# The Radiation Crosslinking of Poly(vinyl Chloride) with Trimethylolpropanetrimethacrylate. III. Effect of Diundecyl Phthalate: Chemical Kinetics of a Three-Component System

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## Synopsis

The radiation chemistry of poly(vinyl chloride) (PVC) blended with trimethylolpropanetrimethacrylate (TMPTMA) and diundecyl phthalate (DUP) has been examined. This three-component mixture contains a base resin (PVC), a crosslinking sensitizer (TMPTMA), and a physical modifier (DUP). These are the basic components in any radiation-curable coating. The kinetics and mechanism of the crosslinking reactions were studied with reference to the dependence on radiation dose and blend composition. The polyfunctional TMPTMA underwent polymerization incorporating the PVC into a 3-dimensional network. DUP remained chemically inert during the irradiation, not being bound to the network. However, DUP by plasticizing the macromolecules and diluting the monomer, changed the kinetics extensively. DUP enhanced TMPTMA homopolymerization, TMPTMA grafting, and PVC crosslinking reaction rates. The effect on the competition between polymerization, grafting, and degradation reactions was examined in terms of enhanced mobility of the reacting species. The influence of these kinetic considerations in selecting a blend composition for a coating application was discussed.

## INTRODUCTION

Poly(vinyl chloride) (PVC) in the presence of polyfunctional monomers undergoes rapid crosslinking upon exposure to ionizing irradiation. The monomer needs to be able to be crosslinked by irradiation as well as to incorporate the PVC molecules into the network via grafting reactions. A number of unsaturated monomers have been shown to act as sensitizers for PVC,[1-5] among which the polyfunctional methacrylates and acrylates were found to have the greatest sensitivity. A typical formulation for a radiation-curable coating includes a base resin (e.g., PVC), a crosslinking sensitizer (e.g., polyfunctional monomer), and a plasticizer.[4] The plasticizers are used to obtain the required physical properties for a specific coating application. These crosslinked coatings have higher heat and abrasion resistance than ordinary plasticized PVC. In commercial formulations, additional stabilizers and filler materials are common. However, the fundamental chemistry and physical properties of the systems are determined by the three components noted above. We have selected the system of PVC blended with trimethylolpropanetrimethacrylate (TMPTMA) and diundecyl phthalate (DUP) as a representative example of such radiation-curable coatings.

In previous papers, the effects of irradiation temperature, irradiation dose, and thermal treatment of a PVC/TMPTMA blend were discussed.[6,7] It was

shown that there was an initial preference for TMPTMA homopolymerization after which PVC molecules were bound into the network. Increasing the irradiation temperature primarily increased all the reaction rates equally. However, dehydrochlorination of the PVC did begin to compete with the grafting and crosslinking mechanisms at the high temperatures (>80°C). Post-irradiation thermal treatment was shown to markedly alter the physical properties of the irradiated blends. This was caused by the reactions of residual monomer molecules and unreacted double bonds in the crosslinked network. TMPTMA does not use all of the available double bonds to form the network.

Over a wide range of blend compositions the crosslinking rate was found to be proportional to the TMPTMA concentration. As the TMPTMA concentration decreased, soluble graft copolymers were produced in addition to insoluble networks. A GPC–LC technique provided compositional information on the gel and sol fractions, which was then used to discuss the kinetics in terms of a competition between homopolymerization, grafting and degradation reactions.[7]

We will now consider the three component blends of PVC, TMPTMA, and DUP in terms of the molecular crosslinking mechanism. This paper will investigate the chemical kinetics of network formation in these blends.

## EXPERIMENTAL

Poly(vinyl chloride) with $\overline{M}_n$ = 60,000 g/mol was obtained from Goodrich Co. Trimethylolpropanetrimethacrylate (TMPTMA) (1)

$$CH_3CH_2C(CH_2\!-\!O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{C}\!=\!CH_2)_3$$

(1)
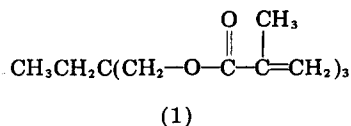
was procured from Ware Chemical Corp. and the plasticizer diundecyl phthalate (DUP), was obtained from Monsanto Co.

The TMPTMA monomer (with thermal stabilizers) plus DUP was added gradually to the PVC in a high speed blender at 60–70°C. The resulting powders were roll-milled to ensure adequate mixing and then compression-molded in a steam press at 150–160°C for 2.5 min to produce sheets 100–400 $\mu$m thick. The compositions of the blends were checked by gel permeation chromatography (GPC) and chlorine elemental analysis (see Table I).

Irradiations were carried out with a Dynamitron electron beam accelerator using 1.5 MeV electrons at currents of 0.4–1.0 mA, to doses up to 50.0 Mrad. The irradiations were carried out under a nitrogen atmosphere at room temperature (20–23°C) as previously described.[6]

The gel content was determined by (1) Soxhlet extraction and (2) gel permeation chromatography (GPC). In the Soxhlet process, 1–2 g of material was placed in a cellulose thimble and extracted for 20–25 h with refluxing tetrahydrofuran. The insoluble material was dried at 80°C to constant weight (required 45–60 min). This was defined as the gel content of the sample.[7]

The technique for the GPC analysis of the two component blends has been described elsewhere.[8] The simple extension to this three component blend required a column set consisting of seven $\mu$-Styragel columns having porosities

TABLE I
Blend Compositions[a]

| Blend | Composition | | | |
| | % PVC from | | | |
| | GPC | % Cl | % TMPTMA | % DUP |
|---|---|---|---|---|
| A | 100 | 100 | 0 | 0 |
| B | 91 ± 1 | 91 ± 1 | 9 ± 1 | 0 |
| C | 77 ± 2 | 74 | 18 ± 2 | 0 |
| D | 62 ± 2 | 63.5 | 32 ± 2 | 0 |
| E | 91 ± 1 | — | 0 | 9 ± 1 |
| F | 78 ± 2 | — | 0 | 20 ± 1 |
| G | 81 ± 1 | 78 | 8.5 ± 1 | 8 ± 1 |
| H | 73 ± 2 | 75 | 18 ± 1 | 7 ± 1 |
| I | 61 ± 1 | — | 29 ± 2 | 6 ± 1 |
| J | 64 ± 2 | 62 | 17 ± 1 | 16 ± 1 |

[a] All blends contain 2–4% dibasic lead phthalate as thermal stabilizer. ·

of $10^6$, $10^5$, $10^4$, $10^3$, 500, 100 and 100 Å, respectively. The latter three columns were necessary to obtain baseline resolution between TMPTMA, DUP, and $CCl_4$ (internal standard). A typical analysis time was 40 min at a flow rate of 2 mL/min.

For infrared spectroscopy, films were cast from 1% solutions (in tetrahydrofuran) onto KBr windows and teflon surfaces. The former may be analyzed as prepared; the latter was lifted from the teflon surface prior to spectral analysis. Samples were irradiated up to 50 Mrad. From the infrared spectra, unsaturation was measured using the ratio of the absorbance at 1630 cm$^{-1}$ to that at 690 cm$^{-1}$ and to that at 630 cm$^{-1}$. The 1630 cm$^{-1}$ resonance arises from the C=C stretching mode, while the 690 cm$^{-1}$ and the 630 cm$^{-1}$ resonances are from C—Cl stretching modes.[9,10] Using the absorbances at 690 cm$^{-1}$ and 630 cm$^{-1}$ for internal reference avoids any effects of thickness variations across the films. A Perkin-Elmer Spectrophotometer Model 597 was used.

## RESULTS

Figure 1 shows the percent gel versus radiation dose for the blends. Blends containing TMPTMA show low incipient gel doses (less than 0.1 Mrad). Crosslinking rates were initially high, but after approximately 1.0 Mrad the rates decreased markedly. A conversion limit was approached asymptotically at high dose; a limit determined by blend composition. Blends with no TMPTMA (pure PVC or PVC/DUP blends) showed no significant gel formation.

Figure 2 shows the subset of blends which have 7 ± 2% DUP. The more TMPTMA present the higher was the initial rate and final conversion of the crosslinking reactions, as shown in Figure 3. An upper limit for gelation rate will be 0.5% gel/rad, the homopolymerization rate of pure TMPTMA. The qualitative relationship was similar to that previously found for PVC/TMPTMA blends with no DUP present.[7] However, the absolute values of the rates were higher with DUP present. Holding TMPTMA content constant at 17 ± 1% and varying the DUP content produced the kinetic data shown in Figures 4 and 5.
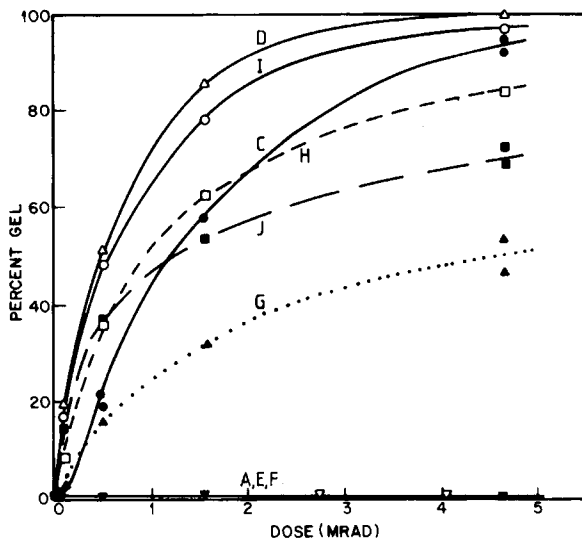
Fig. 1. Percent gel vs. irradiation dose.  Blend designations are adjacent to curves (see Table I).

As the %DUP was *increased* the initial gelation rate *increased* while the final conversion after 5 Mrad *decreased* (Fig. 5).

To determine the compositional changes during irradiation (e.g., the chemical nature of the gel), the soluble fractions were analysed by GPC.  A typical chromatogram for the three-component blends is shown in Figure 6.  As the irradiation dose increased, the soluble fraction decreased with TMPTMA and PVC being incorporated into the gel.  TMPTMA reacted faster than PVC.  Generally, the PVC molecules with the higher molecular weight were preferentially cross-linked into the network, since they have more potential sites for reaction and binding to the network.  The DUP peak remained unchanged throughout the irradiation.  The DUP was chemically inert and was not bound or entangled into the network.
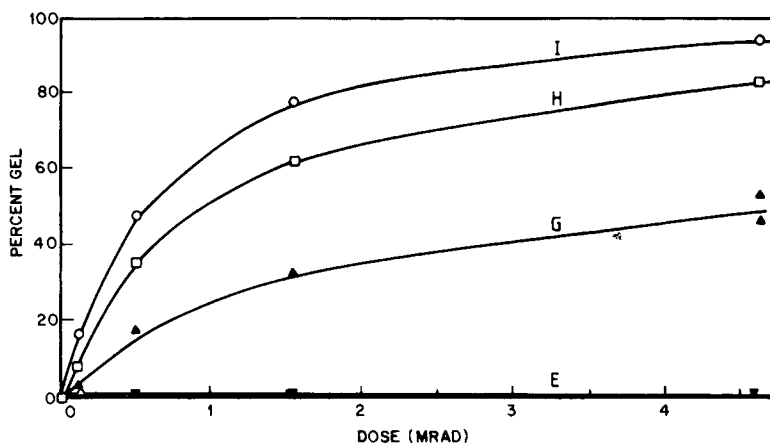


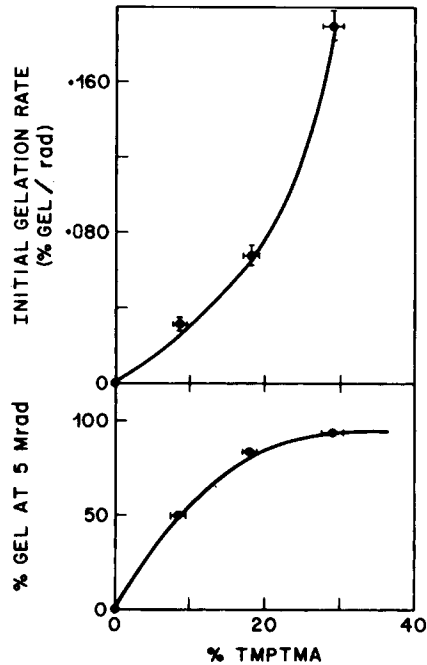Fig. 2.  Percent gel vs. dose for blends with 7 ±2% DUP.  Blend designation as in Figure 1.

Fig. 3. Initial gelation rate and % gel (5 Mrad) vs. % TMPTMA in blends with 7 ± 2% DUP.

Figure 7 shows the incorporation of PVC and TMPTMA into the gel as a function of dose for three representative blends.   Blends C and D have no DUP present.   Initially both PVC and TMPTMA were incorporated rapidly with a small preference for TMPTMA crosslinking.   At high doses (i.e., high conversion) the incorporation rates decreased.   At this stage, depletion of TMPTMA resulted in the PVC crosslinking reactions becoming most important for further gel formation.   Addition of DUP enhanced both rates initially; compare blend J to
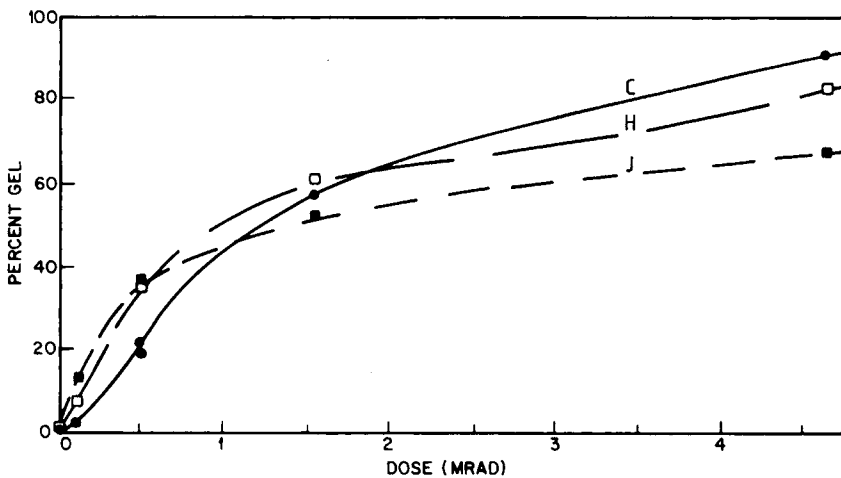


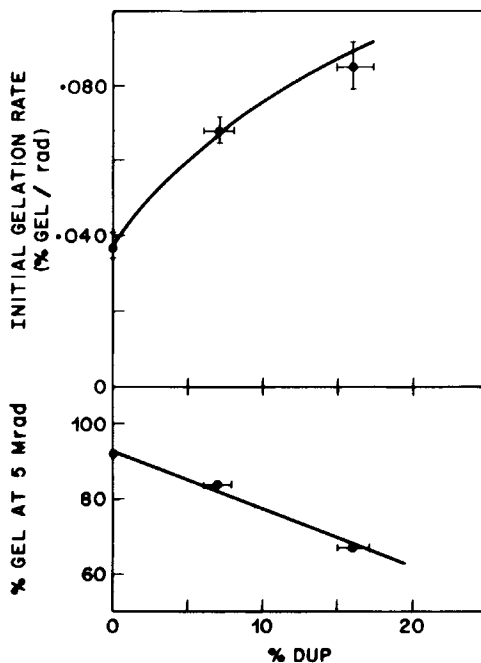Fig. 4. Percent gel vs. dose for blends with 17 ± 1% TMPTMA.   Blend designation as in Figure 1.

Fig. 5. Initial gelation rate and % gel at 5 Mrad vs. % DUP in blends with 17 ± 1% TMPTMA.

blend C. For example, the TMPTMA homopolymerization was enhanced such that for blend J all TMPTMA has been crosslinked before 20% of the available PVC was locked into the network. To see the effect of DUP addition on the incorporation rates, the data in Figure 7 was normalized by plotting percent
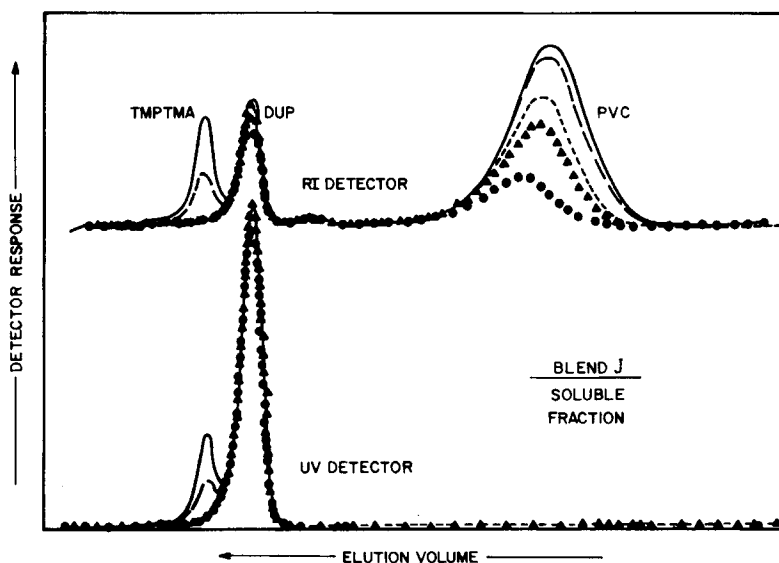


Fig. 6. GPC profiles for soluble fractions of blend J. Refractive index (RI) and ultraviolet (UV) detector traces are shown as a function of elution volume. (——) 0 Mrad; (– –) 0.1 Mrad; (- - -) 0.5 Mrad; (▲) 1.55 Mrad; (●) 4.64 Mrad.
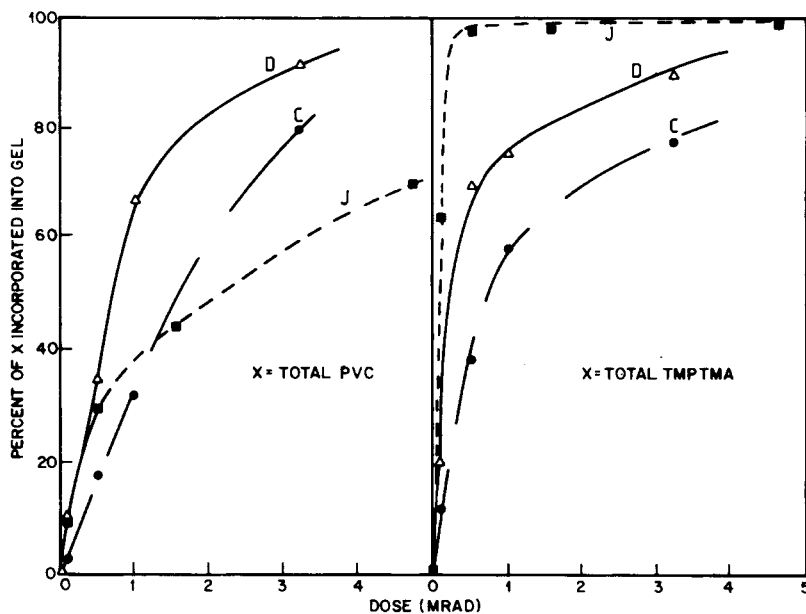
Fig. 7. Percent of PVC and TMPTMA incorporated into the gel as a function of radiation dose. Blend designation adjacent to curves (see Table I for composition).
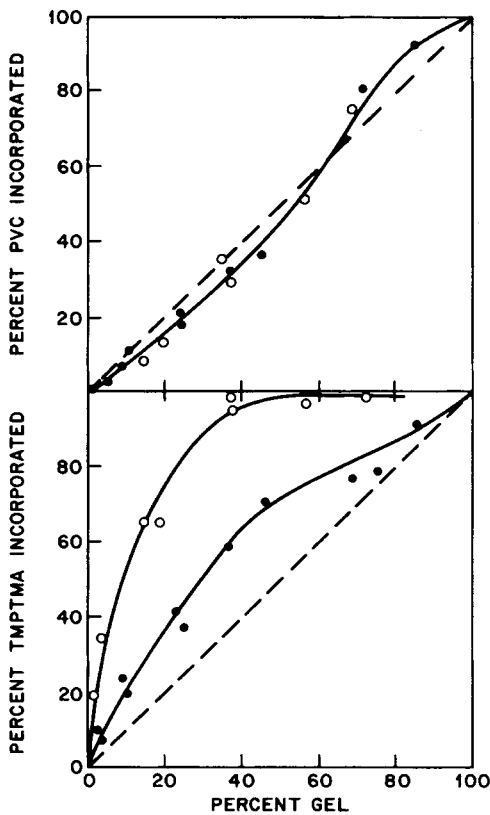


Fig. 8. Percent of PVC and TMPTMA incorporated into gel vs. % gel (i.e., extent of reaction). (O) Blends with DUP (J and G); (●) blends with no DUP (B, C, D).
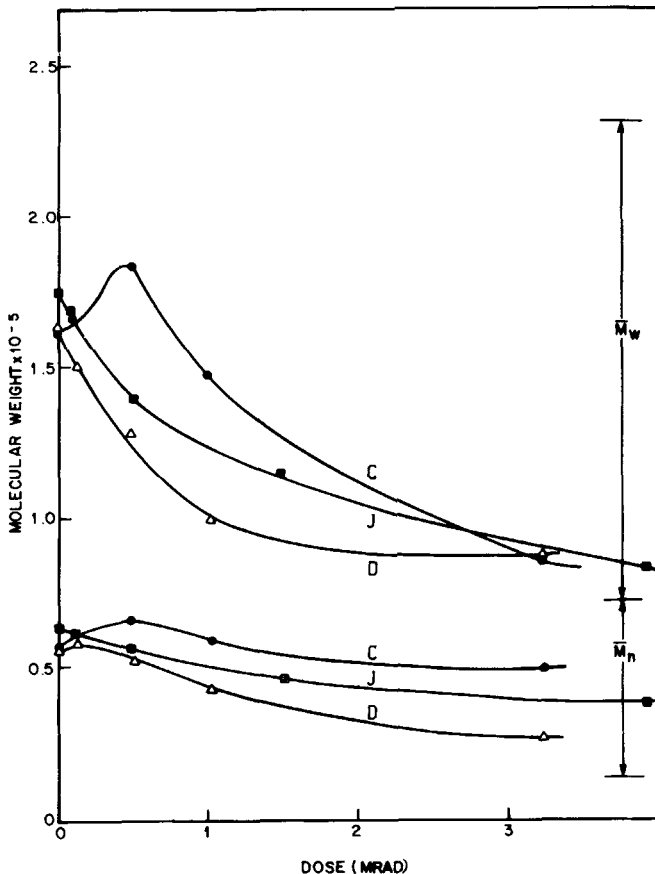
Fig. 9. $\overline{M}_n$ and $\overline{M}_w$ of soluble PVC vs. radiation dose. Blends C, D, J: see Table I for composition.

incorporated versus percent gel (i.e., extent of reaction) and is shown in Figure 8. Data from all the blends is included in Figure 8. For TMPTMA incorporation two distinct curves were found, one for blends with DUP present and one for blends without DUP. For PVC incorporation similar behavior was found for all the blends.

If uniform crosslinking occurred, the dashed lines in Figure 8 would result, that is, blend composition would equal gel composition across the entire range. With PVC/TMPTMA blends, a small preference for TMPTMA incorporation over PVC incorporation was found. This preference was reversed at high conversion when TMPTMA had been depleted. With DUP present, the preference was large enough that the crosslinking reaction became a distinct two step process: (1) the formation of the TMPTMA network and (2) PVC grafting onto that network. Since DUP was chemically inert during the irradiation, its mechanical properties (plasticization and dilution of the blends) would be expected to be responsible for this behavior.

The competition between (1) homopolymerization of TMPTMA and (2) grafting of the PVC onto the network can be examined by determining the molecular weight characteristics of the soluble PVC fractions (Figs. 9 and 10). The
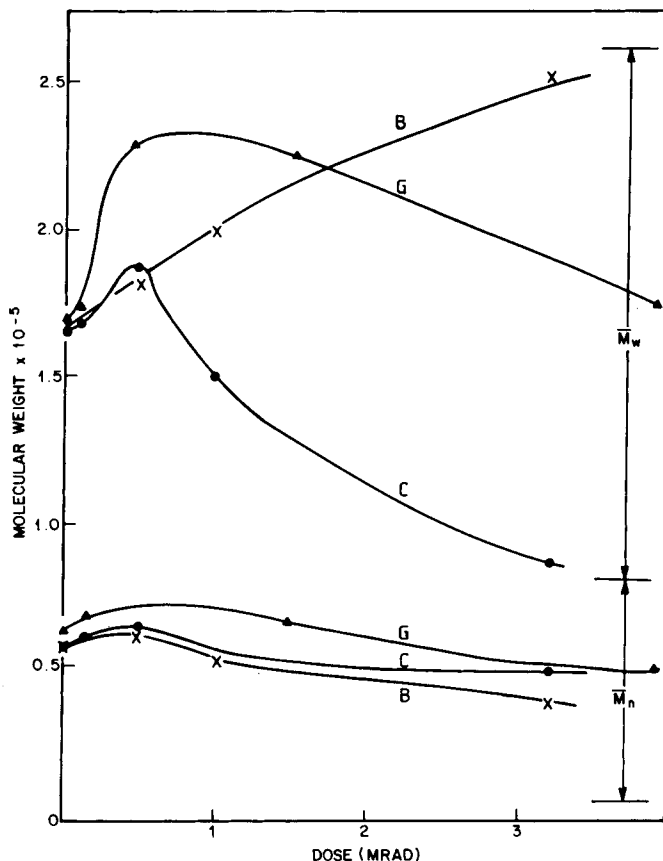
Fig. 10. $\overline{M}_n$ and $\overline{M}_w$ of soluble PVC vs. radiation dose. Blends B, C, G: see Table I for composition.

weight average molecular weight $(\overline{M}_w)$ has been found to be more sensitive to the changes than the number average molecular weight $(\overline{M}_n)$.[7]  If TMPTMA homopolymerization was favored, then a TMPTMA-rich network rapidly forms and the PVC molecules are slowly crosslinked or grafted onto the gel.  Since larger PVC molecules have more possible sites for reaction, they have a higher probability of becoming bound to the gel and therefore the average molecular weight of the soluble fraction will decrease (blends J and D in Fig. 9) as the radiation dose increases.[11]  The increases observed in $\overline{M}_w$ in Figure 10 are assumed to arise from PVC–(TMPTMA)$_x$ and PVC–(TMPTMA)$_x$–PVC graft structures. Since pure PVC showed no significant crosslinking in this dose range (Table II), the crosslinked PVC molecules were formed via TMPTMA grafts.  For the macromolecules to be soluble, $x$ will be small, e.g., 1–4.  When the grafting reactions compete efficiently with homopolymerization for the TMPTMA molecules, then $\overline{M}_w$ will increase.  The more dilute that a blend was in TMPTMA, the higher was the probability of a TMPTMA molecule being grafted to PVC instead of homopolymerizing to another TMPTMA molecule.  This is illustrated by considering blend C (Fig. 9 and 10) in which the grafted and crosslinked products resulted in an initial $\overline{M}_w$ increase.  Further crosslinking reactions,

TABLE II
Molecular Weight of Irradiated PVC

| Irradiation dose (Mrad) | $\overline{M}_n \times 10^{-5}$ (g/mol) | $\overline{M}_w \times 10^{-5}$ (g/mol) | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|
| 0 | 0.60 | 1.48 | 2.5 |
| 0.5 | 0.54 | 1.59 | 2.9 |
| 1.0 | 0.54 | 1.56 | 2.9 |
| 2.0 | 0.55 | 1.53 | 2.8 |
| 4.0 | 0.50 | 1.75 | 3.5 |

however, bound the soluble macromolecule onto the insoluble network, and, therefore, the $\overline{M}_w$ of the soluble fraction decreased. In Figure 10, three of these dilute blends are shown. With the PVC/TMPTMA blends of less than 10% TMPTMA (e.g. blend B), the $\overline{M}_w$ value monotonically increased across the dose range examined. Upon adding DUP to such a blend (blend G, Fig. 10), the formation of PVC–(TMPTMA)$_x$–PVC structures was enhanced, and $\overline{M}_w$ rose faster (compare blend G with blend B, Fig. 10). The shape of the $\overline{M}_w$ plot will depend on the mobility and concentration of (1) the residual double bonds in the PVC–(TMPTMA)$_x$–PVC molecules, (2) the residual TMPTMA molecules, and (3) free radicals, chiefly methacrylate-type free radicals.[6,7] The kinetic competition between different reaction pathways was affected by the plasticizing ability of DUP since this will affect the mobility of the reacting species. For example, this increased mobility would increase the rate at which PVC–(TMPTMA)$_x$–PVC structures were bound onto the network. This effect resulted in the decrease of $\overline{M}_w$ for blend G at high dose (Fig. 10).

There were minor amounts of grafting and crosslinking during the mechanical mixing of the blends.[7] Thermally induced grafting may be assumed to account for the small variations of the initial molecular weights in Figures 9 and 10. Crosslinking as measured by Soxhlet extraction was less than 3% prior to irradiation (Figs. 1, 2, 4). However, without thermal stabilizers present in TMPTMA, homopolymerization will be initiated. For example, if blend C is prepared without TMPTMA stabilizers, then homopolymerization is 90% complete prior to irradiation.

The residual double bonds noted above were determined via IR spectroscopy. For the PVC/TMPTMA blends (no DUP) the onset of gelation occurred with minimal consumption of double bonds. For example, 80% gelation was obtained using only ~30% of the available double bonds as seen in Figure 11. On average,
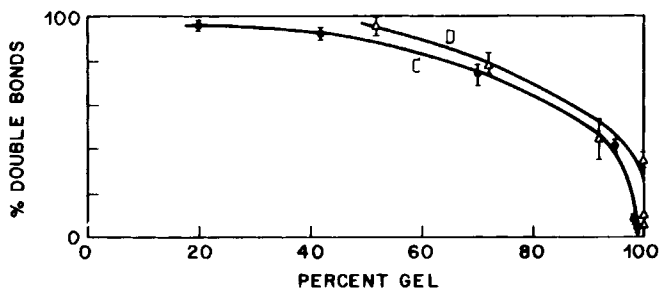


Fig. 11. Percent residual double bonds vs. % gel. Blends with no DUP (see Table I).
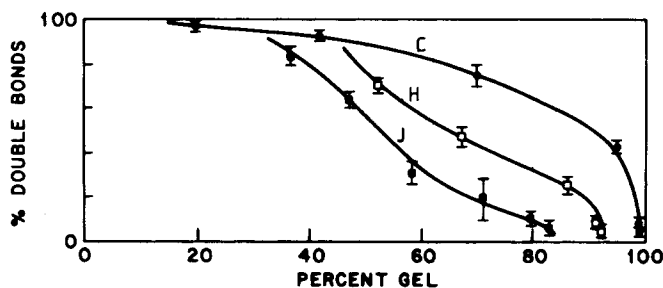
Fig. 12. Percent residual double bonds vs. % gel for blends with 17 ± 1% TMPTMA (blends C, H and J; see Table I).

only one of the three double bonds per TMPTMA molecule was used in the initial network formation.   The residual double bonds were restricted but not inert. Although one had obtained 100% gelation, the residual double bonds and methacrylate free radicals diffused together slowly, continuing polymerization and increasing crosslink density.[7]

Figure 12 shows the effect of adding DUP to the blends (TMPTMA is constant at 17 ± 1%).   The more DUP present, the larger was the percentage of double bonds used in obtaining a given percentage gel.   The more DUP present, the higher will be the mobility of the side chains of the bound TMPTMA moieties. Therefore, the double bonds on these side chains reacted faster when DUP was present.   The presence of the chemically inert DUP resulted in an upper conversion limit; note the intercepts on the percent gel axis in Figure 12.   The decay of unsaturation for the subset of blends with DUP = 7 ± 1% is shown in Figure 13.   The competition between grafting and homopolymerization mechanisms can be observed by considering these plots.   The presence of DUP enhanced these effects.   For example, in Figure 13, as the TMPTMA content was reduced, more double bonds were required to build an insoluble network.   Competition to form soluble PVC–(TMPTMA)$_x$ and PVC–(TMPTMA)$_x$–PVC structures depleted the double bonds without forming gel (blend G in Fig. 13).

## DISCUSSION

Upon irradiation of a three-component blend, free radicals were produced in the TMPTMA and PVC molecules.   DUP had a relatively high stability towards
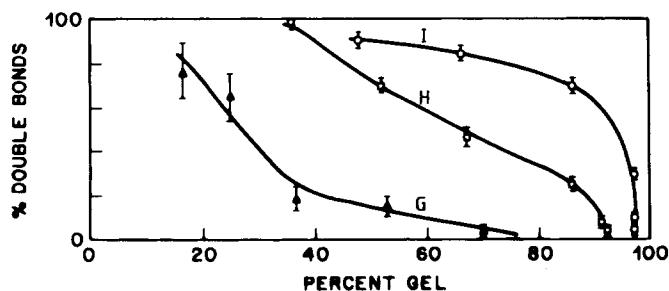


Fig. 13. Percent residual double bonds vs. % gel for blends with 7 ± 2% DUP (blends G, H and I; see Table I).

irradiation. Similar stability has been observed in other aromatic compounds and attributed to energy transfer to the aromatic ring with subsequent nondegradative dissipation of the energy.[12] Radicals will primarily initiate homopolymerization of the TMPTMA or grafting onto the PVC backbone.

In PVC, carbon–chlorine and carbon–hydrogen bonds are the most susceptible to cleavage by ionizing radiation, producing free radical sites on the polymer backbone.[13,14] During irradiation of pure PVC, these radicals would initiate dehydrochlorination and small amounts of main chain scission and crosslinking. The radiation chemical yields for PVC are G(HCl) = 13, G(crosslinking) = 0.3, G(scission) = 0.2 at 25°C.[13–15] This dehydrochlorination proceeds via a chain reaction to produce conjugated double bonds. These unsaturated structures absorb in the UV-visible region, thereby producing discoloration in the PVC. In the blends, the free radical sites are scavenged by TMPTMA, which grafts to PVC and initiates incorporation into the network via structures like PVC–$(TMPTMA)_x$, PVC–$(TMPTMA)_x$–PVC, etc.

The competition between polymerization, grafting, and degradation has been explored previously for the PVC/TMPTMA blends.[6,7] The introduction of DUP into the mixtures enhanced (1) TMPTMA homopolymerization, (2) TMPTMA grafting, (3) PVC crosslinking (at low doses), and (4) reactivity of double bonds. These effects are interrelated. For example, TMPTMA grafting produced precursors for PVC crosslinking. Among the parameters that determine the chemical kinetics of the system are the concentration and mobility of the reactants. The competition between reactions (1), (2), and (3) above are determined by the reactivity and mobility of the double bonds. The ease with which PVC, TMPTMA, and free radicals can diffuse through the matrix and react together will be constantly changing throughout the reaction. With PVC/TMPTMA blends, the medium changes from a flexible PVC resin (plasticised by the monomer) to a 3-dimensional network (strong and brittle).[6,7] With DUP present, the blends remain flexible after irradiation. On a molecular level, this means that the mobility of the reactive species remains high. Until high conversions were reached, the mobility of the reactive sites was enhanced by the presence of DUP and the double bonds were accessible for reaction. For instance, although blend J irradiated to 5 Mrad has 100% of the TMPTMA and 75% of the PVC incorporated into an insoluble network, all the DUP present can be extracted from the network (Fig. 6). The network remains sterically open to penetration by small molecules.

DUP affects the kinetic competition between the homopolymerization, crosslinking, and grafting reactions by controlling the mobility of the reacting species. Let us consider the results shown in Figure 10. With blend B (no DUP) the mobility of the macromolecules was restricted and the reactions of the PVC–$(TMPTMA)_x$–PVC structures to bind to the 3-dimensional network will be slow. With DUP present (blend G) the plasticization allowed reactive sites (free radicals) and residual unsaturation to diffuse together. The result was the rapid incorporation of the PVC–$(TMPTMA)_x$–PVC structures into the gel and, therefore, a decrease in $\overline{M}_w$ of the soluble fraction.

These results show that in the manufacture of crosslinked coatings, the inclusion of DUP would result in energy efficiency, double bond efficiency, and a more stable product. The increase in mobility (due to DUP) produced faster crosslinking, and therefore required less irradiation (less energy). A typical dose

required was 4 Mrad.   Maximum utilization of double bonds (Figs. 12 and 13) allowed one to attain a high crosslink density without using high doses (double bond efficiency).   Since the residual double bonds will be reacting after irradiation, post-irradiation stability will be improved.   These double bonds will scavenge the free radicals that initiate degradation.   One must compromise to attain these advantages; for example, addition of DUP limits the conversion one may achieve.   The mechanical and thermal properties of the blends are equally important as the crosslinking kinetics in determining the required blend composition for a desired coating application.   The physical properties of these three-component blends will be discussed in a subsequent publication.

## CONCLUSION

The molecular crosslinking mechanism in terms of grafting, scavenging, and polymerization reactions of PVC and TMPTMA[6,7] has been found to be consistent when extended to three-component blends.   The addition of a plasticizer (DUP) as a third component in the blends highlighted the role that diffusion and mobility of the reactive species play in the kinetics of gelation.   The initial blend composition determines the formation kinetics and molecular structure of the crosslinked network.

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