Radiation Crosslinking Studies on Branched Polyvinyl Acetate

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Crosslinking and chain scission caused by gamma radiation in branched polyvinyl acetate have been studied. Gel fraction was measured as a function of radiation dose in five well-characterized samples, ranging in structure from almost linear to approximately 1·7 branch points per molecule. Apparent G-values (events per 100 eV of energy absorbed) from random scission and crosslinking, G(S) and G(X) respectively, were obtained from the solubility behaviour at high doses, and G(X) was separately evaluated at low doses from gel point measurements. For each sample the values of G(X) were similar at high and low doses, but they decreased from sample to sample as the branching density increased. All observations were consistent with the supposition that approximately 15 per cent of the branch points are sensitive to radiation and break preferentially prior to the gel point. Several types of branches are known to exist in polyvinyl acetate, which may account for the apparent differences in radiation sensitivity among branches.

THE dominant reactions that alter molecular weight during the irradiation of polymers are random crosslinking and chain scission. In many cases these reactions are proportional to radiation dose over a wide range of doses. The proportionality constants are independent of the initial molecular weight and distribution, and are usually expressed in terms of $G(X)$ and $G(S)$, the number of crosslinks and scissions introduced per 100 eV of absorbed energy. If crosslinking is sufficiently frequent compared to scission, a network structure or gel can be formed. The relationship between weight fraction of gel and radiation dose in any particular polymer is controlled by the structure and molecular weight distribution of the original molecules, and by the values of $G(X)$ and $G(S)$ for the polymer.

The interpretation of gel curves for polymers which are initially linear in structure has been studied extensively[1–8]. However, except for one early investigation[9], almost nothing has been done on the analysis of gelation for molecules that are initially branched. Such an analysis would be useful since many polymers, including biological polymers and low density polyethylene, contain long chain branches which could affect their response to radiation. The purpose of this article is to discuss generally the problem of gelation in branched systems, and to use the results to interpret radiation effects in a series of branched polyvinyl acetates.

Random crosslinking and scission in linear polymers

Random crosslinking theory assumes that all repeating units in the system are equally likely to participate in crosslinks, and that all crosslinks involving the soluble portion of the system are intermolecular[1]. If only random crosslinking takes place and the initial chains are long, a gel first

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appears when the product $\alpha\,(P_w)_0$ becomes equal to unity[10]. The crosslinking density is α, the fraction of repeating units which participate in crosslinks, and the weight-average degree of polymerization of the initial polymer is $(\bar{P}_w)_0$. Beyond the gel point the soluble fraction in the system, s, can be found from[9]

$$s = \int_0^\infty W(r) \exp\{-\alpha(1-s)r\}\,\mathrm{d}r \tag{1}$$

where $W(r)$ is the weight fraction of chains with r repeating units in the initial system.

In general, irradiation which produces a crosslinking density α also introduces a certain amount of random chain scission. When crosslinking is accompanied by random chain scission, the structure of the initial molecules becomes important, and the analysis must be modified. Let β be the chain scission density, the fraction of initial main-chain bonds which undergo scission, and assume that β, like α, is proportional to radiation dose. If scission and crosslinking are statistically independent events, equation (1) can still be used, but $W(r)$ must be replaced by $W(r, \beta)$, the distribution that would prevail if chain scission to the extent of β occurred alone. The function $W(r, \beta)$ is known for linear chains of arbitrary initial distribution[3]. Equation (1) has been used accordingly to calculate gel curves for linear polymers with the condition that β/α is a constant throughout the process[6–8].

Sufficient information to establish $G(X)$ and $G(S)$ can be obtained by examining limited portions of the experimental gel curve. The two regions most commonly studied are the vicinity of the gel point and at the limit of very high radiation doses. With concomitant scission the product $\alpha\,(P_w)_0$ is greater than unity at the gel point since now the criterion for gelation is $\alpha\,[\bar{P}_w(\beta)] = 1{\cdot}0$. Moreover, $\alpha_g\,(P_w)_0$ increases as the initial molecular weight distribution broadens[7].

At the gel point

$$R_g\,(P_w)_0 = \mathrm{f}\,(p_0/q_0)/q_0 \tag{2}$$

where R is the radiation dose, and p_0 and q_0 are the proportionality constants relating β and α to dose: $\beta = p_0R$ and $\alpha = q_0R$. The function $\mathrm{f}\,(p_0/q_0)$ is greater than unity for p_0/q_0 greater than zero. Its value depends on the molecular weight distribution of the original molecules[7], and generally increases as the distribution broadens.

At sufficiently high crosslinking and chain scission densities, Charlesby and Pinner[5] have shown that, for any initial distribution of molecular weights, the solubility and the radiation dose are related by

$$s + s^{1/2} = p_0/q_0 + 1/q_0\,(P_n)_0R \tag{3}$$

where $(P_n)_0$ is the initial number-average degree of polymerization. The constants p_0 and q_0 can thus be obtained from the slope S_∞ and intercept I_∞ of a plot of $s + s^{1/2}$ versus $1/R$ at high values of R.

Differences between branched and linear polymers

Calculation of gelation behaviour for branched polymers is difficult because the changes in distribution caused by scission depend on initial structure. Consider random scission for two molecules with the same total molecular weight but different structure.

A

B

Polymer A is linear, and a random fracture yields fragments of all sizes with equal probability. In polymer B, however, a random fracture is more likely to break the molecule into one small and one large portion. Indeed, for the particular branched molecule shown it would be impossible for scission to yield two equal fragments. A simple calculation shows that, although equal numbers of scissions produce equal changes in the number-average molecular weight, the reduction in weight-average molecular weight is less in Case B than in Case A. In fact, it can be stated quite generally that random chain scission reduces P_w less in branched systems than in linear systems with the same molecular weight distribution. Fewer crosslinks are therefore required to reach the gel point in branched systems, and the product $\alpha_g (P_w)_0$ is closer to unity than for linear polymers of the same initial distribution. Similarly, $f(p_0/q_0)$ must be closer to unity for branched systems than comparable linear systems.

Charlesby and Pinner[5] have already shown that equation (3) is independent of the initial structure of the molecules. Thus, data on branched systems can be analysed in the high dose region without modification. The limiting slope in a plot of $s+s^{1/2}$ versus $1/R$, together with a value of the initial number-average degree of polymerization, $(P_n)_0$, furnishes p_0 and q_0 at high radiation doses. The gel point dose R_g and the value of $(P_w)_0$ furnishes q_0 at low radiation doses, subject to a proper evaluation of $f(p_0/q_0)$ to account for chain scission. The evaluation of $f(p_0/q_0)$ will be discussed after branching in free radical polymerization is introduced in the Experimental Procedure section.

EXPERIMENTAL PROCEDURE

Branching arises in free radical polymerization by reactions between growing radicals and chains formed at an earlier stage in the process[11-13]. Recently we prepared a series of branched polyvinyl acetates with well-defined molecular weight distributions and branching densities[14]. Careful purification of the monomer and very low rates of polymerization yielded polymers whose size and structure were controlled exclusively by the reactions below[13, 15]:

$$\mathrm{P_r\cdot + M} \xrightarrow{k_p} \mathrm{P_r\cdot + 1} \qquad \text{(propagation)} \tag{4}$$

$$\mathrm{P_r\cdot + M} \xrightarrow{k_{tr,m}} \mathrm{P_r + P_1\cdot} \qquad \text{(monomer transfer)} \tag{5}$$

$$\mathrm{P_r\cdot + P_s} \xrightarrow{sk_{tr,p}} \mathrm{P_r + P_s\cdot} \qquad \text{(polymer transfer)} \tag{6}$$

$$\mathrm{P_r\cdot + P_s} \xrightarrow{k_p{}^*} \mathrm{P}_{r\dot{+}\mathrm{s}} \qquad \text{(terminal double-bond polymerization)} \tag{7}$$

Equations (6) and (7) lead to tri-functional branch points. Another feature of the system is that each polymer molecule has exactly one terminal double bond.

The leading moments of the molecular weight distribution can be expressed in terms of the rate constants and the fractional conversion. Values of the monomer transfer constant, $C_m = k_{tr,m}/k_p$, the polymer transfer constant, $C_p = k_{tr,p}/k_p$, and terminal double bond polymerization constant, $K = k_p{}^*/k_p$ can be evaluated from measurements of P_n and P_w as functions of conversion. Polymerizations were conducted to various conversions at 60°C and molecular weights were measured by osmometry and light scattering. The data and the kinetic parameters were recently re-evaluated[16] by statistical curve fitting to obtain $C_m = 2{\cdot}4 \times 10^{-4}$, $C_p = 2{\cdot}3 \times 10^{-4}$, and $K = 0{\cdot}66$. The good fit between theory and experiment lent some confidence to calculated values of properties which were not directly measurable, in particular the branching density b, the average number of branch points per molecule[14].

Five of the samples, ranging in conversion from 13·5 to 71 per cent were selected for the irradiation study. Average degrees of polymerization and calculated branching densities are given in *Table 1*.

Table 1. Properties of polyvinyl acetate samples

Sample	*Fractional conversion in polymerization*	$(P_n)_0$	$(P_w)_0$	b*
A	0·135	4 500	10 100	0·13
B	0·25	4 390	11 100	0·27
C	0·41	5 160	15 700	0·54
D	0·55	5 500	22 000	0·92
E	0·71	6 490	36 200	1·74

*Average branching density: number of branch points in system/number of polymer molecules.

Thin films (3–5 mils) of the samples were cast from a five per cent methanol solution and oven-dried at 50°C. The films were evacuated for one day and sealed in glass tubes at a pressure of approximately 10^{-5} torr. Intrinsic viscosity measurements showed that this preliminary treatment caused no alteration in the molecular weight. The samples were irradiated at 30°C in a cobalt-60 gamma source. The dose rate was approximately $0{\cdot}6 \times 10^6$ rad/h. The tubes were opened after several days, and the soluble portion of weighed samples was extracted by placing the films in a large excess of benzene at room temperature. The gel was isolated, oven-dried in vacuum, and reweighed to determine the soluble fraction.

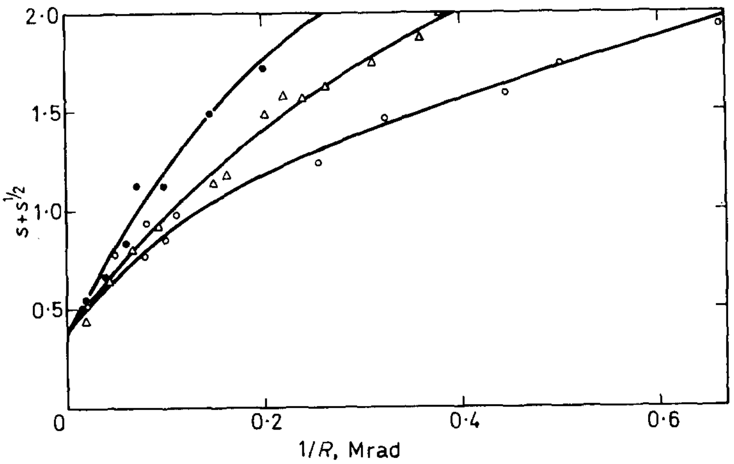


Figure 1—Charlesby–Pinner plots of the solubility data. The closed circles are data for sample A, the triangles are data for sample C, and the open circles are data for sample E

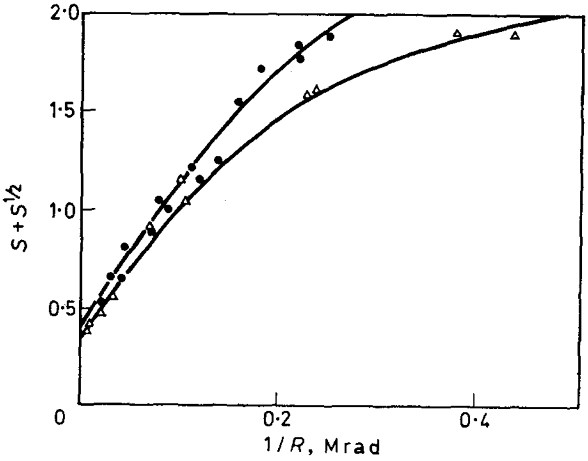


Figure 2—Charlesby–Pinner plots of the solubility data. The closed circles are data for sample B, and the triangles are data for sample D

Table 2. Radiation parameters from Charlesby–Pinner plots

Sample	R_g, rad	S_∞, rad	p_0/q_0*	*Apparent* q_0, rad^{-1} *Gel point*†	*Apparent* q_0, rad^{-1} *High doses*‡
A	$4{\cdot}63\times10^6$	$10{\cdot}0\times10^6$	0·36	$0{\cdot}261\times10^{-10}$	$0{\cdot}22\times10^{-10}$
B	4·16	10·0	0·37	0·266	0·23
C	3·12	8·5	0·33	0·244	0·23
D	2·42	9·8	0·32	0·223	0·19
E	1·79	8·7	0·35	0·187	0·18

*The intercept (at $1/R=0$) of the Charlesby–Pinner plot.
†Calculated from equation (12) on the assumption of random scission and crosslinking alone.
‡Calculated from equation (13) on the assumption of random scission and crosslinking alone.

Charlesby–Pinner plots were made for the five samples, and are shown in *Figures 1* and *2*. The properties of these curves are generally as expected. The intercept at high doses is very nearly the same for all samples, and the gel point dosage R_g decreases as $(P_w)_0$ increases. Furthermore, the curvature of the plots for the low conversion samples is small, and increases for samples with broader distributions. Values of the limiting slope and intercept of the Charlesby–Pinner plot and the gel-point dose are listed in *Table 2* for each sample.

RESULTS AND DISCUSSION

Random scission in branched polymers

Random chain scission amounts simply to a random breaking of the polymer chains at some time after their original formation. A kinetic scheme for the polymerization which supplies the same number of random interruptions during the original generation of the chains, should therefore completely describe the polymer after scission. Stated another way, random scission can be handled perfectly rigorously by being written into the kinetics of polymer growth, arriving at the same results as normal polymerization followed by random scission at some later time.

A simple application of this principle to branched polymers can be made for the system considered by Beasley[17]. In these polymers:

$$(P_w)_0=2/[C_m-C_p\,x/(1-x)] \tag{8}$$

$$(P_n)_0=1/C_m \tag{9}$$

Random interruptions in the growth of polymer chains (due to monomer transfer) are contained in the monomer transfer constant C_m, since C_m can be interpreted as the fraction of encounters between growing radicals and monomer whose outcome is a break in the propagation sequence. If, as before, the fraction of bonds broken by random scission is β, then scission can be accounted for completely by replacing C_m wherever it appears in the Beasley distribution by $C_m+\beta$. Substitution into equation (8) and application of the gel point criterion, $\alpha_g\,(P_w\,(\beta))=1{\cdot}0$, yields

$$\alpha_g(P_w)_0=1/(1-\beta/2\alpha) \tag{10}$$

If α and β are proportional to dose, then

$$f\,(p_0/q_0) = 1/(1 - p_0/2q_0) \tag{11}$$

Thus, $f\,(p_0/q_0)$ is independent of branching and distribution breadth, and the competing effects of distribution breadth and branching density exactly balance one another in determining the effect of chain scission on the gel point.

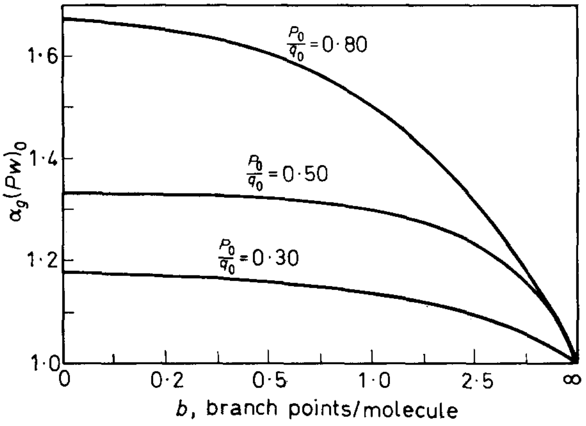


Figure 3—The calculated effect of random chain scission on the gel point for the branched polymers of this study

Although the Beasley distribution was derived for branched free radical polymers it does not happen to apply quantitatively to the polymers used in this study[18]. The basic method of accounting for scission still applies, however. The results of a tedious but not difficult computation appropriate to the experimental polymers[18] are shown in *Figure 3* for three values of p_0/q_0. The product $\alpha_g\,(P_w)_0$ remains nearly constant out to rather high branching densities, and then decreases as the branching density (and the molecular weight distribution breadth) increases still further, approaching unity for sufficiently high branching densities. Thus, at extremely high branching densities the effect of increased branching density is more important than the effect of increased distribution breadth in determining the gel point when chain scission is present. The important point for the present study, however, is that the product $\alpha_g\,(P_w)_0$ is practically constant for the levels of branching density in the experimental polymers. Equation (11) applies and can be used without significant error to calculate q_0 from the gel behaviour. As with the Beasley polymers, correcting the gel point for chain scission is remarkably simple, certainly more so than for linear polymers of comparable distribution breadth. The resulting equations for q_0 are:

$$q_0 = 1/R_g\,(P_w)_0\,(1 - p_0/2q_0) \qquad \text{(gel point)} \qquad (12)$$

$$q_0 = 1/S_\infty\,(P_n)_0 \qquad \text{(high dose range)} \qquad (13)$$

The values of q_0 in the two regions were calculated and are listed in *Table 2*. The values of p_0/q_0 needed in equation (12) were taken from the Charlesby–Pinner intercepts at high doses.

If random scission and crosslinking are the only processes occurring, then q_0 should be the same from sample to sample. If both processes are accurately proportional to radiation dose, then q_0 values at low and high doses should be equal. *Table 2* shows a significant trend in both low and high dose values of q_0 with branching density. Since the effects of random scission and crosslinking have been accounted for, we must conclude that other reactions are occurring as well. The direction of the trend is consistent with a preferential scission process involving the branch points.

A curious result arising from the calculations is that it is possible to obtain gel[18] over a limited range of α values even for polymers with p_0/q_0 greater than 2·0. Thus, a highly branched material can form a gel structure under conditions which render gelation impossible for linear polymers. This gel must, however, disappear again if the radiation is continued indefinitely. Solubility behaviour becomes independent of initial structure at sufficiently high crosslinking and chain scission densities[5], so initially branched systems must approach the behaviour of linear systems eventually.

Preferential scission in branched polymers

The systematic changes in q_0 in *Table 2* suggest the possibility of preferential scission reactions at the branch points. Since both high and low dose values are affected similarly, a sizeable portion of the reaction must occur at the very early stages of irradiation, i.e. prior to the gel point. The effect of preferential scission superimposed on independently occurring random scission and crosslinking is to modify the values of molecular weight needed to calculate q_0. That is, the correct q_0 is obtained by equations (12) and (13) if $(P_n)'$ and $(P_w)'$ are used, the values after preferential scission, rather than $(P_n)_0$ and $(P_w)_0$, the un-irradiated values.

If scission occurs at a fraction m of the branch sites, the number-average degree of polymerization is modified to give

$$(P_n)' = (P_n)_0/(1 + mb) \qquad (14)$$

Since b is simply the number of branch points in the system divided by the number of molecules the new branching density becomes

$$b' = (1 - m)\,b/(1 + mb) \qquad (15)$$

The value of P_w' could be calculated rigorously by methods similar to those used previously to analyse random scission. However, the properties of the un-irradiated polymers are quite accurately related[14] by the equation

$$(P_w)_0/(P_n)_0 = 2\,(1+b) \tag{16}$$

If we assume that the same relationship continues to apply after preferential scission, then

$$(P_w)' = 2\,(P_n)'\,(1+b') \tag{17}$$

and substitution for b' and $(P_n)'$, together with equation (16), leads to

$$P'_w = (P_w)_0/(1+mb)^2 \tag{18}$$

Extensive and detailed calculations of the molecular changes occurring with branch point scission confirm that equations (17) and (18) are quite accurate[16].

If the apparent q_0 values in *Table 2* are represented by q'_0 and the true value by q_0, then the following results are obtained on replacement of $(P_n)_0$ and $(P_w)_0$ in equations (12) and (13) by $(P_n)'$ and $(P_w)'$:

$$q'_0 = q_0\,(1+mb)^2 \qquad \text{(gel point)} \tag{19}$$

$$q'_0 = q_0\,(1+mb) \qquad \text{(high dose region)} \tag{20}$$

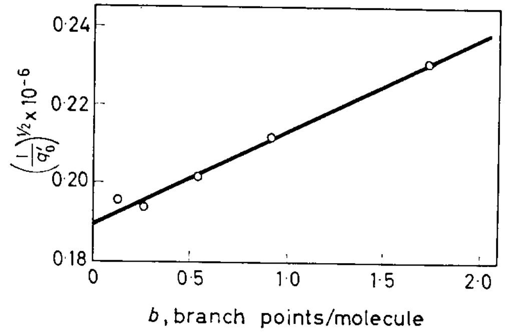


Figure 4—Apparent q_0 from gel point measurements versus initial branching density of the polymers

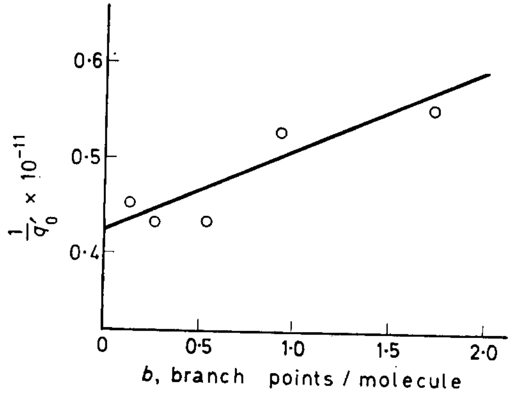


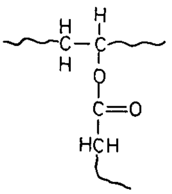
Figure 5—Apparent q_0 from high dose behaviour versus initial branching density of the polymers

Figures 4 and *5* represent the application of these equations to determine m and q_0. In *Figure 4* $(q_0')^{-1/2}$ from the gel point data in *Table 2* is plotted as a function of b, as suggested by the form of equation (19). From the slope and intercept $q_0 = 0{\cdot}28 \times 10^{-10}$ rad^{-1} and the fraction of branch points preferentially broken is $m = 0{\cdot}13$. In *Figure 5* $(q_0')^{-1}$ from the high dose behaviour is plotted as a function of b. The slope intercept yield $q_0 = 0{\cdot}24 \times 10^{-10}$ rad^{-1} and $m = 0{\cdot}19$.

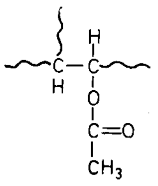
The discrepancy between the values in the two regions is small and in view of the experimental uncertainty, particularly in the q_0 and m deduced at high doses, the difference is probably not significant. We conclude that approximately 15 per cent of the branch points are broken at the earliest stages of irradiation, i.e. prior to the gel point, and that the remaining branch points are not discernibly more sensitive to radiation than ordinary main chain bonds. Furthermore, ordinary random chain scission and crosslinking also occur, at rates that are essentially the same for all samples and proportional to the total radiation dose. Measurements of molecular weight changes in the pre-gel region tend to confirm these conclusions[19]. A detailed study of the pre-gel behaviour of branched and linear polyvinyl acetate and copolymers of vinyl acetate–isopropenyl acetate will be published later.

The G-values for crosslinking and random scission were calculated with average values of $q_0 = 0{\cdot}26 \times 10^{-10}$ rad^{-1} and $p_0/q_0 = 0{\cdot}35$. The results are: $G(X) = 0{\cdot}14$, and $G(S) = 0{\cdot}10$. The only comparable values for polyvinyl acetate were obtained in the course of an extensive study of radiation effects on a single linear sample[20]. The results were $G(X) = 0{\cdot}10$ and $G(S) = 0{\cdot}008$. The only significant difference in conditions was the irradiation temperature, being 50°C in the earlier study and ambient (~30°C) in the present work. The effect of glass temperature ($T_g = 27$°C for polyvinyl acetate) on radiation response is well known, and may account for the differences observed.

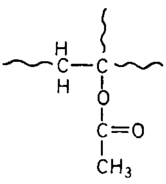
Scission reactions at branch points are not unexpected reactions, and indeed the yields of C_2 to C_4 hydrocarbons in branched polyethylene are explained in just this way[21]. That only a fraction of the branch sites should be extraordinarily sensitive to radiation may be related to the different chemical structures which are possible for branches in polyvinyl acetate. The reactions which originally produce the branch points during polymerization involve the abstraction of a hydrogen atom. Depending on which type of hydrogen atom is removed the following three structures are produced[22]:



A



B



C

Structures A and B would not be expected to be especially radiation-sensitive. However, in structure C the branch carbon atom lacks a hydrogen atom; and, according to observations in many systems, polymers containing main-chain carbon atoms without hydrogen atoms tend to undergo chain scission almost exclusively[23].

Although it is surprising that the reaction should be so specific and should go to completion at such low radiation doses, nevertheless, preferential radiation effects in polymers are not unprecedented. The rapid decrease in the concentration of vinyl groups in high density polyethylene has been discussed by Dole[21]. Keyser *et al.* attributed the sharp initial decrease in the intrinsic viscosity of polypropylene to preferential scission at a few seemingly susceptible groups along the chains[24]. Finally, preferential crosslinking reactions apparently associated with end groups have recently been observed in polystyrene[25]. Such high cross sections for reaction suggest that at some stage the active intermediates in radiation-induced reactions are highly mobile. Whether this mobility is appreciably different in systems of long chain molecules from that in small molecule systems is an important and still unsettled question.

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