

Radiation Crosslinking of Poly(vinyl Chloride)

W. A. SALMON and L. D. LOAN, *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

The mechanism of the electron irradiation crosslinking of poly(vinyl chloride) (PVC) with polyfunctional acrylic monomers has been investigated as part of a program to develop an insulation for distributing-frame wire. These monomers were found to undergo rapid polymerization to form a rigid, three-dimensional network onto which PVC was grafted. Polyfunctionality was necessary for crosslinking to occur, since butyl methacrylate, containing only a single unsaturated bond, did not crosslink readily. On the other hand, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate, each containing three unsaturated groups, gave extremely rapid crosslinking. Trimethylolpropane triacrylate showed 40 times the radiation sensitivity of tetraethylene glycol dimethacrylate, a diunsaturated compound. The rate of disappearance of unsaturation was related inversely to the rate of gel formation. This was attributed to immobilization of unreacted pendant double bonds in the rigid crosslinked network. In the triunsaturated monomers, half the vinyl groups were left unreacted when all of the PVC was insoluble.

INTRODUCTION

Ordinary plasticized poly(vinyl chloride) (PVC), used in large quantities as wire insulation, lacks two properties which are required in certain applications: heat resistance and abrasion resistance. For use in distributing-frame wire in telephone central offices, for example, the insulation must be capable of withstanding temporarily the temperature of a hot soldering iron. In addition, it must resist physical damage by abrasion when wires lying adjacent to it are pulled out of the wire-holding troughs. Crosslinking the PVC greatly enhances these important properties.

Poly(vinyl chloride) by itself is not readily crosslinkable by electron radiation. However, certain polyfunctional unsaturated monomers act as radiation sensitizers and, when added to PVC, give mixtures that crosslink readily upon radiation. Experiments with polyfunctional allyl esters,¹ dimethacrylates,² and divinyl benzene² have been described in the literature; the dimethacrylates gave the highest radiation sensitivity. The dimethacrylate studies, however, were carried out on mixtures complicated by the presence of nonreactive plasticizer, stabilizer, and other filler materials. To obtain an understanding of the mechanism of the crosslinking reaction, a "clean" system containing no such additives is obviously desirable. The present work was undertaken with this objective.

EXPERIMENTAL

The monomers used in this work are listed in Table I. They were all of technical purity. Although they contained 50–100 ppm inhibitor, an additional 0.1% Santonox was added to prevent premature gelling during blending and molding. The PVC was Opalon 660, a high molecular weight ($\bar{M}_w = 120,000$, $\bar{M}_n = 50,000$) homopolymer obtained from the Monsanto Company.

All the mixtures investigated contained 50 phr monomer. They were prepared by adding monomer slowly to the rapidly agitated PVC powder in a high-speed Ronson blender at 80°C.

From these powders, sheets were molded in a heated press at 140°C for 3 min, using 15 tons ram force. The sheet sizes varied from 3 × 3 to 6 × 7 in., and the thicknesses, from 0.020 to 0.045 in. These sheets supplied samples for gel determinations and for tensile tests. For infrared measurements, films 1 × 1 × 0.001 in. were pressed under the same conditions as above, using 1-in. square plates equipped with aluminum foil spacers. In this manner the use of solvents was avoided in the preparation of the samples.

The irradiations were carried out at 80°C under nitrogen in a 5-in.-diam. demountable chamber. The chamber had a thermometer well, holes for circulating nitrogen, and a thin polyethylene window (0.0005 in.) to allow penetration of the electron beam. It was positioned on top of an adjustable hotplate during the irradiations. A Van de Graaff accelerator was used; the voltage was 1 MeV, and the dose rate was 0.01 Mrad/sec.

For gel content determination the irradiated samples were cut into small pieces, enclosed in lens-cleaning tissue, and Soxhlet extracted for 16 hr with tetrahydrofuran; they were then vacuum dried for 16 hr at 100°C. These conditions were found to be sufficient to extract all soluble material. Except where otherwise noted, the term "gel" in this paper refers to total amount of insoluble material in the sample.

TABLE I
Monomers Used in Study

	Abbreviation	Supplier
<i>n</i> -Butyl methacrylate	BMA	Matheson, Coleman & Bell
Tetraethylene glycol dimethacrylate	TEGDM	Ware Chem. Corp.
Tetraethylene glycol diacrylate	TEGDA	Sartomer Resins
Trimethylolpropane trimethacrylate	TMPTM	Sartomer Resins
Trimethylolpropane triacrylate	TMPTA	Sartomer Resins

The swollen gels were weighed after gently blotting excess solvent, and the swelling ratios were determined. "Swelling ratio" refers herein to weight of swollen gel divided by weight of dried gel.

Monomer unsaturation was determined by infrared absorption, using the ratio of the peak at 6.1μ to that at 14.5μ . The 6.1μ peak is due to C=C stretching in the monomer³; that at 14.5μ arises from C—Cl stretching in PVC.⁴ The use of the ratio provided internal standardization and eliminated the effect of thickness variation among the films. A calibration curve was established using a series of TEGDM/PVC mixtures containing 0–100 phr TEGDM. The ratio $R = Abs_{6.1}/Abs_{14.5}$, when plotted as a function of TEGDM content, gave a linear relation over the entire range of composition.

RESULTS

TEGDM/PVC

Figure 1 shows the formation of gel and the disappearance of unsaturation as functions of dose. The gel point occurred at about 0.05 Mrad, at which time about 45% of the initial unsaturation had reacted. The rapid disappearance of this unsaturation strongly suggests a polymerization reaction. The fact that the polymer was soluble up to this point suggests that only a single unsaturated group in each molecule was involved. After the gel point, the gel content rose sharply to approximately 50% at 0.1 Mrad.

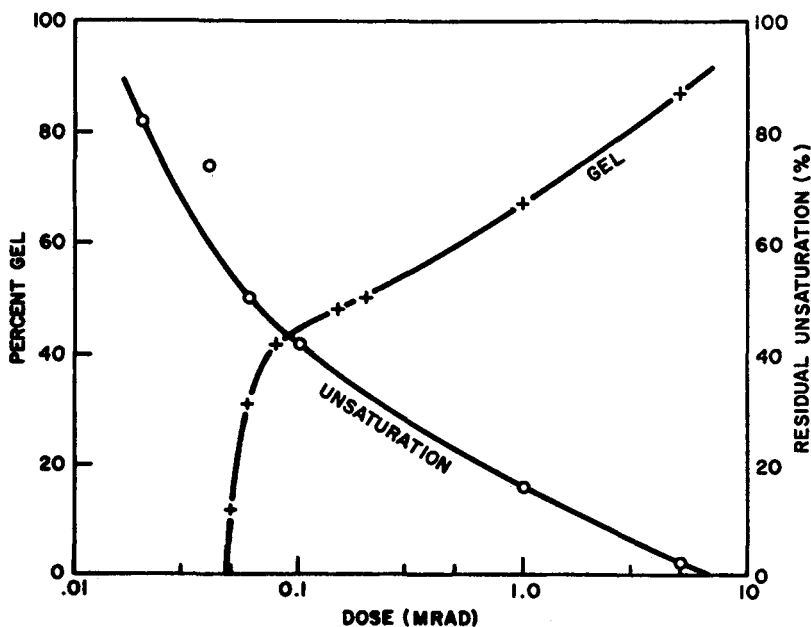


Fig. 1. Per cent gel and monomer unsaturation as a functions of log dose for TEGDM/PVC blends.

TABLE II
Crosslinking of TEGDM and of PVC Calculated
From Chlorine Analysis of Gel

Dose, Mrad	Total gel, %	Chlorine found, %	PVC in gel, %	TEGDM crosslinked, % of total	PVC cross-linked, % of total
0.05	12	15.75	27.7	26	5.0
0.06	31	16.24	28.6	68	13.3
0.08	42	17.16	30.2	88	19.0
0.15	48	19.47	34.2	96	24.6
1.0	67	29.47	51.9	97	52.1
5.0	—	—	—	—	81.0
—	100	—	66.7 ^a	—	100

^aCalculated from formula.

The gel was analyzed for chlorine to determine how much PVC, if any, had become insoluble. The results (listed in Table II along with other quantities derived from the chlorine analyses) are shown in Figure 2. The PVC content was found to be approximately constant at 29% during the period of rapid gel formation. From the chlorine analyses and the known initial composition of the mixture, the amount of crosslinked PVC expressed as per cent of total PVC was calculated. Similarly, the amount of crosslinked TEGDM expressed as per cent of total TEGDM in the mixture was also calculated (see Table I). These values are plotted in

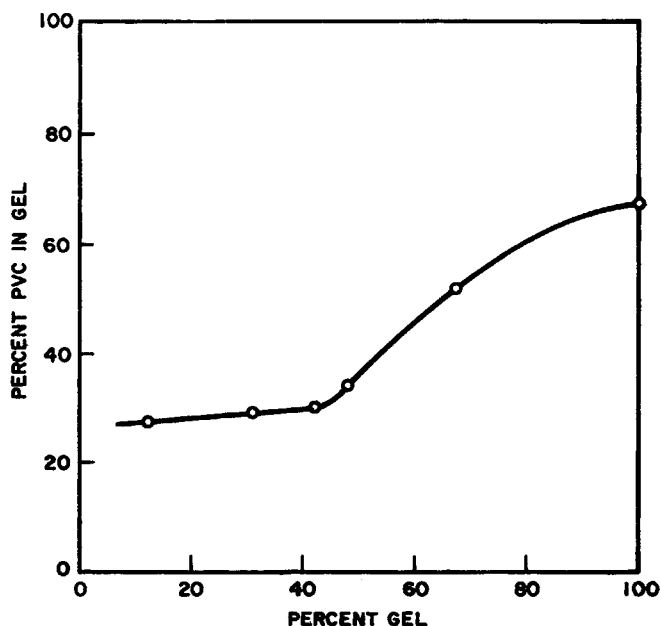


Fig. 2. PVC content of gel.

Figure 3. At a dose of 0.1 Mrad, virtually all of the monomer and 20% of the PVC had been converted into gel. It is interesting to note that at this point 40% of the monomer unsaturation was still unreacted. The final stage of the irradiation, from 0.1 to 5 Mrad, was marked by the con-

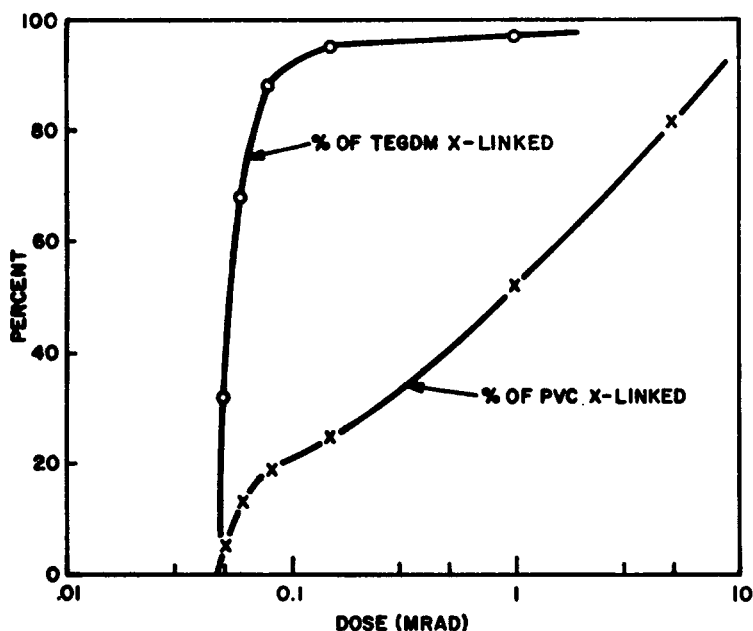


Fig. 3. Per cent of TEGDM and of PVC crosslinked vs. log dose.

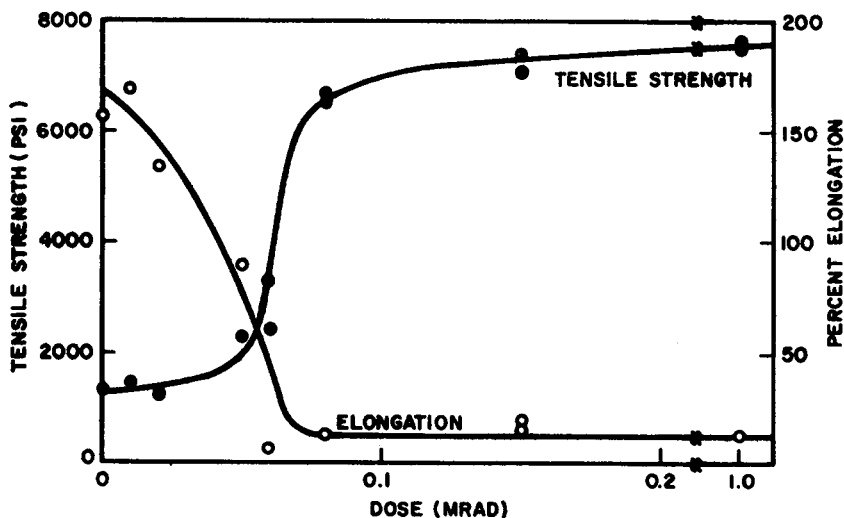


Fig. 4. Ultimate tensile strength and elongation vs. dose (25°C) for TEGDM/PVC blends.

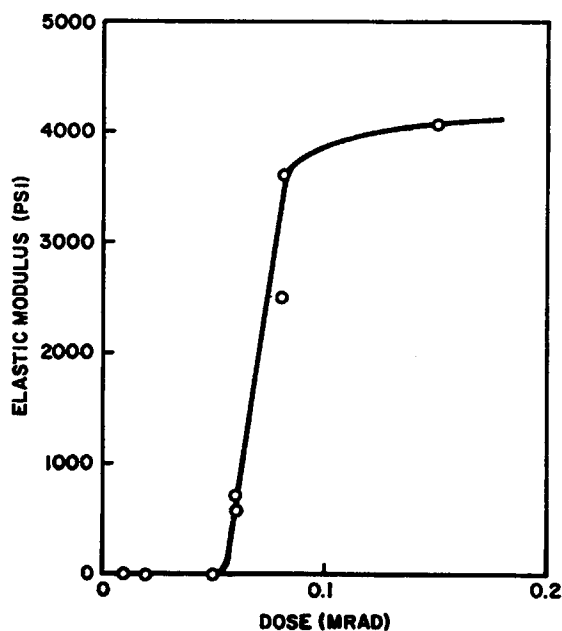


Fig. 5. Elastic modulus vs. dose (100°C) for TEGDM/PVC blends.

tinued but slower crosslinking of PVC. This is shown in Figures 1, 2, and 3.

Physical properties also showed a rapid change in the dose range of 0.05–0.1 Mrad, with much less change at higher doses. Figure 4 shows the tensile strength and the elongation at break, measured at 25°C; Figure 5 shows the elastic modulus measured at 100°C. In a similar manner, the swelling ratio exhibited a rapid decrease in the 0.05–0.1 Mrad region with only a smaller decrease at higher doses.

Other Monomers

A series of monomers containing one, two, and three unsaturated groups was investigated to study the effects of functionality on the crosslinking process and also to compare the behaviors of methacrylates and acrylates. The gelling behavior is shown in Figure 6. BMA did not crosslink readily and formed gel only at relatively high radiation doses.

The triacrylate and the trimethacrylate showed striking behavior. The gelling dose for these monomers was extremely low, about 0.015 Mrad (thus showing that the dose required to deactivate the inhibitor was very small). TMPTA required only 0.1 Mrad to reach 90% gel. This is $1/40$ of the dose required by TEGDM. If we take 90% gel as representative of a fully cured system, TMPTA can be said to have 40 times the radiation sensitivity of TEGDM. Figure 6 shows clearly the order of gelling ability to be tri->di->monounsaturated.

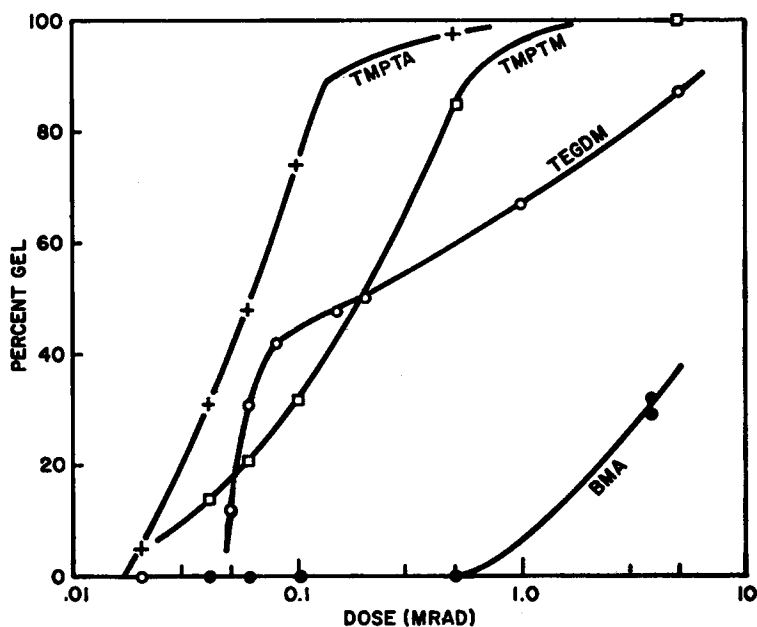


Fig. 6. Crosslinking behavior of blends of PVC with various monomers.

Figure 7 shows the effect of dose on monomer unsaturation. The rates of disappearance of unsaturation lie in inverse order to the rates of gel formation: the triunsaturated monomers showed the lowest rate of loss, while butyl methacrylate showed the highest rate. This finding is in agreement with the hypothesis that early formation of a rigid, three-dimensional network immobilizes the remaining C=C groups, which cannot easily react further with each other, although linking of PVC to this network through them can continue.

Figure 8 shows the unsaturation plotted as a function of gel formation. The triunsaturated monomers reached the gel point when only 15% of the unsaturation had reacted. Subsequent conversion was slow, and finally, at 100% gel, less than 50% of the initial unsaturation had reacted. The diunsaturated monomer underwent an approximately 50% loss of unsaturation before reaching the gelation point, and eventually all the unsaturation reacted. In the monounsaturated compound, nearly all the double bonds had reacted before the onset of gelation.

The swelling ratios, plotted in Figure 9, did not show any consistent differences between the di- and triunsaturated monomers. This would indicate the type of crosslinking to be the same for each class of compounds, at least to a first approximation. At first sight, this conclusion seems incorrect, since higher levels of unsaturation normally result in higher crosslinking densities. However, when it is considered that in the present system the compounds with high unsaturation levels underwent incomplete conversion, this finding is not an unexpected one. Butyl

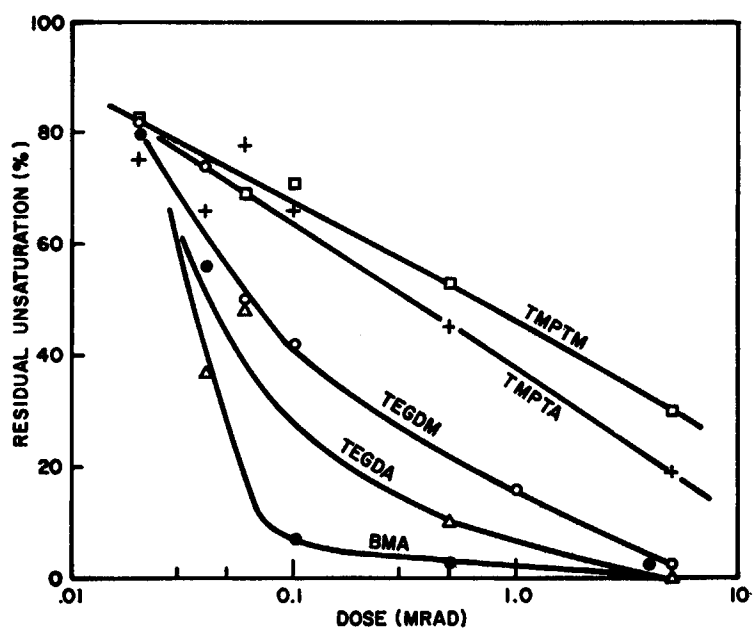


Fig. 7. Effect of dose on residual monomer unsaturation for various PVC-monomer mixtures.

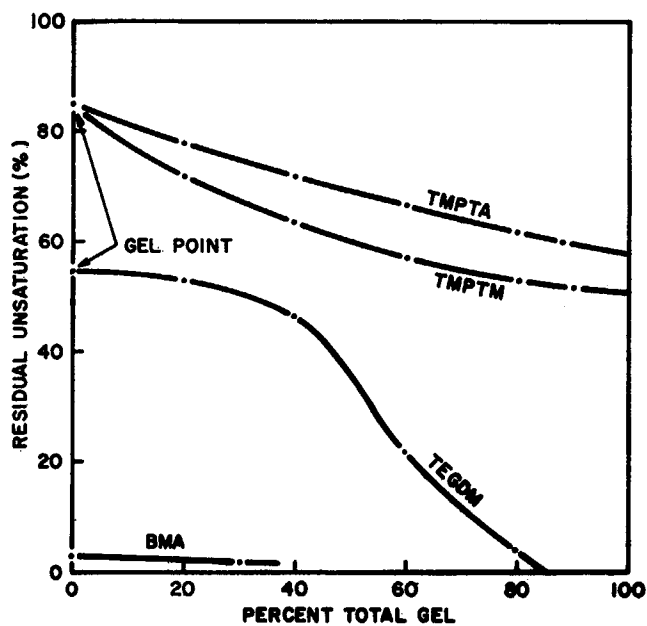


Fig. 8. Residual monomer unsaturation as a function of gel formation.

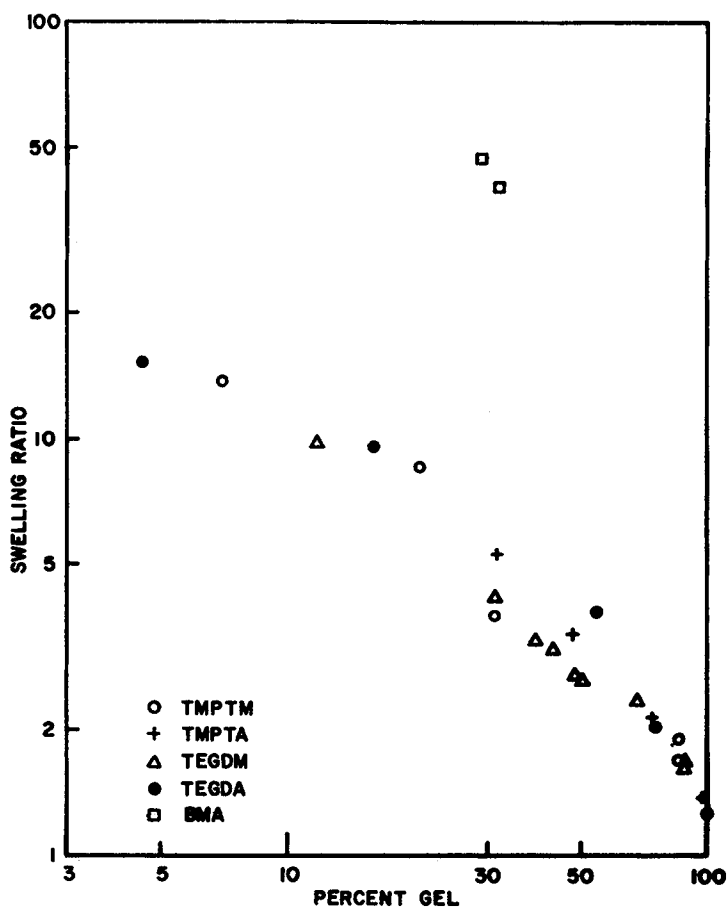


Fig. 9. Swelling behavior of unsaturated monomer-PVC mixtures.

methacrylate, on the other hand, showed ten times the swelling of all the other monomers. This behavior would fit the picture of a PVC network sparsely crosslinked by long, linear chains of butyl methacrylate.

DISCUSSION

Radiation crosslinking of PVC in the absence of additives has been studied quite extensively in the past⁵⁻⁹ and in general low crosslinking yields have been reported. As examples, Charlesby and Pinner⁸ found that a dose of between 15 and 25 Mrad was required for gelation, while Miller⁹ obtained a value of 12 Mrad. The action of polyfunctional radiation sensitizers has also been investigated on a practical level, and Miller⁹ found that 10% of a difunctional monomer reduced the gelation dose to 0.5 Mrad.

Charlesby and Pinner⁸ have carefully analyzed the statistical aspects of radiation crosslinking in the absence of sensitizers and by means of the

now well-known plot of $s + \sqrt{s}$ versus reciprocal radiation dose, where s is the sol fraction. They found $G(\text{crosslinks}) = 0.33$ for PVC. Other investigators^{10,11} have found $G(\text{radicals})$ for PVC to be about 1.6. The analysis for pure PVC is simplified by the single reactant which remains substantially unchanged, from a chemical point of view, throughout the reaction. In the presence of sensitizing monomer, which is consumed through the reaction, the mechanism is more complex as evidenced by the distinctly nonlinear relationship obtained when $s + \sqrt{s}$ is plotted versus reciprocal dose.

We will now discuss the sensitized reaction in a qualitative manner in terms of two stages: the initial stage during which substantial amounts of monomeric additive are present and the second stage where essentially no monomeric additive remains.

The first stage exists up to an irradiation dose of about 0.1 Mrad. It is during the latter part of this stage that the most impressive changes in physical properties, as well as in solubility and swelling behavior, occur. The measurement of unsaturation concentration during this phase indicates a very rapid loss of about 50% of that originally present, a result which is most easily explained by a polymerization mechanism. Presumably the radiation initially produces free radicals of three main types: (1) polymeric radicals formed by loss of a hydrogen or chlorine atom from PVC, (2) the atoms ejected, and (3) low molecular weight radicals derived from the monomer. All of these radicals initiate polymerization. Those formed by removal of atoms from PVC give rise to graft copolymers of methacrylate on PVC and also to methacrylate homopolymer.

The solubility of the initial polymer over a substantial portion of the early dose range further indicates a polymerization involving only one double bond in the monomer molecule to form a chain containing pendant double bonds (Fig. 10a). The crosslinking which occurs during this phase is best explained as a result of occasional growth of a polymer chain through one of these pendant double bonds, as shown in Figure 10b. A very simple analysis (based upon the minimum number of crosslinks necessary to give the observed results) of this phase of the reaction assuming a $G(\text{radicals})$ for PVC of 1.6 and a $G(\text{radicals})$ for monomer TEGDM and poly(TEGDM) (equal to that of methyl methacrylate monomer and polymer⁷) of about 10 indicates that the polymer kinetic chain length is about 150. This may be compared with a value of 1000–10,000 in commercial poly(methyl methacrylate). The $G(\text{crosslinks})$ value is approximately 10, as compared with the previously mentioned value of 0.33 for pure PVC.

As monomer is depleted, the second stage takes over in which all monomer is incorporated into the gel and further crosslinking of PVC is achieved by linking successive molecules of it to the gel. The rate of crosslinking is now substantially reduced, not only because of the reduction in monomer concentration but also because of the sharp increase in viscosity of the system, which hinders the diffusion of pendant unsaturated groups to

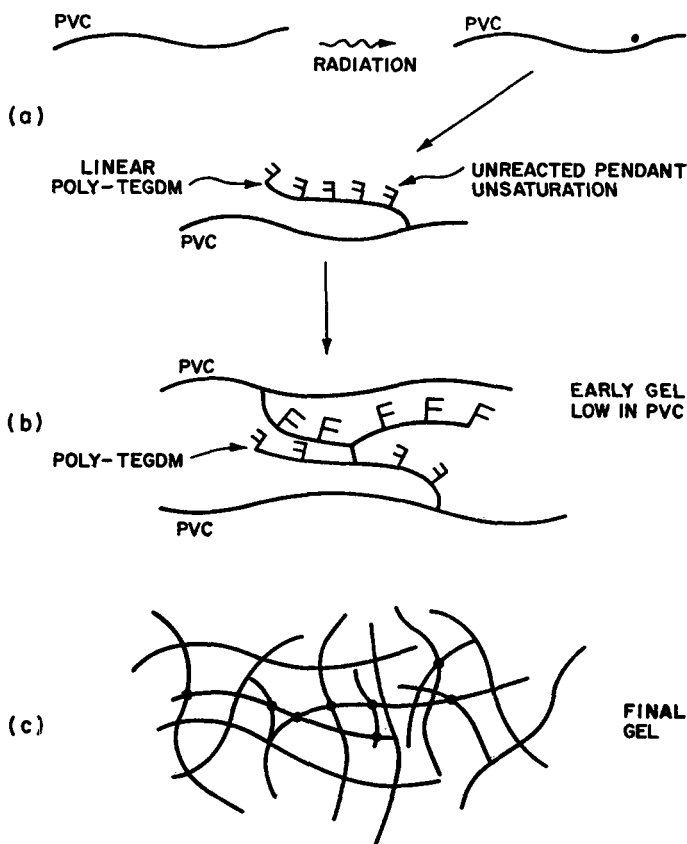


Fig. 10. Crosslinking mechanism.

new radical sites. The crosslinking efficiency of radiation is considerably diminished during this phase—calculation of $G(\text{crosslinks})$ gives a value of about 0.4. The loss of unsaturation continues, but at a much slower rate. At 10 Mrad, virtually all of the unsaturation in the diunsaturated monomers has been reacted, while in the triunsaturated monomers, approximately 20% remains.

Along with this picture of the reaction, it is to be expected that BMA, being monofunctional, propagates linear chains which lack pendant unsaturation and therefore do not undergo crosslinking.

References

1. S. H. Pinner, *Nature*, **183**, 1108 (1959).
2. A. A. Miller, *Ind. Eng. Chem.*, **51**, 1271 (1959).
3. W. M. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).
4. J. Haslam and K. A. Willis, *Identification and Analysis of Plastics*, van Nostrand, Princeton, N.J., 1965, p. 61.
5. A. Charlesby, *Atomic Radiation and Polymers*, Pergamon Press, New York, 1960, p. 142.

6. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, p. 469.
7. *ibid.*, pp. 181-5, 606.
8. A. Charlesby and S. H. Pinner, *Proc. Roy. Soc., Ser. A*, **249**, 367 (1959).
9. A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).
10. R. J. Abraham and D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 1291 (1958).
11. G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).

Received September 3, 1971