (insoluble) fractions that result. After crosslinking, the number of molecules with u monomers,

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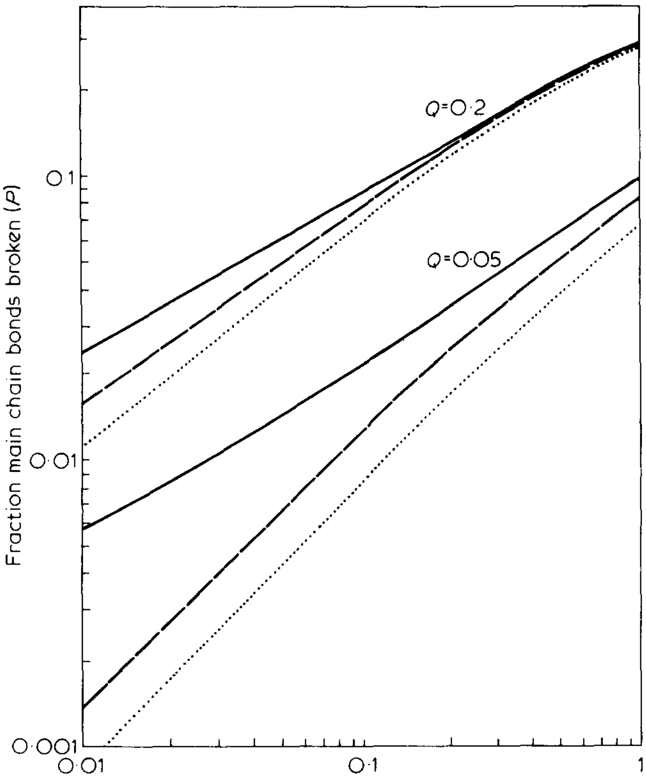

Figure 1 Relationship between solubility, S, and the extent of main chain bond breakage, P, for two levels of crosslink density: Q = 0.2 and 0.05. The variation with chain length at each crosslink density is indicated for three initial chain lengths: $U = \infty$ (——), U = 100 (— — —), and U = 50 (· · · ·)

of which c are crosslinked, is:

$$n_c = N(u)(1-Q)^{u-c}Q^c u!/(u-c)!c! \qquad (3)$$

The total number of crosslinks is QA_1. A fraction t_c of these crosslinks are on molecules that have c links to them, giving:

$$t_c = (1/QA_1)\sum_{u=1}^{U} cn_c \qquad (4)$$

A 'sterile coefficient', S_0, is defined to be the probability that a given crosslink is not connected to the gel through other crosslinks:

$$S_0 = \sum_{c=1}^{U} S_0^{c-1} t_c = \sum_{u=1}^{U}\sum_{c=1}^{u} n_c c S_0^{c-1}/QA_1 \qquad (5)$$

The sterile coefficient can be connected to the actual soluble fraction S in the following way. Solubility is defined by the fraction of molecules that have either no crosslinks at all or sterile ones only:

$$S = \sum_{u=1}^{U}\sum_{c=0}^{u} n_c u S_0^c/A_1 \qquad (6)$$

By introducing the expression for n_c, equation 3, into equations 5 and 6 and evaluating the sums over c, we have for S and S_0

$$S = \sum_{u=1}^{U} uN(u)(1-Q+QS_0)^u/A_1 \qquad (7)$$

and

$$S_0 = \sum_{u=1}^{U} uN(u)(1-Q+QS_0)^{u-1}/A_1 \qquad (8)$$

Comparison of equations 7 and 8 provides the desired relation:

$$S = S_0(1-Q+QS_0) \qquad (9)$$

When equations 1 and 2 for $N(u)$ and $N(U)$ are substituted into equation 8, and the sums evaluated, the closed form that is obtained is given by equation 28 of ref 1. With further algebraic manipulation, this equation can be converted to the following simpler representation:

$$S_0 = a^{U-1} + \frac{P}{U(1-a)^2}\left[2\left(1-\frac{P}{1-a}\right)(1-a^U) + 2U(1+a^U) - U(2-P)(1+a^{U-1})\right] \qquad (10)$$

where

$$a = (1-P)(1-Q+QS_0) \qquad (11)$$

These expressions, along with equation 9, define the solubilization of the crosslinked system. For a given crosslink density Q, and fractional main chain bond breakage P, equations 9, 10 and 11 can be solved iteratively to give S, the expected fraction of the original gel that becomes soluble. *Figure 1* shows illustrative results of such a calculation, in which S is plotted against P for degradation of main chains only (no crosslink cleavage) for hypothetical polymers having two levels of crosslink density, $Q=0.05$ and $Q=0.2$, and three initial chain lengths, $U=50$, $U=100$, and $U=\infty$. Even if an accurate method could be devised for determining the dependent variable P in the whole system (not a trivial matter), it is apparent that the strong dependence of S on U would severely limit the use of such a correlation in estimating an unknown Q, at least for most polymer systems.

The total fraction of main chain cleavage, P, is fortunately not the only important parameter that can be used to characterize polymer degradation in a crosslinked gel. Among various possibilities examined, the most obviously useful is the number of chain ends in the soluble fraction, designated as ν. Although ν could be used to estimate P, a more valuable correlation occurs when it is plotted against the soluble fraction, S. The correlation is essentially independent of U, the initial degree of polymerization, and depends primarily on Q, the initial crosslink density before degradation. This means that the correlation can be applied even to the degradation of an initially heterodisperse crosslinked polymer, thus broadening the theoretical results to include most polymer systems of practical interest.

To calculate ν, we begin by tallying the kinds of molecules or clusters that appear in the soluble fraction after partial solubilization, assuming that everything not attached to the insoluble gel fraction can be leached out. The number of uncrosslinked molecules is determined by summing $n_0(u)$ over all possible u. The number of molecules with one crosslink is a fraction S_0 of the sum of $n_1(u)$ over all u, the number with two crosslinks a fraction S_0^2 of the sum of $n_2(u)$, and so on. The total number of individual molecules appearing in the soluble fraction is

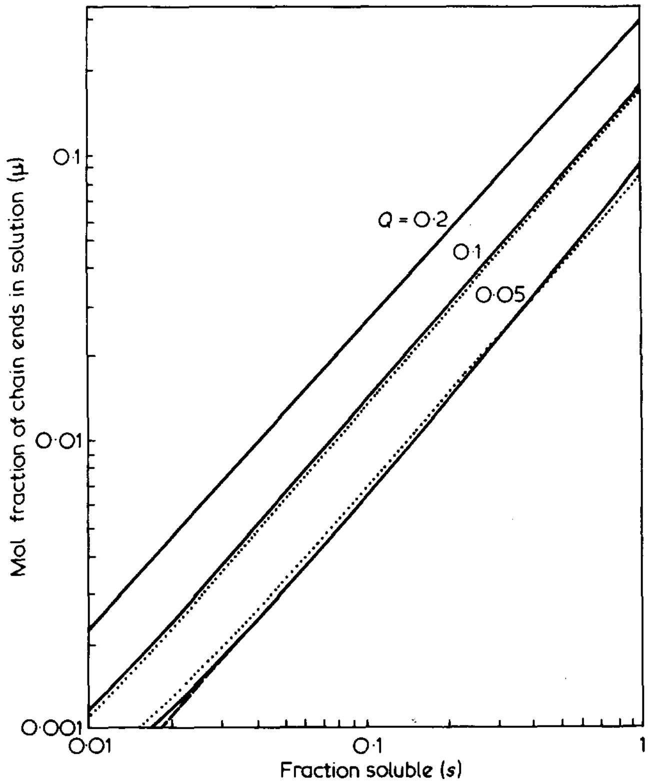

Figure 2 Relationship between solubility, *S*, and the mole fraction of broken chain ends appearing in the soluble portion, *μ*, for three levels of crosslink density: *Q* = 0.2, 0.1 and 0.05. The variation with chain length at each crosslink density is indicated for three initial chain lengths: *U* = ∞ (——), *U* = 100 (– – – –), and *U* = 50 (· · · ·)

the sum of these contributions over all values of the crosslink index c. The total number of chain ends (twice the number of molecules) appearing in the soluble fraction is therefore:

$$v = 2\sum_{u=1}^{U}\sum_{c=0}^{u} n_c S_0{}^c \tag{12}$$

Introducing equation 3 for $n_c(u)$, we have:

$$v = 2\sum_{u=1}^{U} N(u)\sum_{c=0}^{u}(QS_0)^c(1-Q)^{u-c}u!\Big/(u-c)!c! \tag{13}$$

The second sum is the binomial expansion of $(1-Q+QS_0)^u$, which, when substituted, yields:

$$v = 2\sum_{u=1}^{U} N(u)(1-Q+QS_0)^u \tag{14}$$

Now, substituting equations 1 and 2 for $N(u)$ and $N(U)$, we find:

$$v = \frac{2A_0P}{1-P}\sum_{u=1}^{U} a^u[2+(U-1-u)P] + \frac{2A_0}{1-P}a^U \tag{15}$$

where a is given by equation 11.

For the rest of this article, the actual number of chain ends, v, will be replaced by its fraction of the total number possible after complete intermonomer chain breakage. The total number of chain ends possible is, of course, twice the number of monomers present, or $2A_1$ $(=2A_0U)$. The fraction $v/2A_1$ is termed μ. Thus, if the sum in equation 15 is evaluated, terms collected, and the result divided by $2A_0U$, we finally have:

$$\mu = \frac{1}{U(1-P)}\left\{\frac{aP}{(1-a)^2}[2-2a-P)(1-a^{U-1}) + P(U-1)(1-a)] + a^U\right\} \tag{16}$$

The quantity μ can be thought of most simply as the mole fraction of single endgroups in the soluble portion out of the total number of moles of monomers in the original sample.

Figure 2 shows μ plotted against S for four levels of crosslink density, Q, each occurring in polymers of three different initial chain lengths, U. These curves were constructed in the following way. For each case of a particular Q and U, a series of P values was chosen that would produce the complete range of solubilization of the degrading polymer; that is, from the condition of no degradation ($P=0$) to the condition of complete solubility, where $S=S_0=1$. For each P chosen, equation 10 was solved for S_0 by iteration, using a simple computer program. Once S_0 was found, S could be calculated from equation 9, and μ from equation 16.

Because of the way the theoretical model of this paper has been constructed, i.e., by crosslinking uniform chains up to a certain crosslink density, a small correction was applied to those values of μ and S calculated for low initial chain lengths. This correction is needed because of the uncrosslinked chains that would be leached out were a suitable swelling solvent to be applied before the degradation step. In the experimental situation in which an unknown crosslink density is to be investigated, it is assumed that all possible leachable material is removed before degradation is initiated, so no such correction would be needed in practice. For the theoretical expressions, the correction is straightforward. Designating the fraction of original polymer that remains soluble after crosslinking as S^0, the theoretical soluble fraction calculated from P by the above method as S, and the fraction actually solubilized by subsequent degradation as S', we will then have, by material balance,

$$S' = \frac{S-S^0}{1-S^0} \tag{17}$$

and similarly for μ

$$\mu' = \mu - \mu^0 \tag{18}$$

S^0 is found by first iteratively solving equation 10 for S_0^0 with $P=0$:

$$S_0^0 = a^{U-1} = (1-Q+QS_0^0)^{U-1} \tag{19}$$

and using this result in equation 9:

$$S^0 = S_0^0(1-Q+QS_0^0) \tag{20}$$

Similarly, μ^0 is found from equation 16, with $P=0$:

$$\mu^0 = a^U/U \tag{21}$$

Table 1 Theoretical error* between approximate and exact expressions for Q

S	μ	Q_∞	% Error between Q_∞ and Q_{exact}		
			$U = 200$	$U = 100$	$U = 50$
0.1	0.005	0.0385	−3.0	−2.8	−2.4
	0.01	0.0779	−0.9	−2.9	−3.3
	0.025	0.2131	−0.1	−0.4	−1.6
0.5	0.025	0.0303	−1.5	−4.4	−17.7
	0.075	0.0976	−0.2	−0.7	−2.4
	0.15	0.2214	0.0	−0.1	−0.6
0.9	0.05	0.0301	−1.0	−4.8	−20.3
	0.15	0.1015	0.1	−0.4	−1.6
	0.25	0.1934	0.0	−0.1	−0.5

* 'Error' is used here to designate the numeric difference between exact and approximate solutions, rather than in its statistical sense

The curves of *Figure 2*, which now correspond to the experimental situation, were thus plotted from the corrected S' and μ' values. No correction is needed for $U = \infty$, and, in fact, the correction for $U > 100$ is essentially negligible, except at very low crosslink densities.

Useful approximations

It is clear from *Figure 2* that, except for polymers of short chain lengths or very low crosslink density, relatively little error is involved in using the points calculated for $U = \infty$ in place of those calculated for finite chain lengths. Aside from the fact that U is likely to be unknown, a considerable saving of effort is realized by use of the $U = \infty$ expressions, which are of much simpler algebraic form.

For large U, equation 10 approaches the form:

$$S_0 = \left(\frac{P}{1-a}\right)^2 \tag{22}$$

Similarly, equation 16 becomes:

$$\mu = S(1-a) \tag{23}$$

These two expressions can be combined with equation 11 to give, after eliminating P and a:

$$S_0 = \left(\frac{\sqrt{1+\frac{4}{\mu}\left(\frac{S}{\mu}-1\right)}-1}{2\left(\frac{1}{\mu}-\frac{1}{S}\right)}\right)^2 \tag{24}$$

and from equation 9:

$$Q = \frac{S_0 - S}{S_0(1-S_0)} \tag{25}$$

Equations 24 and 25 can be used with experimentally determined values of μ and S to give a direct estimate of Q.

In comparison with Q values calculated 'exactly' from equations 9, 10, 11 and 16, results from using equations 24 and 25 will probably be slightly low. *Table 1* gives an idea of the errors involved over a wide range of Q values and solubilities, where the term 'error' is used in the sense of a deviation between exact and approximate solutions. The errors are calculated as a percentage difference between the 'exact' value of Q calculated for a particular chain length, and the approximate value calculated using an infinite chain length. As seen in the Table, the error incident to using the infinite chain length approximation becomes greater toward lower crosslink densities and shorter chain lengths. As a guide to the kinds of errors that might be expected, the curves of *Figure 3* are of interest. These are contours, calculated for equal error between $Q(U = \infty)$ and Q. The cluster of curves, all for 5% error, also show the effect of extent of solubilization. In general, for a given crosslink density and chain length, the error of using the $Q(U = \infty)$ approximation will be lessened by keeping the amount solubilized as low as is experimentally convenient and precise. No account has been taken in *Figure 3* of actual experimental error, which is bound to increase as the amounts of material handled become smaller. To stay within the indicated error limits, the values of Q and U for the experimental situation should lie above the appropriate line. As a rough guide, the error incurred by using $Q(U = \infty)$ will be 5% or less if the product QU is 2 or more. Since a gel will not form unless $QU > 1$, the region of high error is not extensive.

If some idea of the predominant molecular weight of the crosslinked chains is available, it is of course not difficult to use the exact relations (equations 9, 10, 11 and 16) to find Q. However, even without this knowledge, which is especially difficult to obtain where a distribution of molecular weights is involved, the relative independence of Q on chain length implies that the foregoing approach can usually be used to estimate crosslink density independently of secondary correlations.

Simultaneous breakage of main chains and crosslinks

For some crosslinked polymers, it may be difficult to find a degradation procedure that affects only main chain bonds rather than crosslinks. In such instances, extrapolation of experimental results back to zero degradation time should yield a satisfactory estimate for the initial Q,

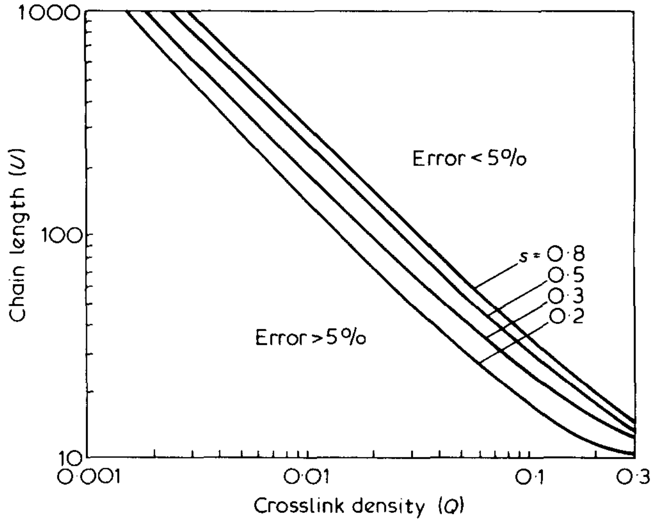

Figure 3 Contours for errors incurred by using relations derived for $U = \infty$ in situations where U is finite. Each of the cluster of contours is drawn for 5% error at four levels of solubilization: S = 0.8, 0.5, 0.3, and 0.2. If a given pair of U, Q values falls below the appropriate contour line for the experimental value of S, then the error in using the approximation will be greater than 5%

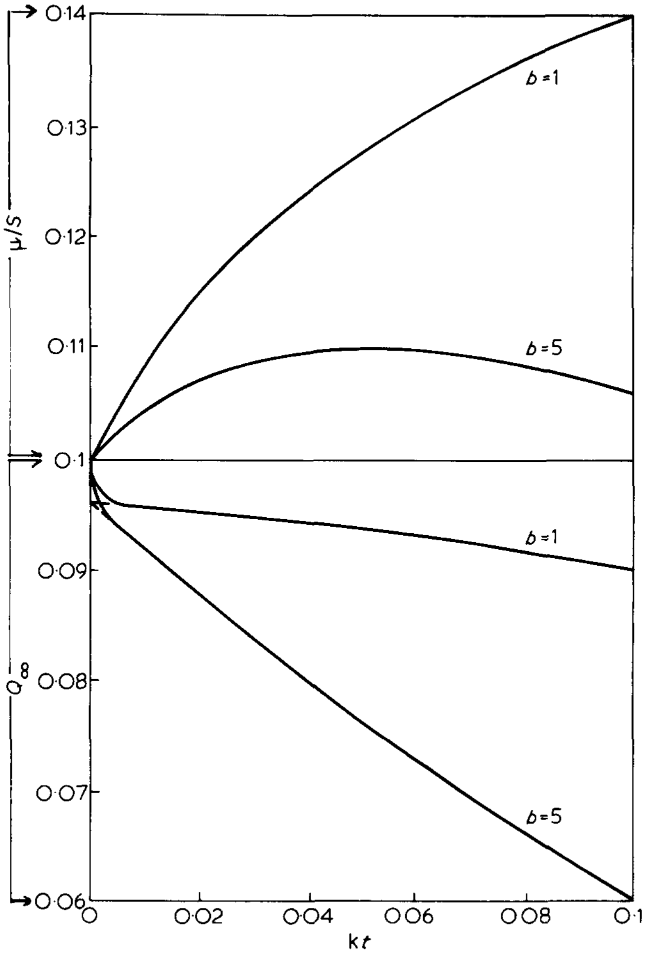

Figure 4 Illustrative examples of the dependence of μ/S and Q on the time of degradation, for experiments in which both crosslinks and main chain bonds are broken simultaneously. The upper two curves are plots of μ/S *versus* kt, for two relative rates of first order crosslink scission. For $b = 1$, the rate constants for main chain breakage and crosslink scission are equal; for $b = 5$, k for crosslink scission, is five times that for main chain breakage. The lower two curves are also for $b = 1$ and $b = 5$, but showing Q *versus* kt. Q is computed from Equations 24 and 25 of the text, derived for $U = \infty$

provided the crosslink density of the sample is reasonaly homogeneous. The quantities to be extrapolated are flexible. An idea of expected behaviour can be obtained from *Figure 4*, which shows the ratio μ/S and $Q(U=\infty)$ plotted for two hypothetical degradation examples. Both P and Q are assumed to follow simple first order kinetics:

$$P = 1 - \exp(-kt) \tag{26}$$

$$Q = Q_0 \exp(-bkt) \tag{27}$$

In these expressions Q_0 is the initial crosslink density before any degradation has occurred, and b is a multiplicative constant that permits varying the relative rates of degradation of P and Q. The abscissa plotted in *Figure 4* is kt. Values of b of 1 and 5 were chosen to represent crosslink scission rates equal to and five times the main chain cleavage rates, respectively. Q_0 was taken as 0.1, and U as 100. Values of S and μ to correspond to the experimental observables were calculated from the 'exact' relations: S calculated iteratively from equations 9, 10 and 11, and μ directly from equation 16. Values of Q for $U=\infty$ were calculated from these 'experimental' values of S and μ using equations 24 and 25. As seen in *Figure 4*, either μ/S or $Q(U=\infty)$ could be used for extrapolation back to zero time. Although μ/S shows more curvature, it extrapolates to the correct value of Q_0. However, the relative linearity of the Q curves may permit less uncertainty in the estimation of Q_0 if data are not available at short times.

Two or more components

The preceding theory has been derived for a single homogeneously crosslinked component. If two or more components are present, or if the crosslinking is not distributed uniformly, then the relationship between solubility and end group concentration will be more complex, but still derivable in a straightforward way from the single component theory. For two components:

$$\bar{S} = S_1 X_1 + S_2 X_2 \tag{28}$$

and

$$\bar{\mu} = \mu_1 X_1 + \mu_2 X_2 \tag{29}$$

where $\bar{S}$ and $\bar{\mu}$ represent the observed solubility and end group concentration for weight fractions X_1 and X_2 of components 1 and 2 which separately would have solubilities S_1 and S_2 and end group concentrations μ_1 and μ_2, respectively. Unless detailed information is available about the solubilization behaviour of the individual components, the data can be analysed by assuming kinetic relationships for the extents of main chain cleavage, P_1 and P_2. The simplest assumption is first order degradation:

$$P_1 = 1 - \exp(-k_1 t) \tag{30}$$

$$P_2 = 1 - \exp(-k_2 t) \tag{31}$$

With knowledge of the crosslink densities of the two components, usually by assumption, equations 11 and 22 can be solved iteratively for S_0, using P values from equations 30 and 31. Only relative values of k_1 and k_2 need be used, since P does not appear explicitly in the results. Once S_0 has been calculated for each component, corresponding S and μ values are determined by equations 9 and 23, and finally $\bar{S}$ and $\bar{\mu}$ can be calculated from equations 28 and 29 above. The process is essentially one of curve fitting to an experimental S–μ curve by repeated estimate of the various unknowns.

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