Chemical modification of polyolefins by free radical mechanisms: a modelling and experimental study of simultaneous random scission, branching and crosslinking

P. E. Gloor*, Y. Tang, A. E. Kostanska and A. E. Hamielec†
McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada
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The chemical modification of polyolefins in the melt, using free radical mechanisms suitable for reactive extrusion, was studied. An algorithm to approximate the solution to an equation for simultaneous random scission and crosslinking[1] is presented. This solution is compared to the classical two-step solutions of Saito[2-5], Flory[6] and Charlesby–Pinner[7], showing significant deviations for the simultaneous random scission and crosslinking case. Suggestions to improve further the scission term of this equation are presented. Experiments were performed using high density polyethylene and peroxides in a minitruder and in small ampoule reactors. Gel fractions, thermal properties and molecular weights were measured. The heats of transition and melting temperatures as measured by differential scanning calorimetry were found to decrease with increasing peroxide level but were independent of reaction temperature. A pure random crosslinking model was found to fit adequately the gel fraction data.

(Keywords: random scission; random crosslinking; reactive processing)

INTRODUCTION

Reactive processing can potentially allow cost-effective conversion of lower cost commodity polymers, such as the polyolefins, to higher priced speciality polymers. Extruders are used because of their low capital costs and high flexibility. Speciality polymers are produced by modifying the molecular weight (either a reduction in the averages and polydispersity in the case of controlled rheology polypropylene, or a build-up of molecular weight in the case of polyethylene) or by grafting functional groups onto the polymer backbone. This grafting process can be accompanied by other changes in the structure and properties of the basic polymer[8].

Moreover, with increased awareness of our extravagant, throwaway lifestyle, and its impact on our environment, recycling of polymers is becoming a highly relevant topic for discussion and research. Plastics with different compositions are difficult to sort and separate, and do not, in general, make blends with good mechanical properties without some form of compatibilization. Reactive processing offers techniques to make compatible blends or alloys[9]. Many reactive-processing techniques involve the introduction of an initiator into the polymer melt, which produces free radicals to commence the modification of the molecular structure of the polymer. However, these free radicals also initiate a host of reactions that may produce other, less desirable modifications. In general, scission, grafting, branching and crosslinking may all occur simultaneously. The difficulty is to promote the desired reactions while suppressing the undesired. To date, much of the work in reactive processing has been of the try it and see approach, and several useful products and techniques have been developed. More fundamental studies are certainly less abundant. These studies may be more difficult, but have greater potential to allow for conceptual leaps than do the more empirical approaches. The optimization process can be facilitated by the use of mathematical models to relate the extent of the reaction, and therefore also the final properties of the polymer, to the processing conditions and the initial polymer properties.

This paper deals with the development of mathematical models to relate the molecular modifications scission, branching and crosslinking to process conditions. The models, based upon generally accepted kinetic mechanisms and certain assumptions about the nature of simultaneous random scission and crosslinking, can predict the molecular weight averages, degrees of crosslinking, scission and branching, and the amounts of sol and gel.

Numerical algorithms to solve the model equations have been developed. One can specify any arbitrary initial molecular weight distribution (e.g. as measured by gel permeation chromatography), the free radical initiator concentration, and the kinetic parameters for scission and termination, and solve for the entire molecular weight distribution, before and after the gel point, as well as the gel fraction and branching frequencies.

The models have unknown parameters which must be estimated by matching the predictions to experiments. In

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* Current address: S. C. Johnson Wax, 1525 Howe Street, Racine, WI 53403-5011, USA

† To whom correspondence should be addressed

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this investigation, experiments were performed with high density polyethylene (HDPE) and peroxides in an extruder and in ampoules. The polymer was analysed for molecular weight and gel fraction. These results were then used to estimate the model parameters.

Before proceeding with a discussion of the present work, some relevant publications will be discussed.

LITERATURE REVIEW

In this section, we briefly review the appropriate literature pertaining to the chemical modification of the polyolefins, emphasizing polyethylene. More thorough reviews have been written by Hamielec *et al.*[1] and Gloor[10]. First, we shall discuss the chemistry of the system, the attempts to model the chemical kinetics, and finally experimental work that has been reported.

The chemistry

In the free radical modification of polymers, a source of energetic radicals is needed, and usually chemical initiators are used. These may be peroxides or azo compounds. These initiators decompose at the reaction temperature to produce free radicals. The initiator radicals can then (i) transfer their reactivity to a polymer chain by abstracting a hydrogen and producing a backbone radical; (ii) terminate with another radical; (iii) react with an unsaturation in the polymer chain to produce an allylic chain-end radical[11,12]; (iv) react with an additive[13,14] or impurity that may be present; or (v) recombine to form some possibly inert product.

Consider the backbone radical and its formation. First, the initiator radical must be sufficiently energetic to abstract a hydrogen. Not all initiator radicals are suitable[15,16]. Secondly, the polymer must have an abstractable hydrogen available, and not all hydrogens are equally labile. The backbone radical will be either secondary or tertiary depending upon whether a branch is present or not. The radical then has a variety of fates. It can (i) undergo β scission to form a chain-end radical and a dead polymer with a terminal double bond; (ii) terminate by combination with another backbone radical, leading to crosslinking and the formation of X branches (tetrafunctional branches); (iii) terminate by combination with a chain-end radical, leading to a Y branch (trifunctional branch); (iv) terminate by disproportionation, leading to an unsaturation; (v) terminate with a primary radical; (vi) transfer its reactivity to another chain; or (vii) react with an additive or impurity, leading to grafting. Polypropylene tends to undergo scission almost exclusively, since most of the backbone radicals formed are tertiary and break easily. Polyethylene homopolymer tends to crosslink, but scission has been observed[8], especially if branches are present. Polypropylene can be made to crosslink at high peroxide concentrations[15] or by using additives that react with the backbone radical before it has a chance to undergo scission[17]. Grafted additives may have radical centres that can terminate by combination with backbone radicals to produce crosslinks. Propagation of the additive species is also a possibility, producing a homopolymer grafted onto the polyolefin backbone.

When sufficient crosslinking has occurred, a three-dimensional network of polymer (gel) is formed that is insoluble in even the best solvents for the polymer. The remaining linear and branched, but still soluble, polymer is defined as the sol. The point at which the first gel appears is the gel point. On the other hand, if only scission occurs, the molecular weight averages decrease, and the width of the distribution changes, approaching $M_w/M_n = 2$ in the limit.

Terminal radicals, produced either by scission or reaction with a terminal unsaturation, can terminate with each other to give chain extension. If one of the terminal radicals is allylic, a backbone unsaturation is produced, probably *trans*-vinyl unsaturation[18]. Scission of radicals at branch points can lead to vinylidene unsaturation[18].

Mathematical modelling

Given this set of chemical reactions, it is possible to develop models to calculate the molecular weights of the polymer being produced. The kinetic modelling methodology is to make mass balances on polymer chains of length r as functions of time and initiator concentrations. Balances are also needed for all the radical species, and, using the stationary-state hypothesis, algebraic equations result. The number of balance equations on a polymer is large (one for each chain length), but it is often possible to (i) solve for about 100 different chain lengths to describe the molecular weight distribution, or (ii) group the mass balances together to yield only the averages. Using this approach, we can make some assumptions about the system (neglecting some reactions) and develop simpler models for specific cases.

Pure scission

Let us now consider the case of pure scission; that is, no crosslinking or grafting. It is possible to postulate that the scission reaction could occur preferentially at the centre, at the ends, or randomly along the chain. For the case where the polymer undergoes only random scission, one can derive a model that gives the entire molecular weight distribution as a function of the degree of scission. This was done by Saito[2–5] for the case of irradiated polymers, but it is certainly applicable for the case of the chemical modification of polypropylene[19]

$$w(r, p) = \left[w(r, 0) + pr \int_r^\infty \frac{2 + p(s - r)}{s} w(s, 0)\, \mathrm{d}s \right] \exp(-pr) \tag{1}$$

where $w(r, p)$ is the weight fraction of polymer of chain length r at degree of scission p, and s also denotes chain length. The degree of scission is the fraction of all repeat units in the polymer that have undergone scission, in this case pure scission, and will be a function of the number of initiator molecules that have decomposed up to this time; thus, there is a relationship between p and reaction time. No assumptions about the initial molecular weight distribution have been made, other than chains are linear.

The model of Suwanda *et al.*[20,21] and Lew *et al.*[22] must be equivalent to Saito's equation since the same chemical reactions are considered and the derivation follows the same path, but the equation is simply in a different form when employed by these authors.

One could use the method of moments to find the molecular weight averages instead of the whole distribution. This was the approach taken by Tzoganakis *et al.*[23,24] and Hamielec *et al.*[1,25], again assuming random scission. However, the moment equations are not closed.

Lower moments are functions of higher moments. Tzoganakis *et al.*[23] and Hamielec *et al.*[25] addressed this problem with different empirical closure equations, and these give rise to the two different models. Tzoganakis *et al.*[23] attempted to fit the initial distribution using a closure rule based on that of Hulburt and Katz[26], whereas Hamielec *et al.*[25] tried to fit the final distribution, assuming it to be the most probable distribution. Zhu[27] addressed this moment closure problem in a more general manner, showing that the closure rule changes with the degree of scission and depends upon the initial molecular weight distribution. The moment closure problem is avoided if one knows the initial molecular weight distribution and uses equation (1).

Ziff and McGrady[28] developed a similar equation while removing the assumption that scission is random. Ballauff and Wolf[29] used a similar approach and found that the model reduces to a set of linear algebraic equations. Monte Carlo-type simulations have also been done by Guaita *et al.*[30] to study the effect of non-random scission to very high degrees of scission. However, it should be pointed out that Triacca *et al.*[19] used equation (1) and found that the random scission assumption appears to be valid for peroxide-induced modification of polypropylene. Non-random scission may be more significant for shear-induced scission.

Pure random crosslinking

For the case of pure random crosslinking (transfer to polymer and termination by combination), one can follow the same approach and perform mass balances on a polymer of chain length r. In doing so, and making the stationary-state hypothesis for radicals and assuming that all radicals terminate with the same rate constant, one can find[1,5,31]

$$\frac{\mathrm{d}w(r,x)}{\mathrm{d}x} = -rw(r,x) + \frac{r}{2}\int_0^r w(s,x)w(r-s,x)\,\mathrm{d}s \qquad (2)$$

and now x is the degree of crosslinking, i.e. the fraction of all repeat units that have a crosslink. We define a crosslink as a branch point, so when two chains are tied together, two crosslinks are needed. The general analytical solution to this equation has not yet been found, and a numerical solution is required. Attempts have been made[32] with moderate success, but a useful numerical solution is presented in this report. It should be noted that we performed only a mass balance on the sol polymer, and thus $w(r)$ will always include only the sol. But the reactions with gel polymer are included. Thus $\int_0^\infty w(r)\,\mathrm{d}r$ is the mass fraction of sol and will equal 1 before the gel point and then fall, as sol is consumed by gel. With this approach the equations show no discontinuity at the gel point.

An alternative approach again is to use the method of moments[1]; however, the moment closure problem occurs after the gel point.

Flory[6] developed a statistical expression to relate the sol fraction s to the degree of crosslinking and the initial molecular weight distribution. (The primary chains in Flory's analysis relate to the initial molecular weight distribution before chemical modification.) The expression is

$$s = \sum_{r=1}^{\infty} w(r,0)[1-x(1-s)]^r \qquad (3)$$

Simultaneous random scission and crosslinking

Now we must address an even more interesting and difficult problem where both random scission and crosslinking are important and occur simultaneously. An approach[2–5] to solving this problem is to consider modification to occur in two steps: random scission followed by random crosslinking. In this manner we can use Saito's scission equation (equation (1)) to determine the molecular weight distribution after the desired degree of scission p. Then we can use the pure random crosslinking equation (equation (2)) on the degraded polymer to determine the new molecular weight distribution after the desired amount of crosslinking x. The total degree of modification is $z = x + p$. If the initial distribution is linear and most probable and the ratio of scission to crosslinking is constant, then this approach leads to the Charlesby–Pinner equation[7]

$$s + s^{1/2} = \frac{2}{xr_{w0}} + \frac{p}{x} \qquad (4)$$

where s is the sol fraction. This equation is widely used (with some slight modifications), even for polymers with initial distributions much broader than random; for example, it has been used by Kwei *et al.*[8] and Capla and Borsig[33], and in a host of papers on irradiation of polyethylene. In sol–gel measurements, the measured quantity $s + s^{1/2}$ is plotted *versus* the reciprocal of the peroxide concentration and a straight line is drawn through the points. The intercept (at infinite peroxide or radiation dose level) gives the ratio of scission to crosslinking p/x. It should be noted that since we expect crosslinking to be a second-order reaction with respect to radical concentration, and scission to be first order, the ratio of scission to crosslinking will change with initial peroxide concentration and as the initiator is depleted (see Appendix).

There is really no reason why the initial molecular weight distribution needs to be random, because one can use any initial distribution in both the scission and crosslinking equation. The assumption of constant scission to crosslinking ratio can also be relaxed. Numerical solutions are needed since the Charlesby–Pinner equation is no longer valid, but still the two-step approach is solvable and the FORTRAN program '2step' was created in this work for this purpose. The real limitations of the Charlesby–Pinner equation lie in the assumptions of (i) independent crosslinking and scission (in two steps); (ii) constant p/x; and (iii) initially linear polymer. Note that there are some other concerns, specifically related to radiation crosslinking, which have been addressed in Babic and Stannett[34].

The problem with the two-step process is simply that scission and crosslinking occur simultaneously, not serially. In fact, for peroxide-induced modification, where the peroxide level will fall with time, one should expect more crosslinking to occur initially, and scission ultimately, and thus p/x will not be constant. Higher peroxide levels enhance crosslinking over scission. Moreover, scission will produce terminal radicals and these radicals could combine with backbone radicals to form Y branches. The two-step process precludes the formation of Y branches, allowing only X branches. Both Y and X branches are observed in practice[35].

Many of the commercial polymers that are chemically modified are not linear (for example, low density

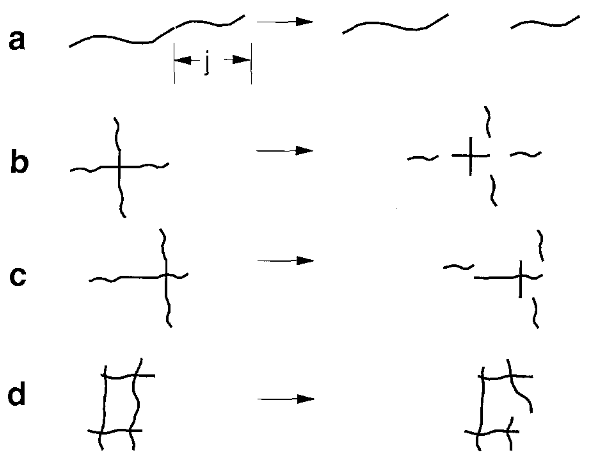


Figure 1 Scission of several branched molecules: (a) a linear molecule; (b) the four ways to make linear chains *j* units long; (c) the three ways to make linear chains *j* units long; (d) scission that does not lead to a new polymer molecule

polyethylene). What kind of chains are produced when these branched molecules undergo scission? This is a key question and at the heart of the problem of modelling simultaneous scission and crosslinking. Consider a linear chain of length r (*Figure 1*). We can count units from one end to find the jth unit. If the chain undergoes scission at the jth unit the products are two linear chains, one of length j, and one $r-j$. We know that we can always make a chain of length j if $r>j$ and it does not matter from which end of the chain we start to count – a cut at the jth unit always makes the same products. However, now consider a tetrafunctionally branched chain. We wish to cut it at the jth unit, but how do we find the jth unit? If we start to count from one end, and count units towards the centre, what do we do at the branch? Suppose that all the arms of the molecule are longer than j units, then we can produce a linear polymer j units long by cutting the jth unit measured from any of the ends, i.e. four different ways. If only three of the four arms are longer than j, we can only make a linear polymer of length j in three ways, and so on. The possible ways to cut a chain, to produce the desired products, depend upon the structure of the branching, and since we have a vast number of possible configurations for the branched polymer, the problem is extremely complicated. It is even possible to cut a unit and not change the total number of molecules in the system.

Zhu[27] (see also Hamielec *et al.*[25]) developed an integrodifferential equation, by extending Saito's work, that accounts for simultaneous crosslinking, scission and grafting, including the production of Y branches

$$\frac{1}{r}\frac{\partial w(r,z)}{dz} = -w(r,z) + 2\alpha\int_r^\infty \frac{w(s,z)}{s}\,ds + \frac{\beta_4}{2}\int_0^r [w(s,z)w(r-s,z)]\,ds + \beta_3\int_0^r\left[w(s,z)\int_{r-s}^\infty \frac{w(m,z)}{m}\,dm\right]ds + \frac{\beta_2}{2}\int_0^r\left[\int_s^\infty \frac{w(m,z)}{m}\,dm\int_{r-s}^\infty \frac{w(m,z)}{m}\,dm\right]ds \tag{5}$$

where z is the degree of modification and α is a group of kinetic parameters related to scission. β_4, β_3 and β_2 are groups of kinetic parameters related to the formation of X branches, Y branches and end linkages, respectively

$$\beta_4 = \frac{k_{tc}R_b^2}{k_\beta R_b + k_{tc}R_b^2 + k_{tc}R_bR_e}$$

$$\beta_3 = \frac{k_{tc}R_bR_e}{k_\beta R_b + k_{tc}R_b^2 + k_{tc}R_bR_e}$$

$$\beta_2 = \frac{k_{tc}R_e^2}{k_\beta R_b + k_{tc}R_b^2 + k_{tc}R_bR_e}$$

$$\alpha = \frac{2k_\beta R_b - k_{tc}R_e^2 - k_{tc}R_eR_b}{2(k_\beta R_b + k_{tc}R_b^2 + k_{tc}R_bR_e)}$$

R_b and R_e are backbone and chain-end radical concentrations, respectively, and are given by using the stationary-state hypothesis for all radical species

$$R_b = \frac{k_{fp}Q_1R_0}{k_\beta + k_tR_t}$$

$$R_e = \frac{k_\beta R_b}{k_tR_t}$$

$$R_t = \left(\frac{fk_dI}{k_t}\right)^{1/2}$$

$$R_0 = \frac{fk_dI}{k_{fp}Q_1 + k_tR_t}$$

R_t and R_0 are the total radical concentration and the concentration of radicals on initiator fragments, respectively. Here it is assumed, in α, that there are two ways to cut a chain to make the desired products. This is exactly correct if the chains are linear. While this assumption is not ideal, it should be better than assuming the two-step model of Saito, since this model can predict the formation of Y branches, whereas Saito's cannot. However, some modifications to this equation yield an equation of the same form that can be solved using the same algorithm as described later in this paper.

Statistical approaches have been put forward by Shy and Eichinger[36], Galiatsatos and Eichinger[37] and Demjanenko and Dusek[38], the last from the theory of branching processes based upon the graph model[39–42].

Experimental and analytical

Several studies on the free radical crosslinking of polyethylene (and copolymers) have been done, including studies of high density polymers, low density polymers, different molecular weights, initiators, temperatures and reaction times, reactions with and without additives, in extruders, batch mixers, moulds, test tubes and thin films. However, for most studies at least one of the following is true.

1. The initial polymer is not completely characterized with respect to molecular weight distribution, copolymer composition, branching and levels of unsaturation.
2. The temperature is not well defined over the entire reaction period. In extruders, and to a lesser extent in batch mixers, the temperature is not very well known for the whole polymer sample. For hot-pressed moulds, test tubes and thin films the heat-up time to reaction temperature may be significant, and is not

often reported. Moreoever, this temperature–time profile may not be reproducible from one experiment to another.

3. The validity of the method of analysis may be suspect, for example using gel permeation chromatography (g.p.c.) to measure quantitatively the molecular weight distribution of the branched polymer.

MATHEMATICAL MODELLING

Of the chemical reactions listed in the previous section, the subset that includes initiator decomposition, radical attack of backbone hydrogen atoms, scission of the chains and termination by combination (*Figure 2*) is chosen. One can perform population balances on chains of various lengths[27] and derive expressions for the molecular weight distribution as a function of degree of modification. This gives rise to equation (5). The degree of modification can be related to the peroxide concentration and the reaction time. The classical solution to this problem has been to use the two-step approach (Saito and Flory). In this work we have developed a numerical solution to equation (5). In the next sections we shall discuss some of the inadequacies of the two-step approach and the numerical solution to equation (5), and present some comparisons between the two approaches.

Some discussion of the two-step approach

Software entitled '2step' was developed to use the two-step approach to find the gel fraction, and for special cases the molecular weight distribution and the molecular weight averages, for a given initial distribution and peroxide level. This model solves differential equations for the initiator concentration, the degree of scission and the degree of crosslinking. Then, given the degrees of scission and crosslinking, Saito's equation (1) for pure random scission and Flory's equation (3) for pure random crosslinking are used to find the gel fractions. One obtains the entire molecular weight distribution for pure random scission. The averages in the pregel region can be predicted. The averages after the gel point can be calculated if we start with the most probable distribution by using equations (43), (44), (47), (48), (49) and (50) of Hamielec *et al.*[1], which were developed from equation (2).

The Charlesby–Pinner equation has been widely used, for example Kwei *et al.*[8], to find the ratio of scission to crosslinking for polyolefins. Let us take a look at how valid this approach is for chemically induced modification. The assumptions of the Charlesby–Pinner equation are that (i) the two-step solution is valid for simultaneous random scission and crosslinking; (ii) the initial distribution is the most probable distribution; (iii) the ratio of scission to crosslinking (p/x) is constant; and (iv) there are random scission and crosslinking. The Charlesby–Pinner equation is used by plotting $s+s^{1/2}$ *versus* the reciprocal of the crosslink density, drawing a straight line through the data, and extrapolating to infinite degrees of crosslinking to find the ratio of scission to crosslinking. *Figure 3* shows the predicted curves for various conditions on a Charlesby–Pinner plot.

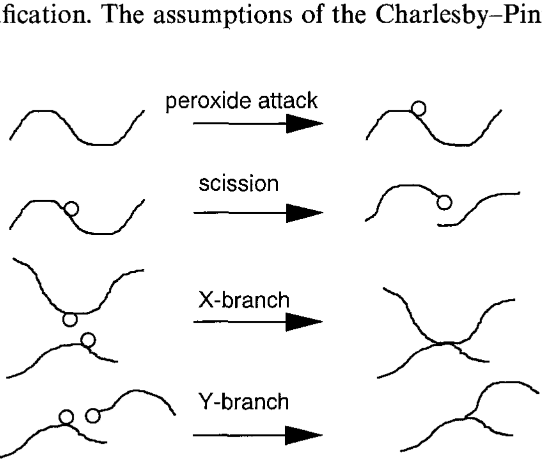


Figure 2 The chemical reactions that modify the polymer molecular structure during simultaneous random scission and crosslinking

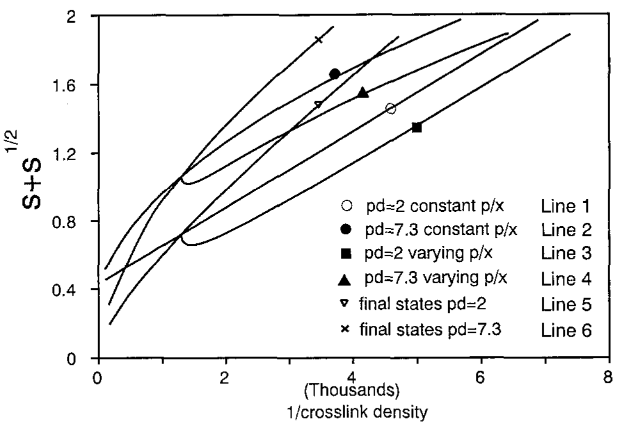


Figure 3 Charlesby–Pinner plots for several two-step solutions: (1) most probable initial distribution and p/x constant; (2) broad distribution and p/x constant; (3) most probable distribution and p/x not constant; (4) broad distribution and p/x not constant; (5) the final values due to different initial peroxide concentrations for the most probable distribution; (6) the final values due to different initial peroxide concentrations for a broad initial distribution

Lines 1 and 2 in *Figure 3* demonstrate the effect of the initial molecular weight distribution. The p/x ratio was held constant at $p/x=0.43$ (by artificially forcing the initiator concentration to be constant). The quantity $s+s^{1/2}$ is calculated as the peroxide causes crosslinking. Line 1 is calculated using the most probable distribution as the initial distribution and is a straight line with intercept equal to 0.43, as expected. Line 2 uses a broader distribution with identical M_w. This line is not straight but curved. However, the intercept will still be equal to 0.43. Thus, fitting a straight line to experimental data where the initial distribution is not the most probable can result in serious error. A more realistic case is given by lines 3 and 4, where the initiator concentration is allowed to fall with reaction, and the ratio p/x is not constant. Line 3 uses a most probable distribution and line 4 uses the broader distribution. The final value of p/x was arbitrarily set to be 0.43 by varying the scission and crosslinking parameters. The initial p/x will be smaller. Notice the trend at higher values of crosslink density – the quantity $s+s^{1/2}$ actually increases with increasing crosslinking. This is because the ratio p/x is increasing and the calculated gel level falls. Lines 1 to 4 all have the same initial peroxide concentration. Lines 5 and 6 are calculated by varying the initial peroxide concentration and calculating the $s+s^{1/2}$ when all the peroxide is consumed. This is usually how the experiments are performed when experimental Charlesby–Pinner plots are made. The ratio p/x is allowed to vary but the scission and crosslinking parameters are set to the identical values as for lines 3 and 4. Lines 5 and 6 do not follow any of the other lines. These lines are closer to being linear, except that the intercept is now not equal to 0.43 but will tend to zero as I_0 increases (see Appendix). These observations lead us to the conclusion that using Charlesby–Pinner plots to find the ratio of scission to crosslinking for peroxide-induced modifications is not valid.

The classical approach assumes that the polymer undergoes the entire amount of scission and then the entire amount of crosslinking. An improvement could be to use a two-step model where the polymer undergoes a small fraction of the total scission, then a small fraction of the total crosslinking. This slightly modified molecular weight distribution is then subjected to an additional small amount of scission followed by additional crosslinking. This process is continued until the desired amounts of scission and crosslinking are reached[43]. This approach still neglects end linking and the formation of Y branches, and requires a numerical solution for the crosslinking step, but may give better results than the classical two-step approach.

Numerical solution of the model equations

It is of interest to solve an equation of the form derived by Zhu[27] for simultaneous random scission and crosslinking (equation (5)). Triacca *et al.*[32] attempted to solve this equation by selecting several chain lengths (200 or so) and solving the resulting differential equations using the package LSODE[44]. The integrals were evaluated using the trapezoid rule. The solution for the pure random crosslinking case was found up to about 80% of the way to the gel point before excessive numerical errors and computational time were encountered.

The following is a more efficient algorithm. First, the molecular weight distribution is discretized, roughly equally spaced on a natural log of chain length scale. About 50 to 100 nodes are used and each node becomes a differential equation to be solved (see *Figure 4*) with either time or the degree of modification as the independent variable. The equation is transformed using $W(r)\,\mathrm{d}r = W'(x)\,\mathrm{d}x$, where $x = \ln r$, to improve the accuracy of the solution, especially that of the integrals. The molecular weight distribution is then interpolated using a natural cubic spline. This provides a smooth interpolation, without excessive waviness, and allows one to solve the integrals in a more efficient manner.

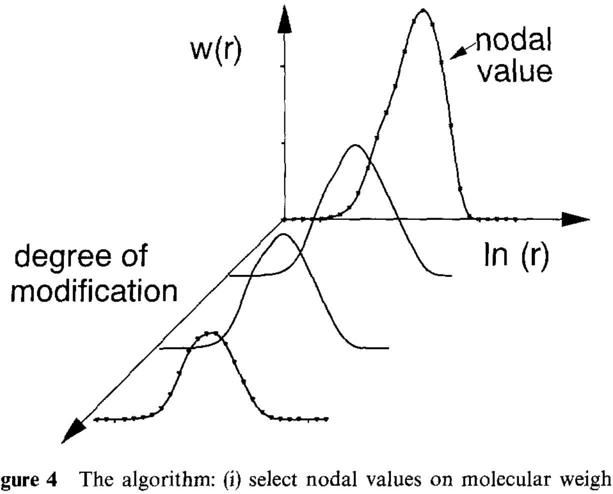


Figure 4 The algorithm: (i) select nodal values on molecular weight distribution to obtain one differential equation for each node; (ii) interpolate between the nodes using cubic splines; (iii) evaluate integrals using Gaussian quadrature, or analytically using the spline; (iv) solve the differential equations using LSODE

These differential equations are then solved using LSODE. Each differential equation has a number of integrals to be solved

integral 1 $\displaystyle\int_r^{\infty} \frac{w(s,z)}{s}\,\mathrm{d}s$

integral 2 $\displaystyle\int_0^r [w(s,z)w(r-s,z)]\,\mathrm{d}s$

integral 3

$$\int_0^r \left[w(s,z) \int_{r-s}^{\infty} \frac{w(m,z)}{m}\,\mathrm{d}m \right] \mathrm{d}s$$

integral 4

$$\int_0^r \left[\int_s^{\infty} \frac{w(m,z)}{m}\,\mathrm{d}m \int_{r-s}^{\infty} \frac{w(m,z)}{m}\,\mathrm{d}m \right] \mathrm{d}s$$

Integral 1 can be evaluated between the nodes by substitution of the spline coefficients for $W(r)$ and solving the integral analytically. To obtain the entire integral we simply sum up the results between all nodes from r to ∞. Notice that this integral also appears in integrals 3 and 4 and thus is solved in the same manner for these cases.

Integrals 2, 3 and 4 are all evaluated over the same region (0 to r), and thus these integrals can be evaluated at the same time. Gaussian quadrature (four integration points) is used to evaluate the integrals between the nodes (or partial regions between the nodes) and then sum up the values for each portion. The differential equations are solved using a predictor–corrector package called LSODE[44].

The sol fraction and the molecular weight averages can be found by integrating over the entire molecular weight distribution. By assuming a cubic for $W(x)$ between the nodes, we can find an analytical solution to these integrals. The sol fraction will be the area under the curve $W(x)$ *versus* x will fall below unity when gel is formed. In this way the gel fraction is calculated. Moreover, when no gel is formed, the sol fraction will give us an indication of the numerical error.

The number of nodes required to represent adequately the initial distribution was investigated by choosing a most probable distribution, discretizing it using a number of nodes and interpolating with the spline, and then comparing approximately 1000 interpolated values with the actual values. The error decreases with increasing number of nodes, indicating that we need at least 25 nodes to approximate adequately the distribution. More than 100 nodes is probably unnecessary. Moreover, if we assume an initial distribution that is most probable, one can derive analytical solutions to integrals 1 to 4 for a specific chain length at zero degree of modification. When three-point Gaussian quadrature was used for the interval between the nodes, the error in the integrals was insignificant.

Comparisons with classical solutions

Pure random scission. For the case of pure random scission, one only needs to evaluate integral 1 for each differential equation, and thus the solution is quite fast. We started with an arbitrarily broad distribution and calculated the molecular weight distributions and averages for increasing degrees of pure random scission. The molecular weight distributions are presented in *Figure 5*. Increasing scission narrows the molecular

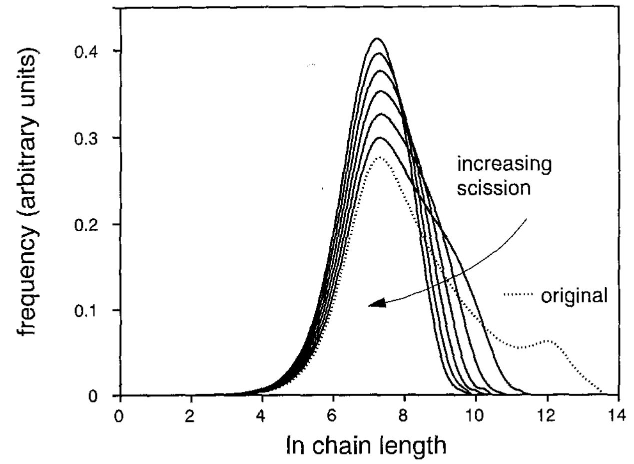


Figure 5 Molecular weight distribution for pure random scission

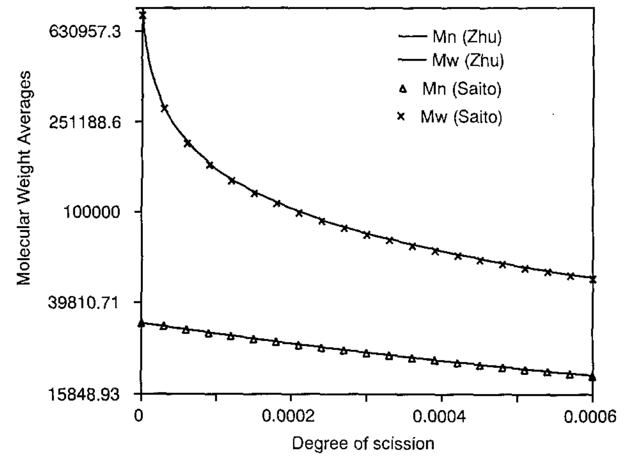


Figure 6 Molecular weight averages for pure random scission

weight distribution to approach the most probable. This is a somewhat trivial result, as Saito[5] has presented an analytical solution for this case (equation (1)); however, this exercise provides the opportunity to check part of the numerical solution. The error in the calculation, as indicated by the sol fraction, is less than 1% for 100 nodes. *Figure 6* compares the molecular weight averages calculated by us to those predicted by Saito. The agreement is excellent.

Pure random crosslinking. Next we test pure random crosslinking using an initial distribution that is most probable. The weight average molecular weight is 250 000. *Figure 7* reveals that the molecular weight distribution first broadens, as higher molecular weight material is created, before the gel point. After the gel point the molecular weight distribution of the sol narrows as the gel grows by preferentially consuming the higher molecular weight sol material. In the postgel region the molecular weight distribution and the averages describe the sol fraction only, and the area of the peak is equal to the sol fraction.

There are two parameters that we use to control the error of the solution, namely the tolerance for LSODE and the number of nodes. Increasing the number of nodes or reducing the tolerance for LSODE increases the time for the solution of the model. The relative tolerance for LSODE seems to have little effect on the error as long as it is set to be less than about 10^{-3}. *Figure 8* shows the gel fraction as a function of the crosslink density for different numbers of nodes. In all cases the gel fraction becomes slightly negative before the gel point and then rises to become positive. Increasing the number of nodes tends to make the negative deviation sharper and moves the gel point closer to the gel point predicted by Flory (equation (3)). At higher gel fractions all solutions approach the values predicted by Flory (equation (3)).

Since we assumed the most probable distribution for the initial molecular weight distribution, the gel fraction and the molecular weight averages can be calculated from equations (43), (44), (47), (48), (49) and (50) of Hamielec *et al.*[1]. *Figure 9* shows how the weight average molecular weight, as predicted by Flory, grows to infinity at the gel point, and then falls after the gel point. The numerical solution does not go to infinity but shows a smooth transition through the gel point. The peak becomes sharper as the number of nodes is increased. The number average molecular weight follows the same increasing–decreasing trend but remains finite right through the gel point. The number of nodes does not greatly influence the number average. In all regions, except very near the gel point, the numerical solution and the classical solution are in excellent agreement.

Simultaneous random scission and crosslinking. The numerical solution of equation (5) compares quite well

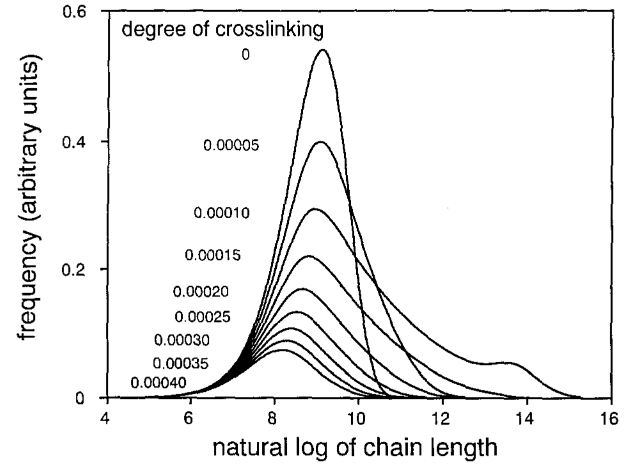


Figure 7 Molecular weight distributions as a function of the crosslink density

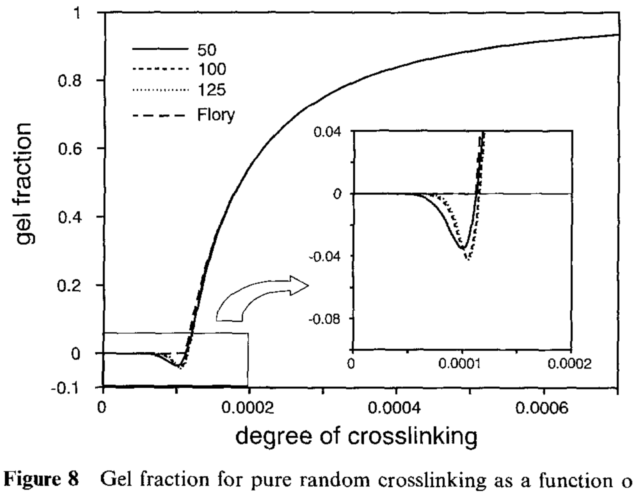


Figure 8 Gel fraction for pure random crosslinking as a function of the crosslink density and the number of nodes

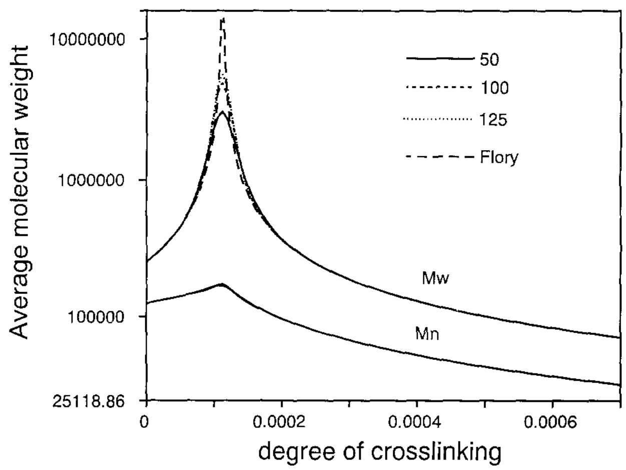


Figure 9 Average molecular weights as a function of crosslink density and the number of nodes

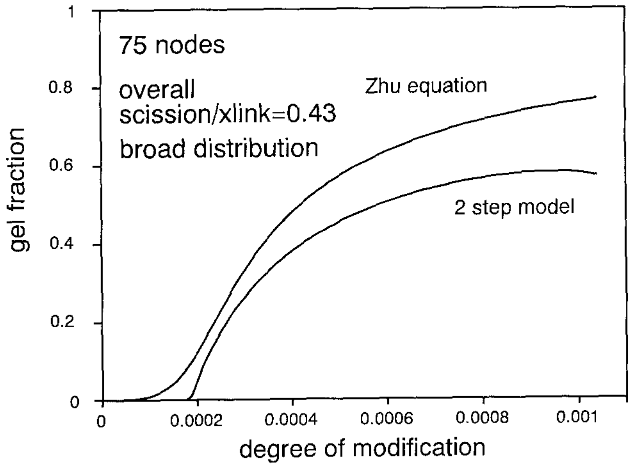


Figure 10 Comparison of the gel fractions predicted for simultaneous random scission and crosslinking using equation (5) and the two-step solution

with the classical solutions for pure random scission and pure random crosslinking; however, this equation was derived to describe the case of simultaneous random scission and crosslinking. Let us consider simultaneous random scission and crosslinking of an initial distribution which is broader than the most probable distribution, using both equation (5) and the two-step solution. We set the parameters such that we obtain the overall ratio of scission to crosslinking $p/x=0.43$, and use 75 nodes for the numerical solution. *Figure 10* compares the gel fraction predictions. The simultaneous solution predicts that the gel point occurs at lower degrees of crosslinking and gives a higher gel fraction over the entire range. At large degrees of modification the two-step solution predicts a reduction in the gel fraction. Equation (5) shows a continuous rise in gel fraction. The reduction in the gel fraction seems to be an unreasonable consequence of the two-step assumption. If one considers the branching frequencies, one can see that there can be a significant contribution to the molecular weight due to Y branches. *Figure 11* shows the predicted branching frequencies *versus* the degree of modification. In this case there are more X branches than Y branches, and the rate of branching appears to change slightly as the initiator decomposes, with the rate of X branching decreasing and the rate of Y branching increasing. Higher initiator concentrations favour X branches over Y branches. The two-step model neglects the Y branches, and thus must underestimate the molecular weight build-up and the gel fraction. Zhu's model (equation (5)) assumes that the termination rate constant for the production of Y branches is equal to that for the production of X branches. In fact, the termination rate constant for the production of Y branches may be larger because of steric difficulties in getting two backbone radicals together to form an X branch.

The average molecular weights, in the pregel region, agree quite well (*Figure 12*), except at the gel point where the two-step solution predicts an infinite weight average molecular weight. Calculation of the two-step averages after the gel point for this arbitrarily broad distribution was not done and so no comparison was possible here.

Figure 13 shows the results of a calculation for various degrees of modification, and compares the final results to that given by the two-step approach. Here, the two-step approach is implemented by solving equation (5) for pure random scission up to degree p, and then for pure random crosslinking up to degree x. The two-step approach seems to overestimate the size of the high molecular weight tail.

In summary we can list the following points.

1. The numerical solution to equation (5) compares quite well with the classical solutions for pure random

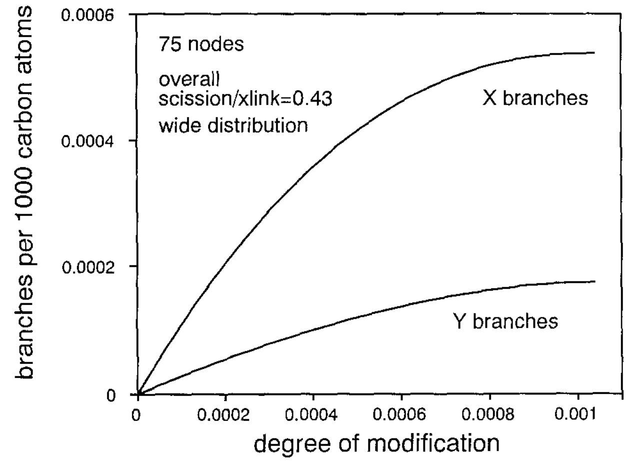


Figure 11 X and Y branching frequencies for scission and crosslinking. Frequencies are as branches per thousand carbon atoms

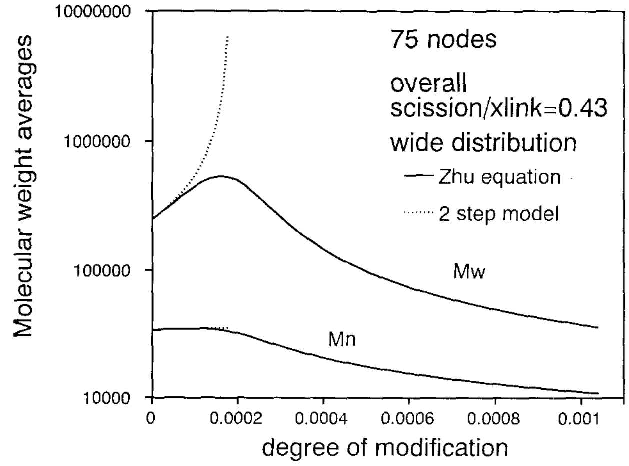


Figure 12 Comparison of the molecular weight averages predicted for simultaneous random scission and crosslinking using equation (5) and the two-step solution

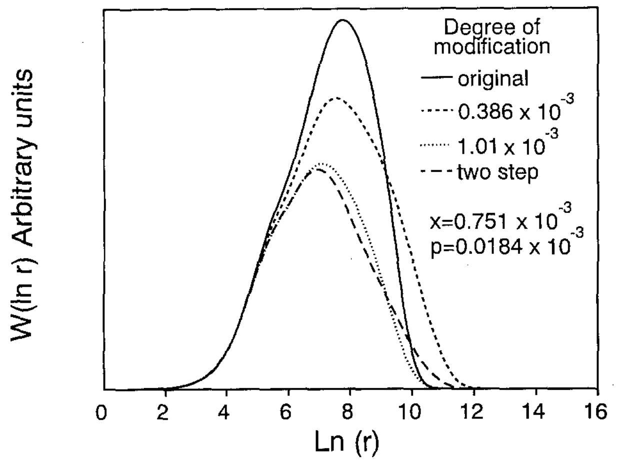


Figure 13 Molecular weight distributions during simultaneous random scission and crosslinking as calculated by solving the complete equation (5) all at once or by solving it in two steps

scission and crosslinking. There is some disparity between the molecular weight averages near the gel point for pure random crosslinking.

2. For simultaneous random scission and crosslinking, equation (5) predicts the gel point to occur at lower degrees of modification than does the two-step solution. Higher gel fractions are predicted by equation (5) at all degrees of modification.
3. Unlike the two-step model, which predicts a reduction in the gel fraction at higher degrees of modification, equation (5) shows a continuous increase.
4. The number and weight average molecular weights predicted by both methods in the pregel region do not differ greatly.

Modifications for scission of branched polymers

The equation for simultaneous random scission and crosslinking developed by Zhu[27] assumes that the chains that undergo scission are linear. This means that each chain has two ends, and thus there are two possible ways to cut the chain to create a smaller chain of specified length. To modify a chain of length r to create a chain of length s $(s<r)$, one can cut the chain s units from either end. On the other hand, branched chains will have more than two ends per molecule and thus the possibilities should increase; however, the number of possibilities will not equal the number of ends, but will also depend upon the placement of the branch along the backbone. Moreover, in some cases, especially for gel, a scission will not create a second molecule. We need to make some assumptions about the average branching structures; for instance, assume the polymer molecules are linear[27], stars or combs, and so on.

Let us make the first step, and assume that all the polymer molecules are stars, and all the branches are the same length and radiate from the centre of the polymer molecule. Based upon the branching frequencies and the degree of scission, one can easily calculate the number of ends per molecule.

1. Each scission adds two ends and increases the number of polymer molecules by one.
2. Each Y branch formed reduces the number of ends by one, and reduces the number of polymer molecules by one.
3. Each X branch formed does not change the number of ends, but reduces the number of polymer molecules by one.

Therefore the total number of polymer molecules is given by

$$Q_0 = Q_0' + [p-(x+y)]Q_1$$

where Q_0' is the initial number of polymer molecules, p is the degree of scission and x and y are the numbers of X branches and Y branches per repeat unit. Q_1 is the first moment of the polymer molecular weight distribution and is a constant. The number of ends equals

$$E = 2Q_0' + (2p-y)Q_1$$

The total number of ends per polymer molecule is then given by E/Q_0. Making this ratio and using the initial number average chain length calculated by $r_{\mathrm{n}0} = Q_1/Q_0'$ we can find that

$$e = \frac{E}{Q_0} = \frac{2+(2p-y)r_{\mathrm{w}0}}{1+(s-y-x)r_{\mathrm{w}0}}$$

Let us consider a star polymer of length r with e branches, each of length r/e. If one wishes to cut this polymer molecule to create a second polymer molecule of length n we must consider four cases.

Case 1:	$n<(r/e)$	e possibilities to create a polymer molecule of length n by cutting off n units from any branch.
Case 2:	$(r-r/e)<n<r$	e possibilities. One can cut $r-n$ off any end to get a polymer molecule n units long.
Case 3:	$(r/e)<n<(r-r/e)$	zero possibilities since we would have to cut off more than r/e from any end.
Case 4:	$n>r$	zero possibility of creating a polymer molecule of length n.

The term for the production rate of polymer molecules of length n by scission of a branched molecule of length r having e ends is

$$\alpha \int_n^\infty \phi \frac{W(r)}{r} \mathrm{d}r$$

where $\phi = e$ if $n<r/e$ or $n>(e-1)r/e$ and $\phi=0$ otherwise. Thus we can break this integral up into two integrals

$$\alpha \int_n^\infty \phi \frac{W(r)}{r} \mathrm{d}r = e\alpha \int_n^{en/(e-1)} \frac{W(r)}{r} \mathrm{d}r + e\alpha \int_{en}^\infty \frac{W(r)}{r} \mathrm{d}r$$

Notice that this reduces to the case given by Zhu[27] if $e=2$. A simple illustration of the effects can be made if we assume that the molecular weight distribution is the most probable distribution

$$w(r) = \tau^2 r \exp(-\tau r)$$

Branched polymer molecules will most likely have a distribution broader than the most probable. We can substitute this expression into the integrals above and solve them analytically. We can also ratio this to the integral assuming linear chains to determine the relative

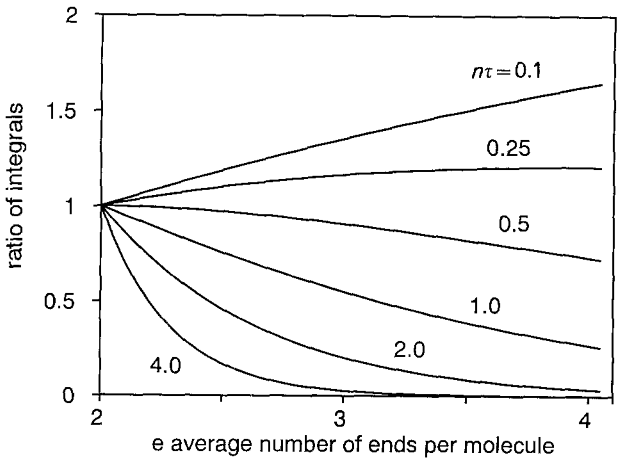


Figure 14 The ratio of the scission of star molecules to linear molecules as a function of the number of ends per polymer molecule and the relative length of the polymer molecule to be formed by scission ($n\tau$). The most probable distribution is assumed

change in the scission term. This equation then becomes

$$\frac{\text{scission of stars}}{\text{scission of linear molecules}} = \left(\frac{e}{2}\right)\left\{1 - \exp\left[n\tau\left(1 - \frac{e}{e-1}\right)\right] + \exp[n\tau(1-e)]\right\}$$

Figure 14 shows the results of this calculation for several values of $n\tau$, the relative length of the molecule to be formed by scission, and several average ends per molecule. For small values of $n\tau$ the ratio is larger than unity, and in the limit as $n\tau$ gets smaller the ratio will equal $e/2$. This result is expected since, when we are making small molecules by scission, nearly all of the branches are longer than the desired molecule, and thus they can all be used. However, as $n\tau$ gets larger the ratio falls below unity, reaches a minimum and then rises to some final value above unity. Work is currently underway to determine the effect of this modification and others, including the comb structures[45].

EXPERIMENTAL

Modification of polyethylene

The polyethylene (HDPE) powder used was Novacor W50555-H with average molecular weights (as calculated by g.p.c.) of around $M_n = 10\,000$ and $M_w = 180\,000$.

The HDPE was coated with the peroxides Lupersol 101 (2,5-dimethyl-2,5-di(t-butylperoxy)hexane, Atochem) and Lupersol 130 (2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, Atochem) (see *Table 1*). This was accomplished by dissolving the desired amount of peroxide in acetone (BHD Inc.) and adding this to the polymer. Additional acetone was added to create a slurry which was well shaken. This slurry was placed in an aluminium pie dish and the acetone was allowed to evaporate for at least 48 h. The sample was stirred occasionally during the evaporation time. The polymer/peroxide mixture was then heated either in the minitruder or in ampoules and the resulting modified polymer was analysed for either gel content or molecular weight.

Minitruder experiments

Several experiments were performed using a minitruder (Randcastle Inc.) having a single 0.25 inch screw, a 24:1 *L/D* barrel and three heated zones with temperature controllers to control within 1°C. The maximum throughput was approximately 120 g h^{-1} at a maximum speed of approximately 115 r.p.m. The r.p.m. were controlled by tachometer feedback.

All polymer powders were screened through a 20 mesh sieve to help ensure adequate feeding. The throughput of the minitruder was measured for polypropylene (isotactic powder, Shell KY-6100) at 200°C and was found to be a linear function of the r.p.m.

$$Q = 0.3669(\text{r.p.m.}) \qquad (\text{mg s}^{-1})$$

The mass of polypropylene contained in the barrel and die was measured using a carbon black tracer at several r.p.m. and at 200°C. On average, the mass was 1.051 g. This allows the calculation of an approximate residence time (see *Figure 15*)

$$\tau = \frac{2.8637 \times 10^3}{(\text{r.p.m.})} \qquad (\text{s})$$

Extrusion experiments were then performed at r.p.m. settings to allow at least enough residence time for 99% consumption of the peroxide added at the temperature selected using the decomposition rate given by Atochem[46]. The usual experimental conditions used for polyethylene modification were as given in *Table 2*, with extra experiments and replicates performed to test the influence of r.p.m. and peroxide/polymer mixing techniques. Varying the r.p.m. settings (5, 10 and 30 r.p.m.) did not influence the gel fractions. Replicate mixtures of nearly identical peroxide levels were made to find the variability of this part of the experiment. This was found to introduce less uncertainty than that demonstrated by the gel fraction analysis.

Table 1 Initiator decomposition rates[a]

Peroxide	Frequency factor A (s^{-1})	Activation energy E (cal mol^{-1})	Molecular weight	Activity (%)
Lupersol 101	8.73×10^{15}	37 180	290.4	92.0
Lupersol 130	7.88×10^{15}	38 130	286.4	92.5

[a] $k_d = A\exp(-E/RT)$, where T is the temperature in kelvin and $R = 1.987$ cal mol^{-1} K^{-1} (1 cal = 4.2 J) (ref. 44)

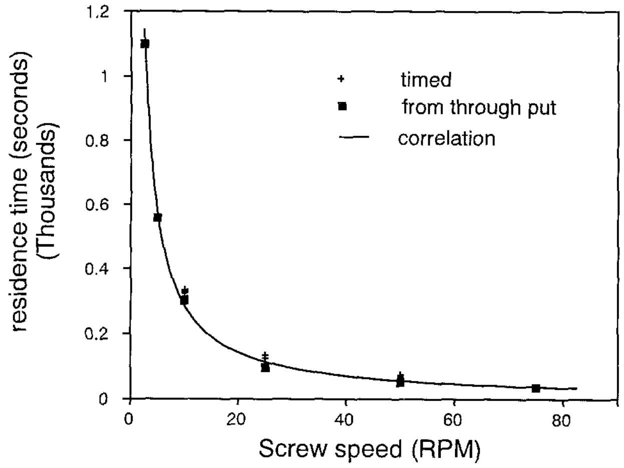
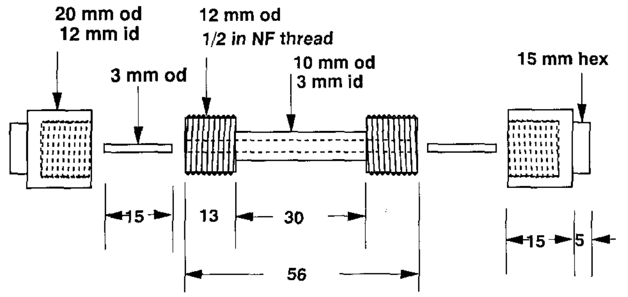


Figure 15 Residence times for the minitruder calculated by measuring the time for a carbon black plug to pass through the extruder (+), by measuring the mass throughput and the mass of polymer in the barrel (■), and from the correlation (——)

Table 2 Usual experimental conditions for polymer modification in minitruder

Temperature (°C)	Peroxide	Peroxide level (wt%)	R.p.m.
190	Lupersol 101	0.2–0.88	10
200	Lupersol 101	0–2	10
200	Lupersol 130	0–1.4	10
230	Lupersol 101	0–2	30
230	Lupersol 130	0–1.4	30



material: aluminum
not to scale
measurement in mm
sizes are approximate

Figure 16 Exploded view of a typical ampoule. Sizes are approximate and may vary slightly from ampoule to ampoule

Ampoule experiments

In order to determine the effect of the extruder mixing, some reactions with polyethylene were performed in small aluminium ampoules in a heated oil bath. *Figure 16* shows a typical ampoule. The insides of the ampoules were coated with a silicone mould-released compound (Moulders Supply Ltd) to allow the sample to be removed from the ampoule. The polymer, coated with peroxides as in the minitruder experiments, was placed in the ampoules and packed tightly to facilitate good contact between the powder particles to obtain a homogeneous polymer/peroxide mixture. The ampoules were closed and suspended in an oil bath at the desired temperature for the desired time. The samples were then cooled, cut up, and analysed for gel content.

The approximate centreline temperature was measured using a thermocouple and pure polymer. The thermocouple was placed by first melting some polymer in the ampoule, and then drilling a hole down the centreline of the cooled polymer. The thermocouple was then placed in the hole. These profiles showed that the centreline reached 99% of the bath temperature after only a few seconds. The ampoule experiments were performed using Lupersol 130 since the crosslinking efficiency of this peroxide showed a small temperature dependence and the half-life was much larger than the heat-up time (*Figure 17*).

The ampoule experiments were performed at 200°C using Lupersol 130 in concentrations of 0.218, 0.88 and 1.37 wt% with replicates at the highest peroxide level.

Molecular weight measurement

The molecular weights of the linear polymers were measured using a Waters 150-C gel permeation chromatography apparatus. Three columns obtained from American Polymer Standards (AM gel 10^6 A, 15 μm; AM gel linear, 15 μm; AM gel 500 A, 15 μm and a guard column) were used. 1,2,4-Trichlorobenzene (TCB; J. T. Baker Chemical Co.) with 2,6-di(t-butyl)-*p*-cresol (Fisher Scientific) stabilizer added was the eluent. Column and injector temperatures were 135°C and the flow rate was 1.0 ml $\min^{-1}$. Around 300 μl of a 0.1 wt% polymer solution in TCB was injected. The samples were made up using the same TCB as the mobile phase for the g.p.c. About 60 min were allowed for each analysis and 5 min allowed between injections.

Because of the errors introduced by the long branches in the g.p.c. analysis, even though they may be approximately corrected for by using viscometry or light scattering[47,48], the branched polymer was only qualitatively analysed using g.p.c.

Narrow polystyrene standards (Tosoh Corporation set D) were used to calibrate the g.p.c. apparatus. The Universal calibrations using $K = 1.21 \times 10^{-4}$ and $a = 0.7070$ for linear polystyrene[49] and $K = 5.260 \times 10^{-4}$ and $a = 0.700$ for polyethylene[50,51] were used for analysis of the HDPE. The results were then checked against broad polyethylene standards (American Polymer Standards and Polymer Laboratories) and by an independent analysis performed by American Polymer Standards.

The raw chromatograms were recovered from the g.p.c. software as ASCII files and smoothed, and then the calibration curves were used to convert the chromatograms to molecular weight distributions for use in the models.

Measurement of gel fraction

The gel fraction was determined using ASTM D2765 with some modifications[50,51]. The polymer sample to be analysed was divided into three specimens, each approximately 0.5 g. If needed, the polymer was cut into small pieces. A specimen holder was made of 400 mesh stainless steel cloth as per the ASTM D2765. The polymer and the specimen holder were weighed and suspended in approximately 350 g of boiling (190°C) decahydronaphthalene (decaline, Aldrich Chemical Co.) for at least 72 h. It was observed that if the extraction time was less than 48 h, the results showed unacceptable variance. Moreover, extraction for longer than 72 h did not significantly change the measurement. Approximately 3 g of Antioxidant 2246 (American Cyanamid) was added

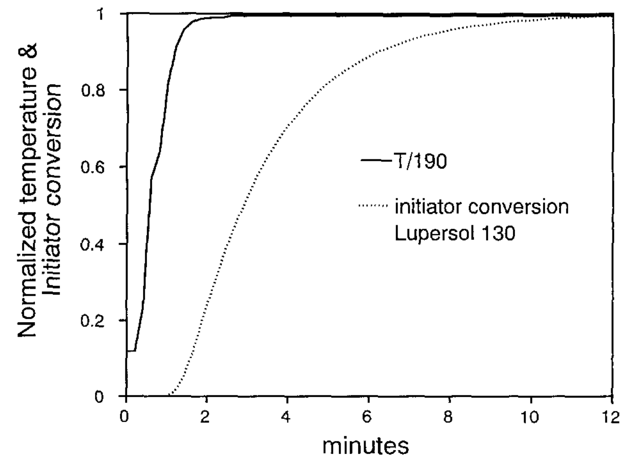


Figure 17 Centreline temperature profile and initiator conversion for Lupersol 130 in aluminium ampoules at 190°C. Temperature is normalized by division by 190. Initiator conversion is the fraction of the initiator that has decomposed

to the decaline to prevent oxidative degradation. The sample was then removed, dried at room temperature for 24 h, and then vacuum dried at 145–150°C for 24 h. The sample and the specimen holder were then reweighed and the sol fraction was calculated on the basis of the loss of polymer during the extraction process.

The technique was developed by measuring the gel content of polyethylene that was subjected to gamma irradiation for a range of doses.

For some samples, the sol was collected, filtered and dried for further analysis.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) was used (ASTM D3417)[52] to find the heats of transition and the transition temperatures for polymers with different peroxide levels by either melting or crystallizing the polymer. Moreover, the d.s.c. was used as a small chemical reactor. The d.s.c. used was a DuPont 910 differential scanning calorimeter with an LNCA II cooling attachment. The polymer, coated with peroxides, was placed in the d.s.c. pan and hermetically sealed. The temperature was increased to the desired reaction temperature (160 or 180°C) and held for sufficient time to consume 99.9% of the peroxide (Lupersol 101) (see *Figure 18*). All heating and cooling rates were 10°C min^{-1}. After the reaction was complete, the ASTM temperature profile was run and the heats of transition and the peak temperatures of transition were recorded.

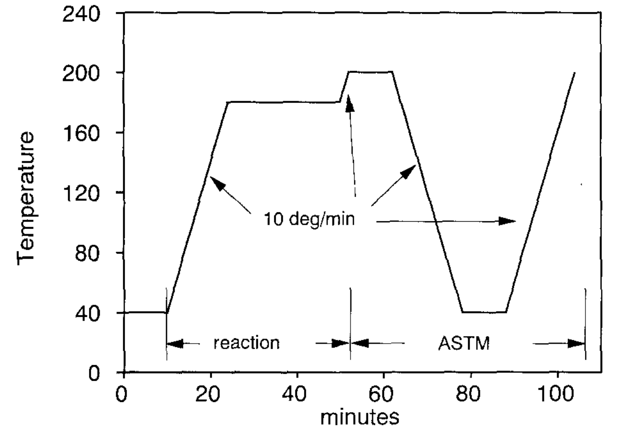


Figure 18 Temperature profile for d.s.c. experiments. Where polymer modified in ampoules was tested, only the ASTM section was used

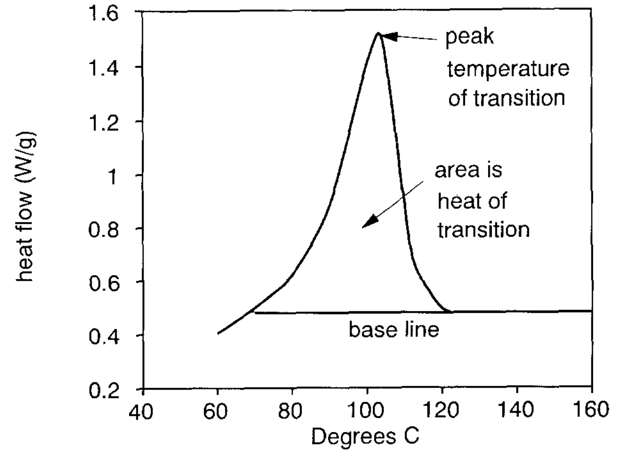


Figure 19 Typical thermal response profile for d.s.c. using the ASTM method

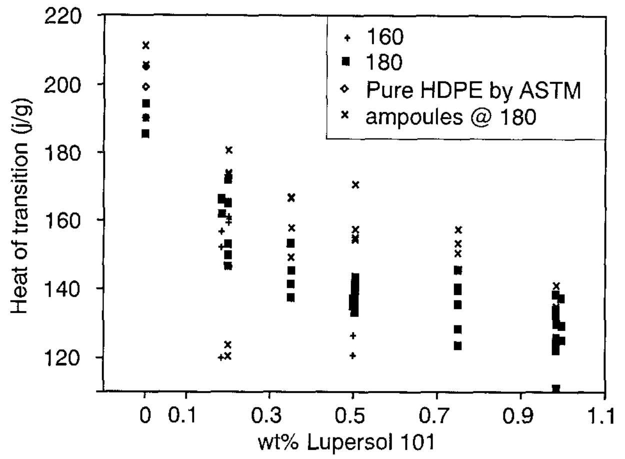


Figure 20 The heat of crystallization as a function of the peroxide level and reaction temperature. This heat was measured by cooling the sample from 200 to 40°C

A typical cooling transition peak is shown in *Figure 19*. The baseline was always selected to be a horizontal line as shown in this figure. Using the common nomenclature, the area of this curve is the heat of crystallization and the peak temperature is the crystallization temperature. The heating peak has a similar shape but with negative heat flow. The area is called the heat of fusion and the peak is the temperature of fusion.

DISCUSSION

The experimental results are presented and discussed first on their own and compared to model predictions where applicable.

Differential scanning calorimetry

Several experiments were performed with coated polymer powder at 160 and 180°C and with polymer modified in ampoules at 180°C. In all cases the peroxide used was Lupersol 101. *Figure 20* shows that the heat of crystallization is reduced with increasing peroxide levels. The heat of crystallization should be proportional to the amount of crystalline polymer formed, and thus the modification is reducing the crystallinity by introducing defects into the polymer molecules, or by reducing the mobility of the molecules to inhibit crystal growth. However, the heats of transition for polymer modified at 160°C, 180°C and in the ampoules are statistically equal, and thus either the polymer is being modified to the same degree for all the temperatures, or d.s.c. is not sensitive enough to resolve the difference.

The peak temperature of transition, as shown in *Figure 21*, also demonstrates a reduction with an increase in peroxide level; and again, no significant difference could be found between polymer modified at 160°C, 180°C or in ampoules.

The heat of fusion and the peak temperature of fusion, as measured by heating the sample from 40 to 200°C, showed the same trend. The heat of fusion was approximately 25% larger than the heat of crystallization, and the peak temperature of fusion was about 20% larger than the temperature of crystallization.

If one can say that the change in the thermal properties, as measured by d.s.c., is caused by the degree of modification by the peroxide, it appears that the reaction temperature has no effect on the degree of modification.

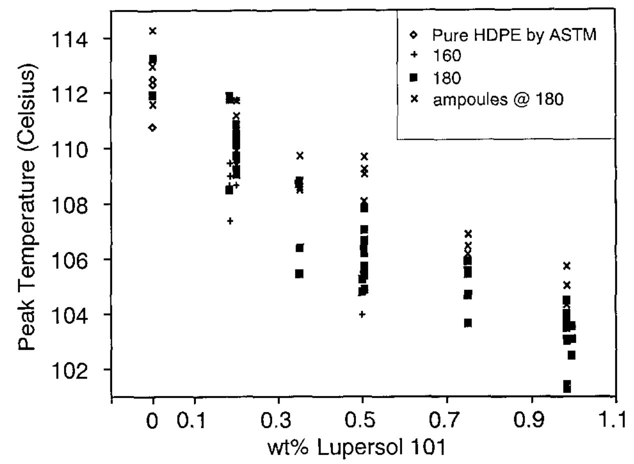


Figure 21 The peak temperature of transition as a function of the peroxide level and reaction temperature. This temperature was measured by cooling the sample from 200 to 40°C

Extrusion experiments

First, some overall observations about the minitruder experiments will be presented. It was possible to extrude the polyethylene even when it contained the highest amounts of peroxides used. As the peroxide content increased, the extrudate became rougher, and finally began to form flakes instead of a continuous fibre. Polymer powder coated with higher amounts of peroxide tended to aggregate near the hopper wall and did not feed as easily into the barrel of the extruder.

Several experiments were performed where polymer was extruded in the absence of peroxide and the gel level measured to determine if there was any modification occurring due to the extruder. The gel levels measured for these conditions were less than 3%. The gel level was also measured for virgin, unextruded polymer powder and was found to be, on average, 2.8%. It should be noted that the gel measurement technique is biased slightly to give higher gel levels. It is easier to extract not enough polymer than to extract too much, and thus we expect the measured gel level to be slightly higher than the actual level. For this reason we can accept that gel levels less than 3% actually represent zero gel. Furthermore, the simple act of extruding the polymer does not significantly increase the gel level in the absence of peroxides.

Figures 22, 23 and *24* show the gel fraction *versus* the amount of Lupersol 101 for experiments performed at 190, 200 and 230°C, respectively. In all cases the gel level increases with increasing peroxide except at the highest peroxide level, where it actually decreases. The gel levels appear to be quite similar for polymer extruded at 190 and 200°C but somewhat lower for that extruded at 230°C.

Figures 25 and *26* show the gel levels for polymer extruded at 200 and 230°C, respectively, in the presence of Lupersol 130. Unlike the difference found for Lupersol 101, the gel levels for both 200 and 230°C appear to be quite similar. In fact, except for the higher peroxide levels, the gel fractions are quite similar to those found for Lupersol 101 at 190 and 200°C. For pure random crosslinking, one would expect (see Appendix) that the only temperature dependence, and difference between peroxides, would be with respect to initiator efficiency. If the efficiencies for Lupersol 101 and Lupersol 130 were to be equal, and independent of temperature, one would expect the same gel levels, for pure random crosslinking, for both initiators at all temperatures. This seems to be true for the lower peroxide levels and all conditions except for Lupersol 101 at 230°C. The efficiency of the peroxide at 230°C seems to be markedly lower than for all the other cases, but why? One could postulate that the efficiency of Lupersol 101 has a strong temperature dependence. However, this is not demonstrated by the

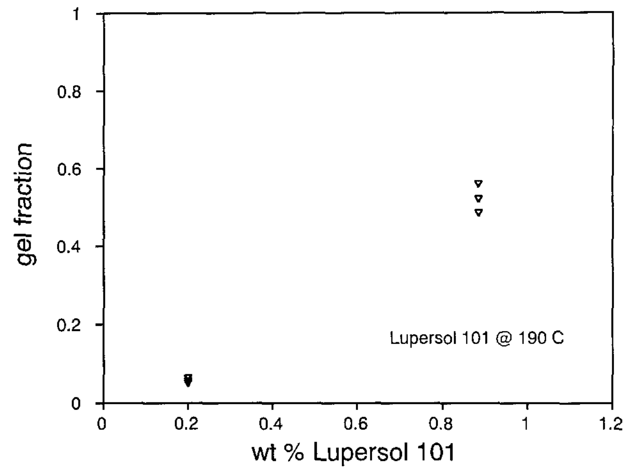


Figure 22 Gel fractions measured for minitruder experiments performed at 190°C using Lupersol 101 initiator

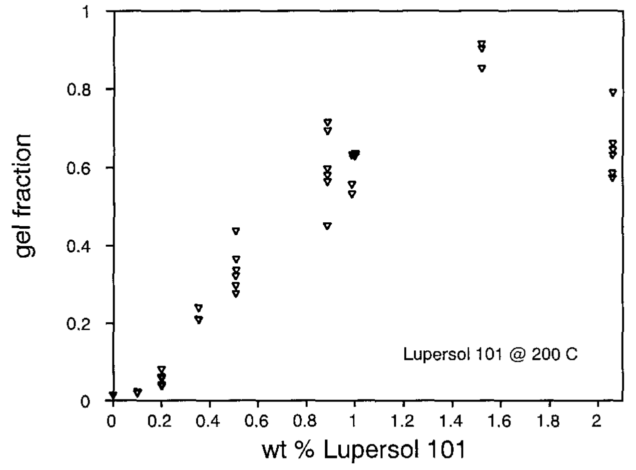


Figure 23 Gel fractions measured for minitruder experiments performed at 200°C using Lupersol 101 initiator

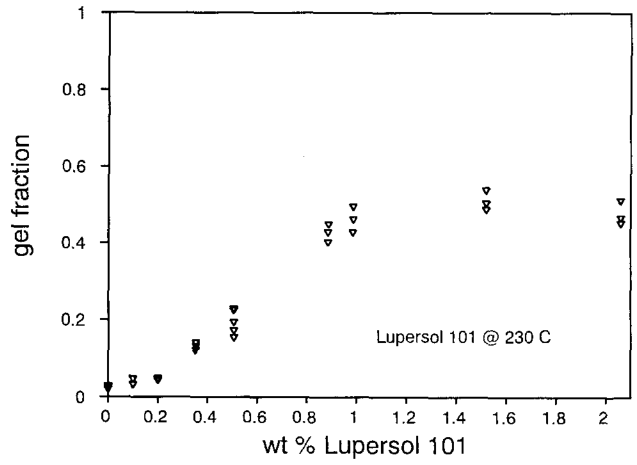


Figure 24 Gel fractions measured for minitruder experiments performed at 230°C using Lupersol 101 initiator

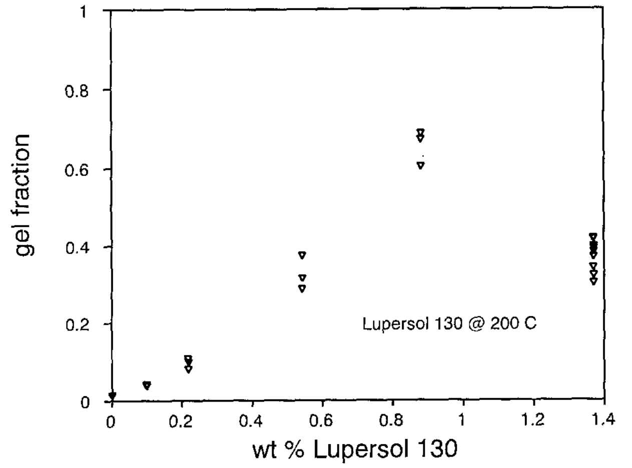


Figure 25 Gel fractions measured for minitruder experiments performed at 200°C using Lupersol 130 initiator

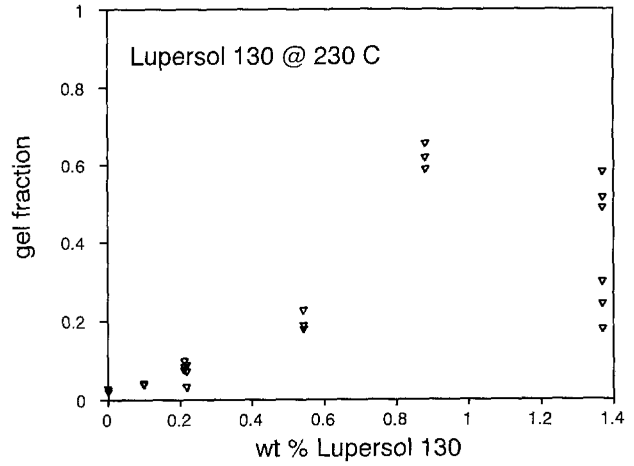


Figure 26 Gel fractions measured for minitruder experiments performed at 230°C using Lupersol 130 initiator

190 and 200°C curves, which have statistically equal averages. The polymer could be experiencing more scission at 230°C, but this should be a function of the polymer and not the initiator, and the curve for Lupersol 130 at 230°C does not show this reduced gel level. Notice that this set of conditions (Lupersol 101 at 230°C) has the shortest lifetime for the peroxide. It could be that the peroxide is being depleted before the polymer has had adequate time to melt and mix in the extruder, thus reducing the gel fraction.

The second major observation is that the gel fraction seems to be reduced by high levels of peroxides. The reduction is shown for both peroxide types and at all temperatures, except at 190°C where the highest peroxide level was not used. Moreoever, replicate experiments were performed to confirm the phenomenon. One possible reason is that increased scission is occurring at the elevated peroxide levels, although this is only borne out by a two-step model and not by the solution to equation (5). Another possibility is that this result is due to extruder effects. It was noted that the higher peroxide levels did not feed as well, or possibly the extruder was causing shear degradation of the gel. Increased crosslinking will certainly reduce the diffusion rates of the macroradicals, possibly reducing the macroradical termination rate and the gel fraction. The variance of the high peroxide measurements was also larger than that of the low peroxide measurements.

The reasons for doing ampoule experiments are two-fold: first, to determine if the extruder mixing plays a significant role in the level of gel formed; and secondly, to shed some light on the reason for the reduction in the gel level at higher peroxide levels. These experiments were performed using Lupersol 130 at 200°C. The gel levels obtained at 0.218 and 0.88 wt% agree quite well with the gel fractions obtained in the minitruder for those peroxide levels. The gel fractions observed are presented in *Figure 27*. This indicates that the effect of extruder mixing is not a significant influence on the gel level for these peroxide concentrations. However, the ampoules also show a decline in the gel level at higher peroxide levels (1.37 wt%). Again, the variability of these results is quite high relative to the results at lower peroxide levels.

Comparison between model predictions and experimental data

Parameter estimation method. If either pure random scission or pure random crosslinking under isothermal conditions is considered, the model reduces to a single-parameter model (see Appendix)

$$\mathrm{d}p/\mathrm{d}t=\phi_p k_d^{1/2} I^{1/2} \tag{6}$$

or

$$\mathrm{d}x/\mathrm{d}t=\phi_x k_d I \tag{7}$$

where I is the initiator concentration, k_d is the initiator decomposition rate constant and is known, ϕ_p is the parameter for pure random scission, ϕ_x is the parameter for pure random crosslinking, and p and x are the degrees of scission and crosslinking, respectively. Once we know either p or x we can calculate the sol molecular weight distribution and gel fractions using Saito's (equation (1)) and/or Flory's (equation (3)) equation and the initial molecular weight distribution.

We must simply estimate either ϕ_p or ϕ_x from molecular weight or gel fraction data. The non-linear least-squares package UWHAUS[53] that uses the Marquardt[54] method was used. The program '2stepEst' was created to use the two-step model to fit the parameters. The two-step model is still valid for pure random crosslinking or pure random scission. For pure random scission, the molecular weight averages can be used, and for pure random crosslinking, the gel fraction was used.

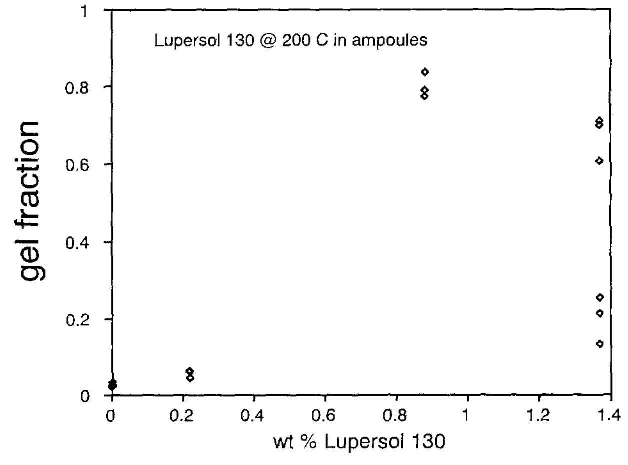


Figure 27 Gel fractions measured for ampoule experiments performed at 200°C using Lupersol 130

Table 3 Parameter estimates for pure random crosslinking

Peroxide	Temperature (°C)	Peroxide levels used	Crosslinking parameter	Approximate 95% confidence interval
Lupersol 101	190	All	0.69	(0.84, 0.54)
Lupersol 101	200	All	0.78	(0.88, 0.68)
Lupersol 101	230	All	0.49	(0.54, 0.43)
Lupersol 101	200	<2 wt%	0.83	(0.93, 0.74)
Lupersol 101	230	<1.0 wt%	0.57	(0.61, 0.53)
Lupersol 101	190 and 200	<2 wt%	0.82	(0.90, 0.73)
Lupersol 130	200	All (no ampoules)	0.48	(0.62, 0.35)
Lupersol 130	230	All	0.46	(0.59, 0.34)
Lupersol 130	200	<1 wt%	0.78	(0.95, 0.62)
Lupersol 130	230	<1 wt%	0.85	(1.01, 0.69)
Lupersol 130	200	All ampoule data	0.64	(1.14, 0.14)
Lupersol 130	200	Ampoule data <1 wt%	1.06	(1.38, 0.75)
Lupersol 130	200 and 230	<1 wt%, including ampoules	0.64	(0.80, 0.48)
Lupersol 101 and 130	190, 200 and 230	All	0.60	(0.66, 0.54)
Lupersol 101 and 130	All except Lupersol 101 at 230	All except highest concentration	0.82	(0.89, 0.74)

Polyethylene modification. The observation that reaction temperature does not influence the gel fraction, except for Lupersol 101 at 230°C, indicates that pure random crosslinking should be adequate to fit these data. In fact, one should be able to fit all the data for a given peroxide using the same crosslinking parameter. Moreover, no significant difference in the thermal properties was found by using different reaction temperatures. This implies that the degree of modification is independent of temperature and thus supports the pure random crosslinking hypothesis. In addition, if the peroxide efficiency is the same for both peroxides, a single crosslinking parameter value should represent all of the data.

The pure random crosslinking model was fitted to a variety of the data (see *Table 3*). First, the parameter was estimated for each peroxide type and each temperature separately. Moreover, estimates were found by neglecting the higher peroxide concentrations, where the gel levels fell. Considering Lupersol 101, the parameter estimates for data collected at 190 and 200°C were not statistically different; however, the data collected at 230°C were significantly lower. If the higher peroxide concentrations were neglected, the crosslinking parameter values estimated were slightly higher.

Similarly, there was no significant difference in the crosslinking parameters found for Lupersol 130 at 200 and 230°C, both collected from the minitruder and from ampoules. Neglecting the higher peroxide levels also gave rise to slightly higher parameter values.

The gel data for Lupersol 101 at 190 and 200°C, neglecting the higher peroxide concentrations, were combined and the crosslinking parameter found. Similarly, the gel data for Lupersol 130 at 200 and 230°C, including the ampoule data but neglecting the high concentration data, were combined to estimate the crosslinking parameter. It was found that the estimated values from these sets of data were not significantly different. To this point, the only significantly different parameter value was for Lupersol 101 at 230°C, supporting the analysis that these data are somewhat suspect. Finally, all of the data, except for Lupersol 101 at 230°C, were used to estimate a single crosslinking parameter, which came out as 0.816 l mol^{-1}. The data and the model are presented in *Figure 28*.

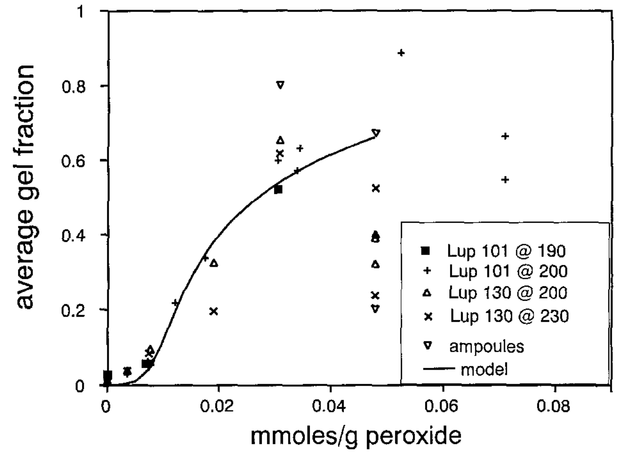


Figure 28 Pure random crosslinking model predictions, using a single crosslinking parameter and average gel fraction data

This same set of data was used in an attempt to fit both crosslinking and scission, using the two-step model, and the scission parameter found was not significantly different from zero. The pure random crosslinking model appears to be adequate to fit these gel fraction data. Moreover, the initiator efficiencies for Lupersol 101 and Lupersol 130 appear to be nearly equal and independent of temperature.

Using the present model, one can predict the molecular weight averages of the sol polymer and compare them to the approximate molecular weights measured by g.p.c. *Figure 29* shows that the comparison between the

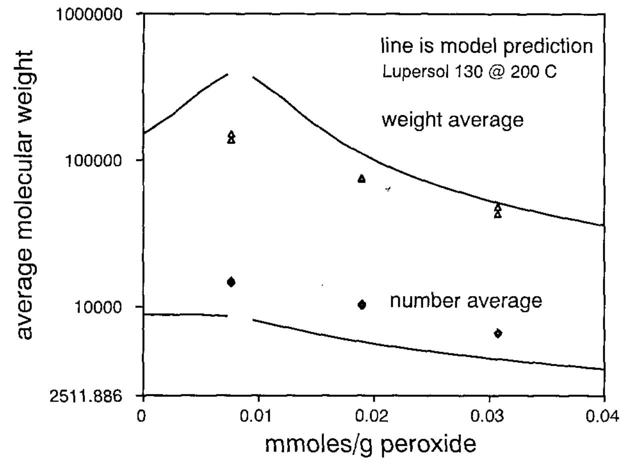


Figure 29 Pure random crosslinking model predictions for the sol molecular weight averages. The molecular weight data were measured by g.p.c. and are therefore only approximate for branched polymer

predicted and the measured values is reasonable for polymer modified by Lupersol 130 at 200°C. The predicted trend is observed, i.e. both the number and the weight average molecular weights decrease with peroxide level and the polydispersity of the polymer is also reduced. The measured average molecular weights must be considered only approximate since g.p.c. is not strictly valid for a branched polymer and will underestimate the higher averages (M_w), especially for a more branched polymer, near the gel point.

CONCLUDING REMARKS

1. The use of the classical Charlesby–Pinner equation to find the ratio of scission to crosslinking for chemically induced modification is not valid. Some modifications in the two-step approach may give rise to some improvement.
2. A numerical solution to an equation for simultaneous random scission and crosslinking has been developed. This equation allows the calculation of the gel fraction and the entire molecular weight distribution for the sol, both before and after the gel point, for any arbitrary initial distribution.
3. Although the numerical solution to this equation agrees quite well with the classical solutions for pure random scission and crosslinking, it does demonstrate a significant difference for the simultaneous random scission and crosslinking case. This equation should more accurately represent the true behaviour, since the assumptions made in its derivation are not as restrictive as the two-step assumption. Modifications have been recommended to improve further the validity of the terms for the scission of branched polymer molecule by assuming the polymer molecules to be stars.
4. The thermal properties and heats and temperatures of transition all decreased with increasing peroxide concentration, but did not appear to be functions of the modification temperature.
5. A pure random crosslinking model is adequate to describe the gel formation of polyethylene. The initiator efficiencies for Lupersol 101 and 130 are not significantly different and are independent of temperature in the range 190–230°C. The pure random crosslinking hypothesis is supported by the observation that the thermal properties, as measured by d.s.c., are not functions of the reaction temperature.
6. It is important to use experimental conditions that allow adequate melting and mixing before the initiator is completely consumed when studying chemical modification of polymers via radical mechanisms.

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APPENDIX

Calculation of the rates of peroxide-induced scission and crosslinking

A balance on total radicals, using the stationary-state hypothesis, gives

$$R=(f/k_t)^{1/2}(k_d I)^{1/2}$$

where I is the initiator concentration, k_t is the overall termination rate constant, k_d is the initiator decomposition rate constant and f is the initiator efficiency which includes the number of radicals produced per initiator molecule. The initiator concentration is given by the differential equation

$$\mathrm{d}I/\mathrm{d}t=-k_d I$$

A balance on backbone and chain-end radicals, using the stationary-state hypothesis, yields

$$R_b=\frac{k_{fp}Q_1 R}{k_{fp}Q_1+k_t R+k_\beta}$$

$$R_e=\frac{k_\beta R_b}{k_t R+k_{fp}Q_1}$$

where R_b and R_e are the concentrations of backbone and chain-end radicals, respectively; Q_1 is the first moment of the polymer molecular weight distribution, and is also the number of polymer repeat units per unit volume; k_β is the β scission rate constant; and k_{fp} is the transfer to polymer rate constant. If we can say that $k_t R \ll k_{fp}Q_1$, then substituting for R we get

$$R_b \approx \left(\frac{k_{fp}Q_1}{k_{fp}Q_1+k_\beta}\right)\left(\frac{fk_d}{k_t}\right)^{1/2} I^{1/2}$$

$$R_e \approx \left(\frac{k_\beta}{k_{fp}Q_1}\right)\left(\frac{k_{fp}Q_1}{k_{fp}Q_1+k_\beta}\right)\left(\frac{fk_d}{k_t}\right)^{1/2} I^{1/2}$$

The rates of scission and crosslinking are

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}t}&=\frac{k_\beta R_b}{Q_1}\\&=\left(\frac{k_\beta}{Q_1}\right)\left(\frac{k_{fp}Q_1}{k_{fp}Q_1+k_\beta}\right)\left(\frac{fk_d}{k_t}\right)^{1/2} I^{1/2}\\&=\phi_p k_d^{1/2} I^{1/2}\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t}&=\frac{k_{tc}R_b^2}{Q_1}+\frac{k_{tc}R_b R_e}{Q_1}\\&=\left(\frac{k_{tc}}{Q_1}\right)\left(1+\frac{k_\beta}{k_{fp}Q_1}\right)R_b^2\\&=\left(\frac{k_{tc}}{Q_1}\right)\left(1+\frac{k_\beta}{k_{fp}Q_1}\right)\left(\frac{k_{fp}Q_1}{k_{fp}Q_1+k_\beta}\right)^2\left(\frac{fk_d}{k_t}\right)I\\&=\phi_x k_d I\end{aligned}$$

where k_{tc} is the termination by combination rate constant and p and x are the degrees of scission and crosslinking, respectively. This evaluation predicts that the rate of crosslinking will be first order in initiator concentration, and the rate of scission of half order. Higher initiator concentrations should give rise to increases in crosslinking. For pure random crosslinking, the parameter reduces to the group

$$\phi_x=\frac{k_{tc}f}{Q_1 k_t}$$

This analysis assumes (i) that the kinetic constants are equal for all radical types; (ii) the stationary-state hypothesis for all radical types; (iii) $k_t R \ll k_{fp}Q_1$; (iv) random scission and random crosslinking; and (v) constant volume and therefore constant Q_1.

If we relax the $k_t R \ll k_{fp}Q_1$ assumption, then we can write

$$R_b=\frac{\theta}{\phi_1\theta+\phi_2}$$

where $\theta=(k_d I)^{1/2}$, $\phi_1=k_t/k_{fp}Q_1$ and

$$\phi_2=\left(\frac{k_{fp}Q_1+k_\beta}{k_{fp}Q_1}\right)\left(\frac{k_t}{f}\right)^{1/2}$$

The rate of pure random scission is given by a three-parameter model

$$\frac{\mathrm{d}p}{\mathrm{d}t}=\frac{k_\beta}{Q_1}\frac{\theta}{(\phi_1\theta+\phi_2)}$$

where the parameters are k_β, ϕ_1 and ϕ_2. The rate of pure random crosslinking is also given by a three-parameter model

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k_{tc}}{Q_1}\left(\frac{\theta}{\phi_1\theta+\phi_2}\right)^2$$

where the parameters are k_{tc}, ϕ_1 and ϕ_2. Now the rate of crosslinking will be less than first order with respect to initiator concentration and the rate of scission will be less than half order. However, if $\phi_1\theta \ll \phi_2$ we return to a single parameter for crosslinking and a single parameter for scission. An order of magnitude analysis can be done to test this.

Basis: 1000 g of polyethylene, density 1000 g l^{-1}
0.1 wt% initiator of molecular weight 300 g mol^{-1} and having

$k_d = 8.73 \times 10^{15} \exp(-37\,182/RT)$, or $6 \times 10^{-2}\ \mathrm{s}^{-1}$ at 200°C

$k_t = 10^7 \quad (\mathrm{l\,mol^{-1}\,s^{-1}})$

$k_{fp} = 10^3 \quad (\mathrm{l\,mol^{-1}\,s^{-1}})$

We can calculate the group $\phi_1 = k_t/k_{fp}Q_1$, where $Q_1 = (1000\ \mathrm{g\,l^{-1}})\ [\mathrm{mol\ (28\ g)^{-1}}] = 36\ \mathrm{mol\,l^{-1}}$, so

$$\phi_1 = \frac{10^7}{(10^3)(36)} = 278$$

and

$$\theta^2 = k_d I$$
$$= (6 \times 10^{-2}\ \mathrm{s^{-1}})(0.1\ \mathrm{wt\%}/100)(1000\ \mathrm{g\,l^{-1}})[\mathrm{mol\ (300\ g)^{-1}}]$$
$$= 2 \times 10^{-4} \quad (\mathrm{mol\,l^{-1}\,s^{-1}})$$
$$\theta = 1.4 \times 10^{-2}$$

Therefore $\phi_1\theta = (278)(1.4 \times 10^{-2}) \approx 4$ and

$$\phi_2 = \left(\frac{k_{fp}Q_1 + k_\beta}{k_{fp}Q_1}\right)\left(\frac{k_t}{f}\right)^{1/2} \geqslant \left(\frac{k_t}{f}\right)^{1/2}$$
$$\approx (10^7)^{1/2} \approx 3000$$

Since $\phi_1\theta/\phi_2 \approx 4/3000 \ll 1$ we are justified in using $\phi_1\theta \ll \phi_2$, and therefore in using a single parameter for scission and a single parameter for crosslinking.

Isothermal conditions to final states

Given the rates of scission and crosslinking derived above, and the initiator concentration $I = I_0 \exp(-k_d t)$, one can integrate to find the final degrees of scission and crosslinking. For scission we can evaluate

$$p = \int_0^t \frac{\phi_p}{Q_1} k_d^{1/2} I_0^{1/2} \exp(-k_d t/2)\,\mathrm{d}t$$
$$p = \frac{2\phi_p I_0^{1/2}}{k_d^{1/2}}[1 - \exp(-k_d t/2)]$$
$$= \frac{2\phi_p I_0^{1/2}}{k_d^{1/2}} \qquad \text{at } t = \infty$$

The number average molecular weights for pure random scission are given by

$$\frac{M}{M_n} = \frac{M}{M_{n0}} + p$$

where M is the molecular weight per repeat unit. Substitution for p yields

$$\frac{M}{M_n} = \frac{M}{M_{n0}} + \frac{2\phi_p I_0^{1/2}}{k_d^{1/2}}$$

Therefore a plot of M/M_n *versus* $2I_0^{1/2}k_d^{-1/2}$ should give a straight line with slope ϕ_p.

For pure random crosslinking

$$x = \int_0^t \frac{\phi_x}{Q_1} k_d I_0 \exp(-k_d t)\,\mathrm{d}t$$
$$x = \phi_x I_0[1 - \exp(-k_d t)]$$
$$= \phi_x I_0 \qquad \text{at } t = \infty$$

This analysis provides a very interesting result. Except for initiator efficiency, the final degree of crosslinking is independent of the initiator type. Initiators with vastly different decomposition rates, but similar efficiencies, would give the same final degree of crosslinking. Moreover, if both the efficiency and termination are weak functions of temperature, the final degree of crosslinking will be independent of temperature. Scission will still depend on the initiator decomposition rate.

The final ratio of scission to crosslinking will then be a function of the initiator concentration and decomposition rate

$$\frac{p}{x} = \frac{2\phi_p}{k_d^{1/2}\phi_x I_0^{1/2}} \qquad \text{at } t = \infty$$

and thus p/x will not be constant for experiments using different initial peroxide concentrations and will tend to zero as I_0 increases.

Considerations for bifunctional initiators

Both Lupersol 101 and Lupersol 130 have two peroxide groups per initiator molecule, and thus are bifunctional initiators. This introduces some modifications to the equations as derived for a monofunctional initiator. These differences will only affect the modification *versus* time profiles for either pure random crosslinking or pure random scission, but should not influence the final degree of modification after all of the initiator is consumed. However, for the bifunctional case we will have four radicals produced per initiator molecule instead of two for the monofunctional case. For the simultaneous random scission and crosslinking case, where the radical concentration influences the ratio of scission to crosslinking, the following analysis will be important. This derivation shows the proper way to account for the bifunctional initiators. Consider the following reactions

$$\mathrm{I} \xrightarrow{k_d} \mathrm{R} + \mathrm{R}_1$$

$$\mathrm{R}_1 \xrightarrow{k_d} \mathrm{R} + \mathrm{R}_2$$

where R, R_1 and R_2 are primary radicals, R_1 is a radical with an unreacted peroxide group and R_2 is a diradical since both peroxide groups have decomposed. These radicals can react with polymer backbones to give macroradicals (Y_0) by transfer to polymer. X is a dead initiator product.

$$\mathrm{R} + \mathrm{P} \xrightarrow{k_{fp}} \mathrm{X} + \mathrm{Y}_0$$

$$\mathrm{R}_1 + \mathrm{P} \xrightarrow{k_{fp}} \mathrm{HR}_1 + \mathrm{Y}_0$$

$$\mathrm{R}_2 + \mathrm{P} \xrightarrow{k_{fp}} \mathrm{R} + \mathrm{Y}_0$$

HR_1 is an initiator fragment, no longer a radical, but containing an unreacted peroxide group that can decompose

$$\mathrm{HR}_1 \xrightarrow{k_d} \mathrm{R} + \mathrm{R}$$

These radical species can undergo termination by combination with the macroradicals. Termination between primary radicals is neglected as this is accounted for by the initiator efficiency.

$$\mathrm{R} + \mathrm{Y}_0 \xrightarrow{k_t} \mathrm{P}$$

$$\mathrm{R}_1 + \mathrm{Y}_0 \xrightarrow{k_t} \mathrm{P}_1$$

$$\mathrm{R}_2 + \mathrm{Y}_0 \xrightarrow{k_t} \mathrm{Y}_0$$

P_1 is a macromolecule with a peroxide group that can decompose

$$P_1 \xrightarrow{k_d} R + Y_0$$

Based upon this kinetic scheme, and assuming that the rate constants are equal for all peroxide and radical species, we can derive balances for all the species. Q_1 is the first moment of the molecular weight distribution for the dead polymer and is proportional to the concentration of repeat units in the polymer.

$$\frac{dR}{dt} = 2k_d I + k_d R_1 + 2k_d HR_1 + k_d P_1 - k_{fp} Q_1 R - k_t R Y_0$$

$$\frac{dR_1}{dt} = 2k_d I - k_d R_1 - k_{fp} Q_1 R_1 - k_t R_1 Y_0$$

$$\frac{dR_2}{dt} = k_d R_1 - 2k_{fp} Q_1 R_2 - 2k_t R_2 Y_0$$

$$\frac{dHR_1}{dt} = k_{fp} Q_1 R_1 - k_d HR_1$$

$$\frac{dP_1}{dt} = k_t Y_0 R_1 - k_d P_1$$

$$\frac{dY_0}{dt} = (k_{fp} Q_1 - k_t Y_0)(R + R_1 + 2R_2) - k_t Y_0^2$$

The balance on initiator is given by

$$\frac{dI}{dt} = -2k_d I$$

and a balance on the total number of peroxide groups (PO) is given by

$$\frac{dPO}{dt} = -k_d PO \qquad PO(t=0) = 2I(t=0)$$

and the total number of peroxide groups is also given by

$$PO = 2I + R_1 + P_1 + HR_1$$

The total primary radical concentration R_t can be found from

$$R_t = R + R_1 + 2R_2$$

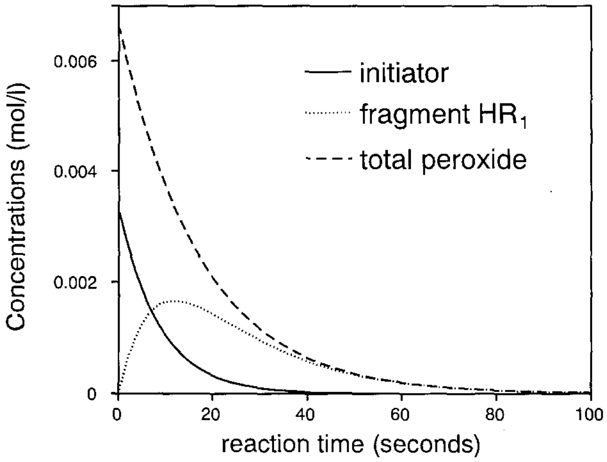

Figure 30 Concentration of initiator, peroxide-containing initiator fragment (HR_1) and total peroxides *versus* reaction time

$$\frac{dR_t}{dt} = \frac{dR}{dt} + \frac{dR_1}{dt} + 2\frac{dR_2}{dt}$$

$$\frac{dR_t}{dt} = 4k_d I + 2k_d HR_1 + k_d P_1 - k_{fp} Q_1 R_t - k_t(R + R_1 + 4R_2)Y_0$$

Solution of these equations (using LSODE and Gear's method), using $k_d = 6 \times 10^{-2}\,s^{-1}$, $k_t = 10^7\,l\,mol^{-1}\,s^{-1}$, $k_{fp} = 10^2\,l\,mol^{-1}\,s^{-1}$ and $Q_1 = 36\,mol\,l^{-1}$, shows that the balance on primary radicals is adequately given by

$$\frac{dR_t}{dt} = 2k_d PO - (k_{fp} Q_1 + k_t) R_t Y_0$$

but not by

$$\frac{dR_t}{dt} = 4k_d I - (k_{fp} Q_1 + k_t) R_t Y_0$$

since PO does not equal $2I$ over the entire course of the reaction because HR_1 rises to a significant level (see *Figure 30*). The total macroradical concentration, given by solution of the differential equations, can also be adequately described (using the stationary-state hypothesis) by

$$Y_0 = \left(\frac{2k_d PO}{k_t}\right)^{1/2}$$