Radiation-Convertible Polymers from Norbornenyl Derivatives. Crosslinking with Ionizing Radiation

H. O. COLOMB, JR., and D. J. TRECKER, *Union Carbide Corporation, Chemicals and Plastics, Research and Development Department, South Charleston, West Virginia, 25303* and F. D. OSTERHOLTZ, *Union Carbide Corporation, Corporate Research Department, Tuxedo, New York 10987*

Synopsis

Vinyl polymers with pendant norbornenyl (bicyclo[2.2.1]heptenyl) groups crosslink rapidly on exposure to ionizing radiation. Analysis (according to Charlesby-Pinner theory) of extraction data from an ethylene–vinyl acetate copolymer and the corresponding ethylene–vinyl norbornenecarboxylate copolymer shows that the unsaturated polymer crosslinks by a chain reaction. At low doses, the kinetic chain length is about 4. Pendant norbornenyl groups accelerate crosslinking of a vinyl alcohol–vinyl acetate–vinyl chloride copolymer and convert poly(vinyl alcohols) and cellulose acetate from degrading to crosslinking polymers. A novel application of the Charlesby-Pinner plot strongly suggests linear dependence of the extent of crosslinking on the norbornenyl group concentration in a series of modified poly(vinyl alcohols). The greater effectiveness of pendant norbornenyl groups, compared to cyclohexenyl groups, demonstrates the importance of the reactivity of the double bond.

INTRODUCTION

Unsaturation in the polymer system can dramatically affect polymer crosslinking induced by ionizing radiation.[1-9] Although details of the mechanism are still controversial,[10,11] vinylene (internal) and, particularly, vinylidene or vinyl (terminal) groups influence the ease of crosslinking of polyethylene, as does unsaturation in natural rubber and polybutadiene.[12-14] Differences in crosslinking behavior among these systems arise from several factors, including differences in polymer morphology and the resultant changes in "usable" vinyl group concentration.[5,14] Crosslinking in these polymers can occur by coupling of polymer chain radicals and by involvement of the unsaturation in interchain free radical processes of short kinetic chain length.[5,12]

The evidence[1-14] for involvement of unsaturation in radiation-induced crosslinking suggests that improvements in curing would be gained through the use of unsaturated groups with (1) high free-radical affinities, (2) no easily abstracted hydrogens (e.g., allylic hydrogens) near the double bond which would favor chain transfer rather than addition to the double bond, and (3) the ability to polymerize by a free-radical mechanism with short

1659

polymer chain lengths, but long kinetic chain lengths. Consistent with this expectation, we now report that norbornenyl (bicyclo[2.2.1]hept-2-enyl) groups, pendant to the polymer chain, significantly increase the curing response of vinyl polymers. The characteristics of the chemical reactivity of the norbornene group include high methyl-radical affinity (50),[15] relatively low reactivity for abstraction of bridgehead hydrogens, and tendency to form low molecular weight polymers under free-radical polymerization conditions.[18]

We are not aware of direct information on abstraction of bridgehead hydrocarbons in unsaturated bicyclo[2.2.1]heptane systems. Since geometry inhibits allylic resonance at the 1-position, evidence for low stability of the analogous *saturated* bridgehead radical and failure of norbornene to chlorinated at the 1-position is good justification for predicting low reactivity of the bridgehead position in the unsaturated system to abstraction by alkyl or α-oxygenated alkyl radicals. See, for instance, Fort and Franklin[16] and Kooyman and Vegter.[17]

EXPERIMENTAL

Irradiations

Approximately 20-mil-(0.5-mm)-thick films of the polymers were stored overnight under nitrogen. Just before irradiation, the samples were sealed into 2-mil polyethylene bags well flushed with nitrogen. The bagged films were irradiated with 1-MeV electrons from a high voltage Engineering Model J Van de Graaff accelerator at dose rates from about 0.1 to 6 Mrads/min. Dosimetry was based on a differential technique using oxygenated ferrous sulfate (Fricke Solution) dosimetry with $0.005M$ $Fe(NH_4)_2(SO_4)_2$; $G(Fe^{+3})$ was taken as 16.[19] Polyethylene cells, cleaned and conditioned by soaking in Fricke solution, were simultaneously irradiated with and without a 20-mil polyethylene absorber over the cell window (2-mil polyethylene). The absorber extended beyond the edges of the cell. The difference in energy received by the two cells was assumed to be due completely to absorption in the polyethylene absorber, whose weight in the portion covering the cell was then used to calculate the dose. The most probable energy loss (calculated by including an allowance of 1.2 for range straggling[21,22]) for 1 MeV electrons passing through 25 mils of polyethylene is approximately 0.11 MeV.[23] There will be little change in the L.E.T. of such electrons,[23] and thus little change in response of the Fricke solution.[19,20]

Polymers

The polymers used in this investigation were prepared by the reaction of a vinyl alcohol polymer (Elvanol 71-24, E. I. du Pont de Nemours), a vinyl alcohol copolymer with vinyl acetate and vinyl chloride (VAGH, Union Carbide Corporation), and other polymers with hydroxyl groups (such as

cellulose acetate Type E383-40, Tennessee Eastman Company) with excess 5-norbornen-2-ylmethyl isocyanate in aprotic solvents using dibutyltin dilaurate as a catalyst. Incorporation of the norbornenylmethyl carbamate in the product was found by elemental analysis for nitrogen. In some cases, methyl isocyanate was then added to react with the remaining hydroxyl groups. The ethylene–vinyl 5-norbornene-2-carboxylate and ethylene–vinyl cyclohexene-3-carboxylate copolymers were prepared by reaction of the corresponding acid chloride with an ethylene–vinyl alcohol copolymer in benzene solution employing pyridine as acid acceptor. Typical experimental procedures follow.

Ethylene–Vinyl Alcohol Copolymer. A 300-g sample of an ethylene–vinyl acetate copolymer (10.2 wt-% vinyl acetate, melt index 2.9 dg/min) was dissolved in 1400 g of toluene by heat and agitation in a 3-liter resin kettle fitted with reflux condenser. Methanol (129 g) was added to the hot (70°C), stirred solution. When the temperature had cooled to 60°C, 23.2 g of a 25% solution of sodium methoxide in methanol was added. The solution was heated to reflux, held there for 3 hr, cooled slightly, and poured into rapidly stirred methanol. The copolymer was recovered by filtration and reslurried in 4 liters of fresh methanol. This was repeated until the methanol filtrate had a pH of 7. The copolymer was then dried for 24 hr in a vacuum oven at 50°C. The copolymer was found to contain 0.5% vinyl acetate by infrared analysis.

Ethylene–Vinyl N-(5-Norbornen-2-ylmethyl)carbamate–Vinyl N-Methylcarbamate Terpolymers. The ethylene–vinyl alcohol copolymer (100 g, 0.204 moles vinyl alcohol) was charged to a 1-liter resin kettle fitted with distillation head and stirrer. Benzene (700 ml) was added and then about 10% of the solvent was azeotropically distilled to remove any water that might be present. The solution was cooled to 70°C and a few drops of dibutyltin dilaurate added. 5-Isocyanatomethyl-2-norbornene (9.6 g, 0.0643 moles) was added and the solution was agitated for 30 min (maintaining the 70°C temperature). Infrared spectroscopy showed that all of the isocyanate had reacted. Methyl isocyanate (12.5 g, 0.219 moles) was then added and the reaction conditions were maintained for another hour. The resin was precipitated and washed in methanol and then dried in a vacuum oven at 50°C.

Ethylene–Vinyl 5-Norbornene-2-carboxylate Copolymer. One hundred grams of ethylene–vinyl alcohol copolymer (0.125 moles of vinyl alcohol per 100 g), 500 ml benzene, and 10 ml pyridine were charged to a 1-liter resin flask fitted with a motor-driven stirring rod, a water condenser (attached to a nitrogen supply and bubbler), a 125-ml dropping funnel, and a thermowell with thermocouple. The solution was heated to reflux and 50 ml of benzene was stripped off. While the solution was refluxing, 5-chloroformyl-2-norbornene (0.131 moles) was added by means of the dropping funnel over a 15-min period. Refluxing continued for 1 hr. The solution was cooled to 40°C and transferred to a 4-liter beaker. Methanol was added slowly with stirring until the solution was cloudy, then 2 liters of

methanol was added quickly. The product was recovered by filtration, washed 3 times in methanol, and dried in an oven at 50°C.

There was 63.3 g (53.1%) of material recovered. The elemental analysis for carbon indicated quantitative conversion of alcohol to ester. *Anal.* Calcd for $(C_{31.5}H_{59.9}O)_n$: C, 83.20%. Found: C, 83.14%.

The DQDA-1818 ethylene–vinyl acetate copolymer used as starting material contained 10% vinyl acetate by weight. The ratio of M_w to M_n by gel permeation chromatography was 3.64. Conversion to the norbornene-containing material gave a polymer with M_w/M_n 3.44. An average value, 3.54, was used for both. Membrane osmometry gave M_n of the modified material as 58,000. Use of an average monomer molecular weight of 32.2 (based on 10 wt-% vinyl acetate in the base resin) gave a number-average degree of polymerization of 1800. M_n of the base resin was 54,000; monomer average molecular weight, 30.0.

Details of the other polymers prepared for this investigation are given in Table I.

TABLE I
Properties of Radiation-Convertible Polymers

Base polymer	Norbornenyl-connecting group	wt-%	Inherent viscosity dl/g
Cellulose acetate	methylcarbamate	24	—
Vinyl chloride–vinyl acetate–vinyl alcohol	methylcarbamate	21	—
Vinyl alcohol	methylcarbamate	10.8	0.79
Vinyl alcohol	methylcarbamate	19.3	0.79
Vinyl alcohol	methylcarbamate	30.0	0.79
Vinyl alcohol	methylcarbamate	70.4	0.79
Ethylene–vinyl alcohol (5.5 wt-%)	carboxylate	15.6	1.16
Ethylene–vinyl alcohol (29.5 wt-%)	(cyclohexene carboxylate)	13.7	—

The method of obtaining the gel content was a modification of a procedure described by Nuenke and Milgrom.[24] The irradiated film samples (approx. 0.25 g) were allowed to stand under nitrogen for at least three days before extraction. The film samples were then cut into small pieces and distributed in the bottom four trays of a five-tray extraction basket, which was placed in an extraction thimble made of 200-mesh stainless-steel wire cloth. The thimbles were placed in wide-mouth 4-oz. jars, and sufficient solvent was added to cover the top tray in the thimble (100 ml). The jars were sealed and placed in a 60°C oven. After four days, the jars were removed from the oven, cooled, and the thimbles were removed from the solution and dried in a 50°C vacuum oven. The gel content was obtained directly from the dry thimble weight. This procedure was repeated using fresh solvent and heating for two days. The gel content was confirmed occasionally by evaporation of solvent and determination of the amount of soluble polymer.

RESULTS AND DISCUSSION

A duplicate series of irradiations was carried out employing an ethylene–vinyl acetate copolymer and the ethylene–vinyl 5-norbornene-2-carboxylate copolymer prepared from it. The relationship of gel fraction or sol fraction to dose was analyzed by the plots shown in Figures 1–4.

The simplest relationship—the variation of gel fraction with dose (Fig. 1)—is significant: it indicates that essentially complete curing
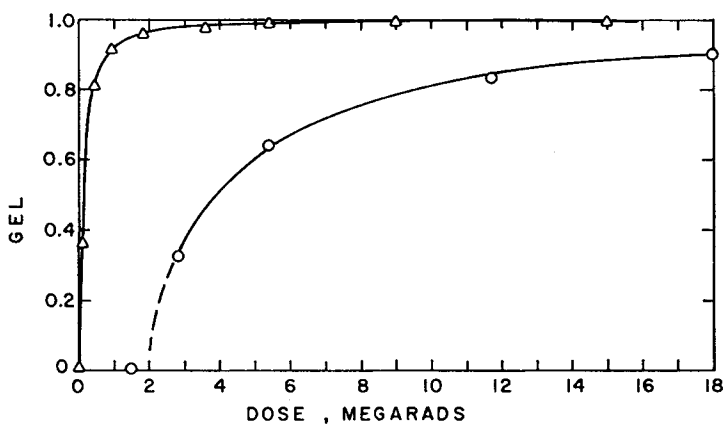

Fig. 1. Gel vs. dose plot; (O) ethylene–vinyl acetate (3.5 mole-% vinyl acetate); (△) ethylene–vinyl norbornenecarboxylate (3.5 mole-%).
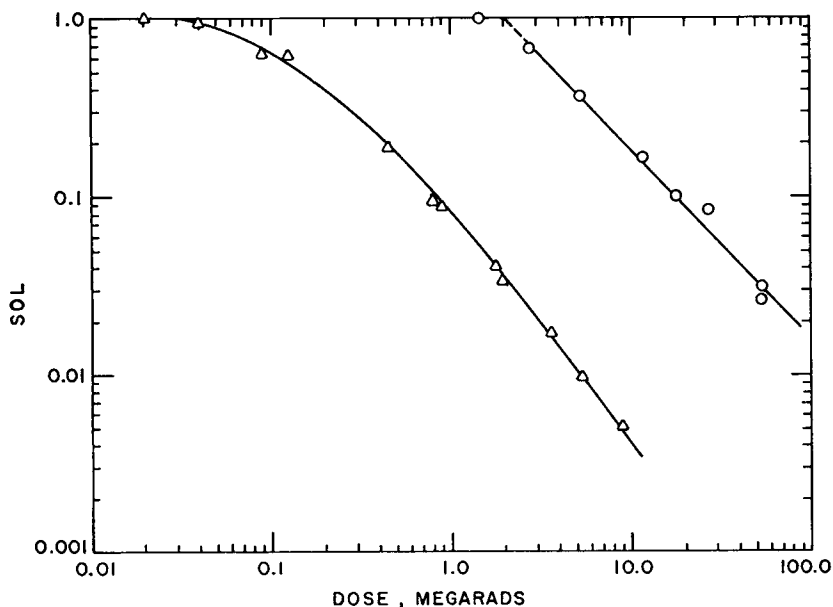
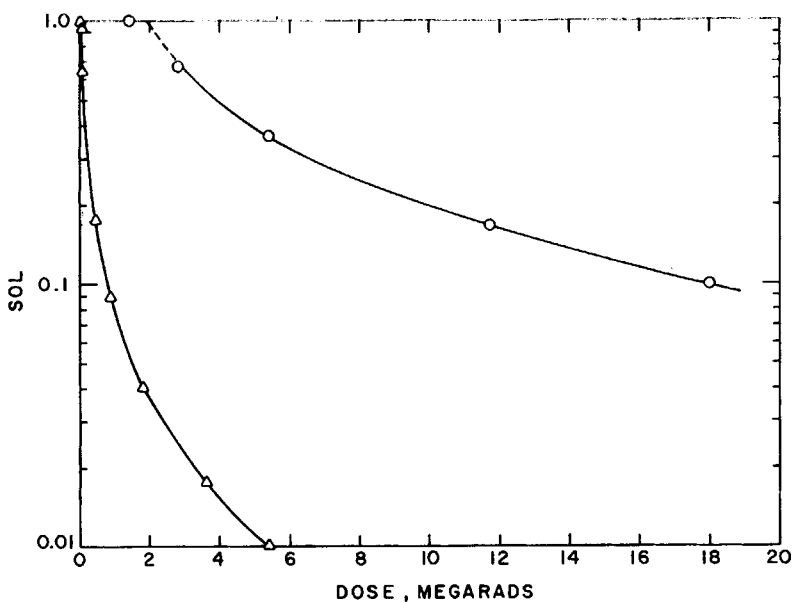Fig. 2. Logarithmic plot of sol vs. dose: (O) and (△) as in Figure 1.

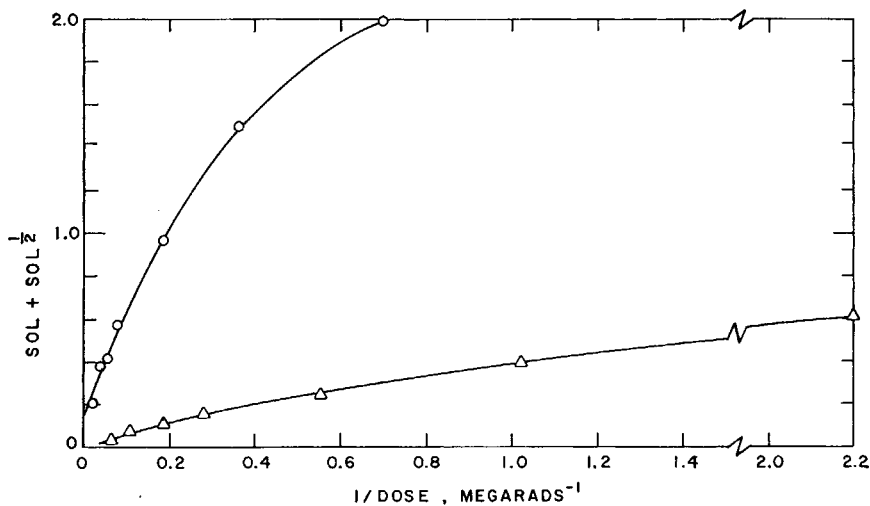Fig. 3. Semilogarithmic plot of sol vs. dose: (O) and (△) as in Figure 1.

Fig. 4. Charlesby-Pinner plot of (sol + sol$^{1/2}$) vs. (1/dose):   (O) and (△) as in Figure 1.

(more than 90% insolubilization) occurs at doses lower than 1 Mrad.   This emphasizes that norbornenyl-containing vinyl polymers are among the most responsive systems to radiation curing that have ever been examined. The reduction in dose required for complete curing of such copolymers is dramatically shown in Figure 1 by comparing the plot of curing for the control ethylene–vinyl acetate copolymer with that of the norbornenyl-modified system.

Figures 2 and 3 show log–log and semilog plots of sol fraction versus dose for the ethylene–vinyl norbornenecarboxylate copolymer and its ethylene–vinyl acetate precursor. The log–log plot (Fig. 2) for the precursor is linear; that of the modified material shows curvature at low doses.

Charlesby[25] has shown that for polymers having random molecular weight distribution, and in which crosslink density is directly proportional to dose, random crosslinking processes (C—H homolysis, followed by interchain coupling) are represented by linear plots of log (sol fraction) versus log (dose). Thus, Figure 2 suggests a random process for the precursor resin, and for the modified resin at higher doses. Charlesby has also shown that, by contrast, linear plots of log (sol fraction) versus dose are indicative of chain processes (interchain telomerizations). Such a plot (Fig. 3) tends toward linearity only at low doses for the modified resin.

On this basis, the results in Figures 2 and 3 suggest that the crosslinking process is a chain reaction at low doses and becomes predominantly a non-chain process at higher doses. Such an interpretation is reasonable if we picture an interchain radical telomerization of norbornenyl groups proceeding until all within close proximity have reacted; then, as the dose increases, crosslinking becomes random—that is, C—H homolysis followed by interchain radical coupling becomes the dominant process.

Such a picture is obviously an oversimplification; we cannot tell a random interchain coupling process from a single addition of a chain radical to a norbornene double bond followed by degradative chain transfer. Also, curves with a similar shape are obtained when the solubility–radiation data for low-density polyethylene samples are plotted in this manner.[25] In these cases, a chain process is not likely; the deviation of the log–log plot near the gel point from a straight line is due to the very broad molecular weight distribution of the low-density polyethylene samples studied. That this deviation does not occur in the log–log plot of the ethylene–vinyl acetate base resin irradiation data may be due to randomization of the molecular weight distribution at the higher doses used.

Nevertheless, there does seem to be a substantial chain element in the crosslinking process. Further consideration of the gel–dose relationships shows the size of this effect. For example, Charlesby[25] has shown that for a random nonchain process the G value for crosslinks formed in a polymer can be estimated at high and low doses by the following equations:

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 r} \tag{1}$$

$$G_{cl} = \frac{0.48 \times 10^6}{M_w \times r_{gel}}. \tag{2}$$

The G-value, analogous to a quantum yield in photochemistry, is defined as the number of events that occur for each 100 eV absorbed by the system. G_{cl} is the G-value for crosslink formation and is twice that for crosslinked sites. In Charlesby's nomenclature, M_w is weight-average molecular

weight, r is radiation dose, r_{gel} is the radiation dose at which gel first begins to appear, u_1 is the number-average degree of polymerization, s is the sol fraction, p_0 is the fraction of monomer units broken per unit dose, and q_0 is the fraction of monomer units crosslinked per unit dose (and is twice the number of crosslinks, since each crosslink requires two crosslinked units).

Figure 4 is a plot of eq. (1). From the slope for the base resin (5.4), and the number-average degree of polymerization (1800), q_0 is 1.03×10^{-4}. Substitution of these values in eq. (3), which defines q_0, gives $G_{cl} = 1.65$:

$$G_{cl} = 0.48 \times 10^6 \, q_0/w = 1.65 \text{ for DQDA-1818.} \tag{3}$$

Alternatively, G_{cl} at low dose may be calculated from eq. (2) and the gel dose (r_{gel}) obtained most conveniently by extrapolation of Figure 2 to the upper axis, to give 2.0 Mrad. Calculation in this fashion gives $G_{cl} = 1.25$ without correction for degradation. A more correct calculation recognizes that some degradation occurs during the irradiations before the gel point. Correction for this degradation, according to Charlesby,[25] may be based on a revised definition of gel point, leading to

$$r_{gel} \times u_2 \times \left(q_0 - \frac{p_0}{2} \right) = 1. \tag{4}$$

If the observed gel point and weight-average degree of polymerization, and the relationship $p_0 = 0.15q_0$ (from the intercept of the Charlesby-Pinner plot), are substituted in eq. (4), q_0 is increased, raising to 1.36 the G_{cl} calculated from the gel point. This treatment requires that p_0/q_0 is independent of dose. This low-dose G_{cl} (1.36) compares reasonably well with the high-dose value (1.65). Differences may be due to errors in molecular weight distribution, extrapolation in Figures 2 and 4, or changes in p_0/q_0 at low doses.

Application of these two types of calculation of G_{cl} to the modified resin gives $G_{cl} = 67$ at low dose (using $r_{gel} = 0.035$ Mrad). Use of the slope of the high-dose end of the Charlesby-Pinner plot gives $G_{cl} = 15$. The magnitude of these values immediately suggests a chain process. This, in turn, renders the results just obtained on the modified resin theoretically groundless, since the Charlesby-Pinner theory as described is based on a random, nonchain crosslinking process, with crosslinking yield (q_0) not a function of dose. However, even though quantitative evaluation of the data lacks adequate theoretical backing, there is no doubt that a highly efficient chain process contributes to crosslinking at low dose.

Charlesby has amplified the treatment of low-dose crosslinking for chain processes.[25] In particular, he has derived the following equation for chain crosslinking of polyester systems:

$$r_{gel} = \frac{0.5 \times 10^6 i^2}{G_i \times M_w}$$

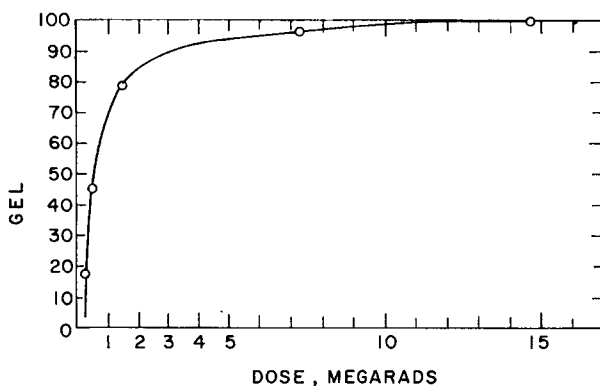$$i^2 = \frac{0.035 \times 2.72 \times 2.05 \times 10^5}{5 \times 10^5} = 0.039. \tag{5}$$

Fig. 5. Gel vs. dose for VAGH, a copolymer of vinyl acetate, vinyl alcohol, and vinyl chloride, modified by reaction with norbornenylmethyl isocyanate.

The derivation requires that there be several reactive sites per weight-average molecule and that i (approximately equal to the reciprocal of the kinetic chain length) be considerably smaller than 1. Unfortunately, eq. (5) requires knowledge of G_i, the G-value for initiation. We might equate this with the G-value for crosslinked sites in the base resin, as a first approximation. This is twice G_{cl}, or 2×1.36. We then obtain $i =$ 0.20, for a chain length of approximately 4.

The striking shape of the gel–dose curves, where rate of gel formation is very high at low dose, is characteristic of several polymers containing pendant norbornenyl unsaturation (Fig. 5,6). The gel point and total insolubles at a given dose are a function of the polymer molecular weight and norbornenyl group concentration. In contrast to normal polymers, and especially at the low doses used for these studies, the gel formation is *not* related to the scission–crosslink ratio of the base polymer. That is, of course, a restatement of the fact that the Charlesby-Pinner treatment is not valid. An illustration of the enhancement of crosslinking is Figure 5, where a vinyl chloride copolymer, which normally has a high scission-to-crosslink ratio, gives 70% insolubilization at 1 Mrad and 90% at 3 Mrad when modified with norbornenyl groups. Similarly, the norbornenyl modification of cellulose acetate, a polymer in which chain scission predominates, provided extensive curing at low doses: 70% insolubilization at 1 Mrad, 90% at 5 Mrad. This is illustrated in Figure 6, where it is shown that, in sharp contrast, the same polymer with a low norbornenyl content developed negligible gel, even at 12.5 Mrad.

The ability of the norbornenyl group to enhance the crosslinking of polymers is striking in these systems and is due to the high reactivity of the double bond toward free radicals. The predominant mode of reaction is probably addition of a free radical on an adjoining chain to the double bond, followed by hydrogen transfer or interchain telomerization. This is consistent with the observed low kinetic chain length (approximately 4).
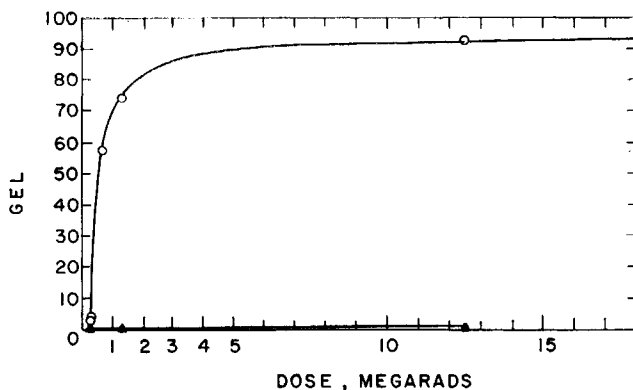
Fig. 6. Gel vs. dose for cellulose acetate E-383-40 reacted with norbornenylmethyl isocyanate: (O) 24% norbornenylmethyl incorporation; (△) 4% norbornenylmethyl incorporation.

Little hydrogen abstraction occurs at the norbornenyl site because of the inactivity of the bridgehead hydrogens.

The importance of the mode of reaction of the double bond in causing crosslinking was demonstrated by comparing the gel–dose curves of an ethylene–vinyl 5-norbornene-2-carboxylate copolymer and an ethylene–vinyl 1-cyclohexene-3-carboxylate copolymer of comparable molecular weight and unsaturation. In the latter, allylic hydrogen abstraction and subsequent interchain coupling should constitute the principal mode of crosslinking since the double bond has a lower methyl affinity (less than 1.0)[15] and the allylic hydrogens are more reactive. Figure 7 shows that norbornenyl-containing system achieved a much lower gel point (0.035
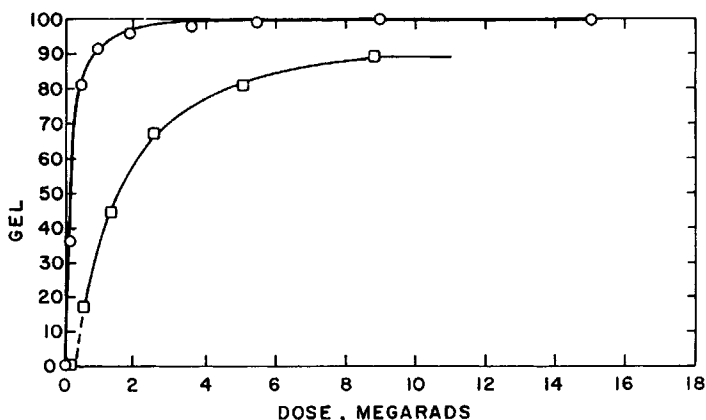

Fig. 7. Gel vs. dose plot: (□) ethylene–vinyl 1-cyclohexene-3-carboxylate copolymer; (O) ethylene–vinyl 5-norbornene-2-carboxylate. Copolymers of comparable molecular weight and unsaturation content.
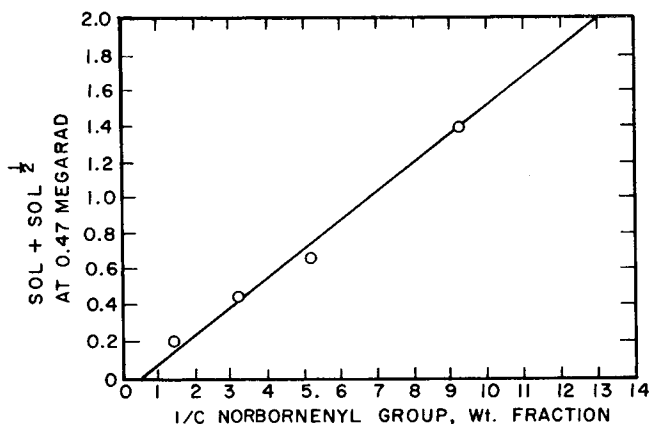
Fig. 8. (Sol $+$ sol$^{1/2}$) vs. reciprocal of concentration of norbornenyl group (w-%) for series of medium molecular weight poly(vinyl alcohols). All samples at a radiation dose of 0.25 Mrad.

versus 0.3 Mrad) and high overall gel than the corresponding cyclohexenyl polymer.

We can illustrate the dependence of crosslinking on the norbornenyl group in another manner. Equation (1) is derived by Charlesby as $s + s^{1/2} = 1/\gamma = 2/\delta$, where γ and δ are the number of crosslinked units per number- and per weight-average molecule, respectively, in a polymer with random distribution. These relationships are then converted to eq. (1), essentially on the basis that dose is linearly related to γ or δ. Thus, we can substitute any other quantity for dose in eq. (1), as long as this quantity is linearly related to γ or δ. Figure 8 is a plot of $(s + s^{1/2})$ versus (1/norbornenyl concentration) for a polyvinyl alcohol modified with various amounts of 5-isocyanatomethyl-2-norbornene, using a constant dose of 0.25 Mrad. Since the molecular weight distribution of this material is unknown, a linear plot is not necessarily expected. That the plot *is* linear is strong evidence for a linear dependence of the extent of crosslinking, at constant low dose, on the amount of norbornenyl group present. Such a linear dependence is consistent with polymerization kinetics in which rate is first order in monomer concentration.

Extrapolation of the line of this plot to the upper axis (where $s + s^{1/2} = 2.0$) gives 7.6% for the norbornenyl concentration in the polymer that would be required for an incipient gel point of 0.25 Mrad. The viscosity-average molecular weight of this polymer is about 65,000. If this is equated to weight-average molecular weight and the polymer were to contain 7.6 wt-% norbornenyl (isocyanatonorbornenyl) groups, it would contain 1.8 mole-%, giving about 27 norbornenyl groups per weight-average molecule.

References

1. M. Dole, D. C. Milner, and T. F. Williams, *J. Amer. Chem. Soc.*, **80**, 1580 (1958).
2. T. F. Williams and M. Dole, *ibid.*, **81**, 2919 (1959).
3. M. Dole, T. J. Stolki, and T. F. Williams, *J. Polym. Sci.*, **48**, 61 (1961).
4. M. Dole, M. B. Fallgatter, and K. Katsuura, *J. Phys. Chem.*, **70**, 62 (1966).
5. T. Okada, L. Mandelkern, and R. Glick, *J. Amer. Chem. Soc.*, **89**, 4790, (1967).
6. B. J. Lyons and C. R. Vaughn, *Adv. Chem. Ser.*, **66**, 139 (1967).
7. B. J. Lyons, *J. Polym. Sci. A*, **3**, 777 (1965).
8. S. M. Miller, M. W. Spindler, and R. L. Vale, *J. Polym. Sci. A*, **1**, 2537 (1963).
9. B. S. Bernstein, G. Odian, G. Orban, and S. Tirelli, *J. Polym. Sci. A.*, **3**, 3405 (1965).
10. I. Auerbach, *Polymer*, **8**, 63 (1967).
11. A. Charlesby, *Adv. Chem. Ser.*, **66**, 1 (1967).
12. G. Vaughan, D. E. Eaves, and W. Cooper, *Polymer*, **2**, 235 (1961).
13. W. W. Parkinson and W. C. Sears, *Adv. Chem. Ser.*, **66**, 57 (1967).
14. A. R. Shultz, *Encycl. Polym. Sci. Tech.*, **4**, 398 (1966).
15. J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 3005 (1961).
16. R. C. Fort, Jr., and R. E. Franklin, *J. Amer. Chem. Soc.*, **90**, 5267 (1968).
17. E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).
18. Unpublished results from these laboratories.
19. H. Fricke and E. J. Hart, in *Radiation Dosimetry*, Vol. 2, F. H. Attix and W. C. Roesch, Eds., Academic Press, New York, 1966, pp. 186–197.
20. F. J. Hassbroek, Brookhaven National Laboratory Report BNL-763, 1962.
21. E. J. Williams, *Proc. Roy. Soc., Ser. A.*, **130**, 310 (1931).
22. L. A. Teichman and E. S. Armstrong, NASA-TN-D-2010, 1963.
23. M. J. Berger and S. M. Seltzer, NAS-NRC Publication 1133, second printing, July, 1967.
24. N. Nuenke and J. Milgrom, *J. Polym. Sci. A-2*, **4**, 158 (1966).
25. A. Charlesby, *Atomic Radiation and Polymers*, Pergamon Press, New York, 1960, Chapters 8–11.