

# **Radiation Crosslinking of Poly(vinyl Chloride) with Trimethylolpropanetrimethacrylate. II. Dependence on Radiation Dose and Blend Composition**

T. N. BOWMER, M. Y. HELLMAN, and W. I. VROOM, *Bell Laboratories,  
Murray Hill, New Jersey 07974*

## **Synopsis**

The radiation crosslinking of poly(vinyl chloride) (PVC) blended with trimethylolpropanetrimethacrylate (TMPTMA) has been examined. The polyfunctional TMPTMA undergoes polymerization incorporating the PVC into a 3-dimensional network. The kinetics and mechanisms of these crosslinking reactions were studied with particular reference to dependence on radiation dose and blend composition. 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 gel permeation chromatography technique provided compositional information on the gel and sol fractions. The competition between polymerization, grafting, and degradation reactions was examined.

## **INTRODUCTION**

A number of insulations and coatings used in high temperature environments are produced by the radiation crosslinking of poly(vinyl chloride) in the presence of polyfunctional monomeric additives. The coatings consist of a 3-dimensional network that has both heat resistance and abrasion resistance, advantages that ordinary plasticized PVC does not possess. A typical sensitizer needs to be able to be crosslinked by irradiation as well as incorporate the PVC molecules into the network via grafting reactions. Polyfunctional monomers that have been shown to act as such crosslinking sensitizers for PVC include, allyl esters,<sup>1</sup> dimethacrylates,<sup>2,3</sup> trimethacrylates,<sup>3</sup> triallyl isocyanurate,<sup>4</sup> divinyl benzene,<sup>2</sup> and triacrylates.<sup>3</sup> The polyfunctional methacrylates and acrylates were found to possess the greatest sensitivity.

The commercial formulations include a variety of secondary additives—nonreactive plasticizers, pigments, stabilizers, and other filler materials—that need to be removed or reduced to minimal quantities in order to investigate the fundamental chemistry of these PVC–monomer systems.

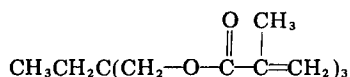
This study continues the discussion into the kinetics and mechanisms of the crosslinking processes involved in the poly(vinyl chloride)–trimethylolpropanetrimethacrylate system. In a previous paper,<sup>5</sup> the effects of irradiation temperature, irradiation dose, and thermal treatment were considered for only one blend composition. 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 higher tempera-

tures ( $>80^{\circ}\text{C}$ ). 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 is a trifunctional monomer).

This paper will discuss the relationship between the chemical kinetics and the network structure over a range of blend compositions. The composition of the gel and sol fractions, investigated by a GPC-LC technique,<sup>6</sup> will be used to investigate the competition between crosslinking, degradation, and grafting reactions.

## EXPERIMENTAL

Trimethylolpropanetrimethacrylate (TMPTMA) from Ware Chemical Corp. and poly(vinyl chloride) from Goodrich Co. were used. The structure of TMPTMA is:



The monomer, together with a thermal stabilizer, was added gradually to the PVC in a high speed blender at  $60\text{--}70^{\circ}\text{C}$ . These powders were compression molded in a steam press at  $150\text{--}160^{\circ}\text{C}$  for 2.5 min to give sheets from  $60\ \mu\text{m}$  to  $400\ \mu\text{m}$  thick. The compositions of the blends, given in Table I, were checked by chlorine elemental analysis and gel permeation chromatography.

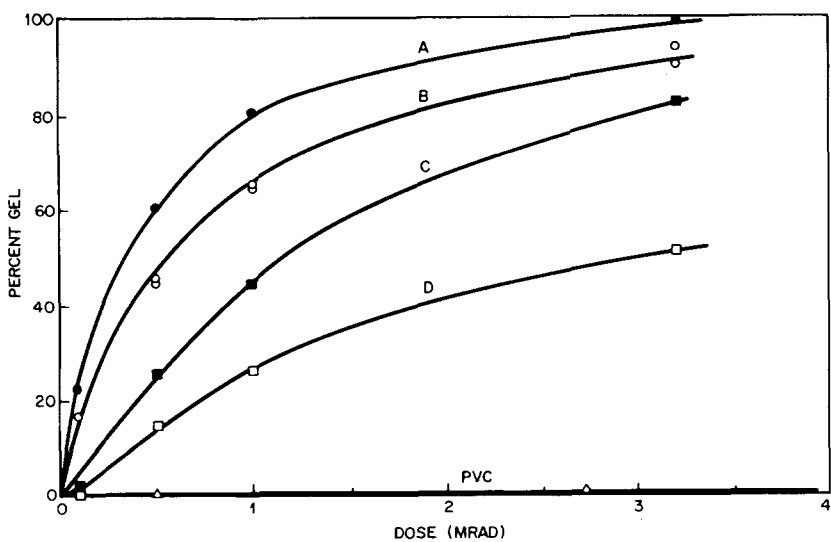
Irradiations were carried out with a Dynamitron electron beam accelerator using 1.5 MeV electrons at currents of 0.4–1.0 mA, to doses up to 4 Mrad. The irradiations were carried out under a nitrogen atmosphere at room temperature ( $20\text{--}23^{\circ}\text{C}$ ) as previously described.<sup>5</sup>

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 temperature in the thimble during the Soxhlet cycle varied from  $63.5^{\circ}\text{C}$  to  $65^{\circ}\text{C}$ —slightly less than the bp of tetrahydrofuran at  $67^{\circ}\text{C}$ . The insoluble material dried at  $60^{\circ}\text{C}$  to constant weight was defined as the gel content of the sample. Chlorine elemental analysis was performed on these gel fractions to determine the extent of PVC incorporation into the network.

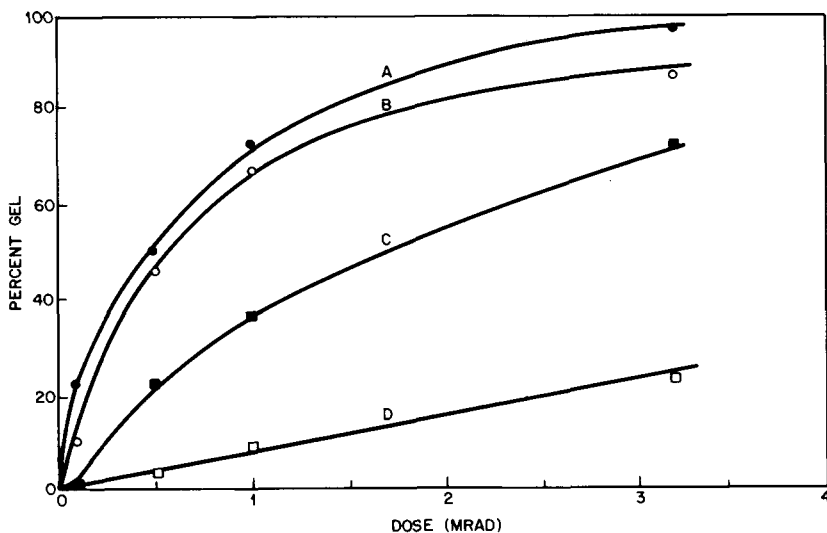
In the GPC analyses, 125 mg of each molded sample was placed in a 25-mL volumetric flask. 20 mL of THF was added and the capped sample was heated at a given temperature ( $50^{\circ}\text{C}$  was found to be the optimum temperature<sup>6</sup>) for 17 h. The solution was stirred continuously by a tiny magnetic spin bar. After cooling to room temperature, the spin bar was removed. 2 mL of a 0.5% by vol-

TABLE I  
Blend Composition

Blend	% PVC	% TMPTMA
A	$59 \pm 2$	$41 \pm 2$
B	$63.5 \pm 1$	$36.5 \pm 1$
C	$79 \pm 2$	$21 \pm 2$
D	$91 \pm 1$	$9 \pm 1$



(a)



(b)

Fig. 1. Percent gel vs. radiation dose: (a) Soxhlet technique; (b) GPC method. Blend A (●); blend B (○); blend C (■), blend D (□). The percentage of TMPTMA in A, B, C, and D are 41%, 36.5%, 21%, and 9%, respectively.

ume solution of  $\text{CCl}_4$  in THF was added followed by additional THF until the mark was reached. The solution was filtered through a  $0.45 \mu\text{m}$  sintered Ag filter.  $100 \mu\text{L}$  of this solution was injected into the GPC. The flow rate was  $2 \text{ mL}/\text{min}$ .

Three well resolved peaks were observed in the chromatograms. They were assigned to PVC, TMPTMA monomer, and  $\text{CCl}_4$ . The areas of the PVC and TMPTMA peaks are a direct measure of the soluble portion of the irradiated sample. The  $\text{CCl}_4$  internal standard area was used to normalize the PVC and TMPTMA areas in order to minimize errors due to injection volume changes.

To obtain absolute component concentrations from the peak areas, calibration curves were obtained using unirradiated samples of TMPTMA, PVC, and  $\text{CCl}_4$ . Both plots (for PVC and TMPTMA) were linear as expected and passed through the origin.

GPC analyses were performed with the Waters Model 244 Liquid Chromatograph. Most results were obtained with refractive index detection. For some runs UV detection was used to detect degradation of PVC molecules. The column set consisted of six microstyragel columns having porosities of  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , 500, and 100 Å. The latter two columns were necessary to obtain good separation between TMPTMA and  $\text{CCl}_4$ . A typical analysis time was 40 min at 2 mL/min. This method is an extension of two previous GPC techniques.<sup>7,8</sup> They dealt with a one-component system, whereas here a complex polymer-crosslinking monomer system is being considered.

## RESULTS

The formation of insoluble gel as a function of dose is shown in Figure 1, for gel fractions determined by the Soxhlet technique (a) or the GPC method (b). The crosslinked network was formed rapidly with an incipient gel dose less than 0.05 Mrad for all blends. The higher the TMPTMA content the more rapid the network was formed; i.e., the initial gelation rate (% gel per unit dose) is proportional to the % TMPTMA (w/w) in the blend. The measurement of gel fraction value is determined primarily by (1) the extraction temperature, (2) the extraction time, and (3) the sample mass-to-solvent volume ratio. The difference between Figures 1(a) and 1(b) arises mainly from item (3) above.<sup>6</sup> The dissolution process in the Soxhlet extraction is less efficient (i.e., gives higher gel content) than for the GPC method at high conversion.

Figure 2 shows the GPC profiles for the soluble fractions of blend B (representative of blends A–C). As the irradiation dose increased the soluble fraction decreased, with the TMPTMA peak decreasing faster than the PVC peak. TMPTMA was preferentially incorporated into the crosslinked network (initially). In Figure 3 the GPC traces for blend D are shown for both the refractive

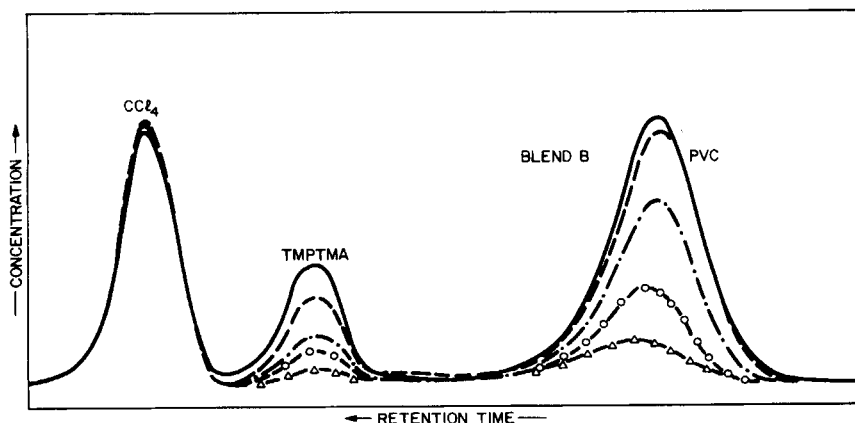


Fig. 2. Refractive index detector response for GPC analysis of soluble fractions from blend B: (—) 0 Mrad; (- - -) 0.1 Mrad; (- · - ·) 0.5 Mrad; (—○—) 1.0 Mrad; (—△—) 3.2 Mrad.

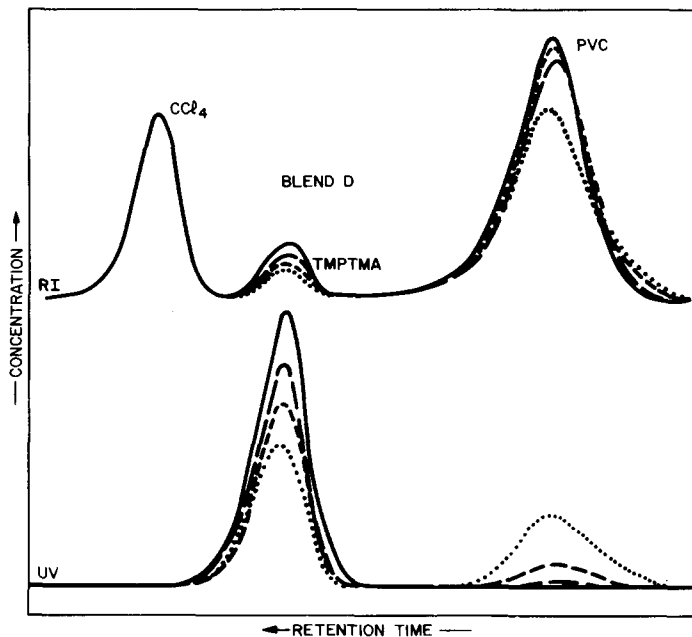


Fig. 3. Refractive index (top) and UV (bottom) GPC detector traces for soluble fractions from blend D: (—) 0 Mrad; (---) 0.5 Mrad; (- - -) 1.0 Mrad; (.....) 3.2 Mrad.

index and the UV detectors. For blends A–C the UV detector trace had a single peak corresponding to the free TMPTMA monomer. Blend D has a second UV peak with the same retention time as PVC. This is due to polyene structures in the PVC formed by dehydrochlorination. This peak may also have a minor contribution due to TMPTMA molecules grafted onto the polymer chain.

Also obtained from the GPC method was the compositions of the soluble fractions (and therefore of the gel fractions) and the molecular weight characteristics of the soluble components. Figure 4 shows the  $\bar{M}_n$  and  $\bar{M}_w$  values for the soluble PVC in the four blends as a function of dose. Pure PVC irradiated to these doses showed no significant variation in molecular weight (Table II). The number-average molecular weight ( $\bar{M}_n$ ) was insensitive to the loss of PVC molecules to the network, showing only a gradual decrease with dose. The weight-average molecular weight ( $\bar{M}_w$ ) was more sensitive. For the soluble PVC in the TMPTMA-rich blends,  $\bar{M}_w$  decreased exponentially with dose. Upon irradiation, no low molecular weight tail was observed to form on the PVC peak.

TABLE II  
Molecular Weights of Irradiated PVC

Irradiation dose (Mrad)	$\bar{M}_n \times 10^{-5}$ (g/mol)	$\bar{M}_w \times 10^{-5}$ (g/mol)	Polydispersity
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

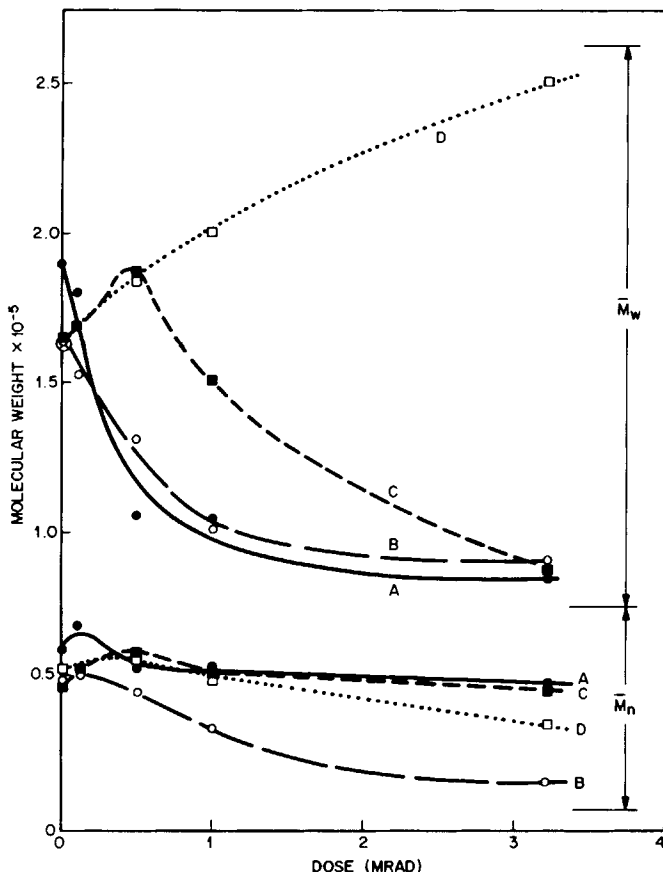


Fig. 4.  $\bar{M}_w$  and  $\bar{M}_n$  for soluble PVC versus radiation dose. Symbols as in Figure 1.

Therefore, the  $\bar{M}_w$  decrease was not due to degradation but to the larger PVC molecules being preferentially bound to the network (in preference to low molecular weight PVC molecules). However, with blend D the  $\bar{M}_w$  increased linearly with dose as the result of high molecular weight products being formed. These soluble high molecular weight products are predicted to be graft copolymers. These copolymers would contain PVC-(TMPTMA) $_x$  and PVC-(TMPTMA) $_x$ -PVC structures with  $x$  being small (less than 4). Blend C showed intermediate behavior with an initial rise followed by exponential decay. At high doses the  $\bar{M}_w$  values from blends A, B, and C approach a common value of  $\sim 80,000$  g/mol.

Figure 5 shows the percentage of PVC in the gel (percentage of gel that is PVC) as a function of percent gel formed. Generally at low conversion less PVC than was available was bound to the network. Initially, blends richer in TMPTMA showed a larger preference for TMPTMA crosslinking than for PVC incorporation into the gel.

The relative rates of incorporation of the available components into the gel are shown in Figure 6 with % PVC and % TMPTMA incorporated into gel plotted vs. dose. After an initial period when TMPTMA and PVC were rapidly bound into the crosslinked network, the incorporation rates decreased. This effect was more pronounced for the TMPTMA-rich blends. The data may be normalized

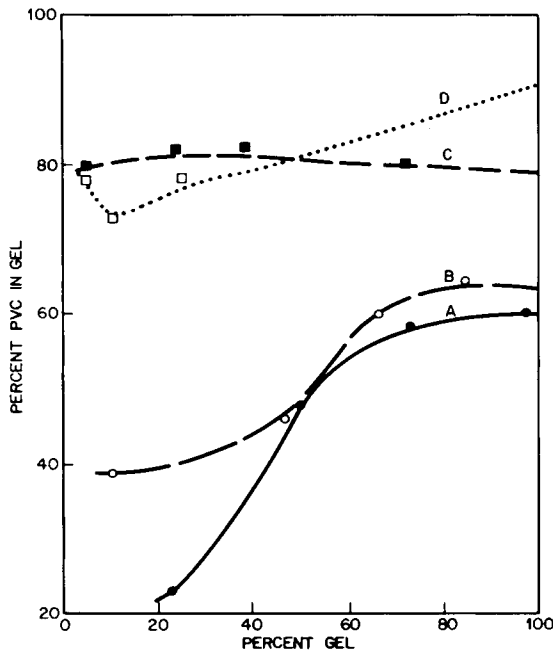


Fig. 5. Percent PVC in the gel vs. percent gel. Symbols as in Figure 1.

by plotting percent PVC or TMPTMA incorporated vs. percent gel, i.e., extent of reaction, as shown in Figure 7. In Figure 7, the dashed line would be followed if equal incorporation in the gel occurred for PVC and TMPTMA, i.e., blend composition = gel composition for all doses. Initially TMPTMA is preferentially incorporated into the gel. As the reaction proceeds and TMPTMA

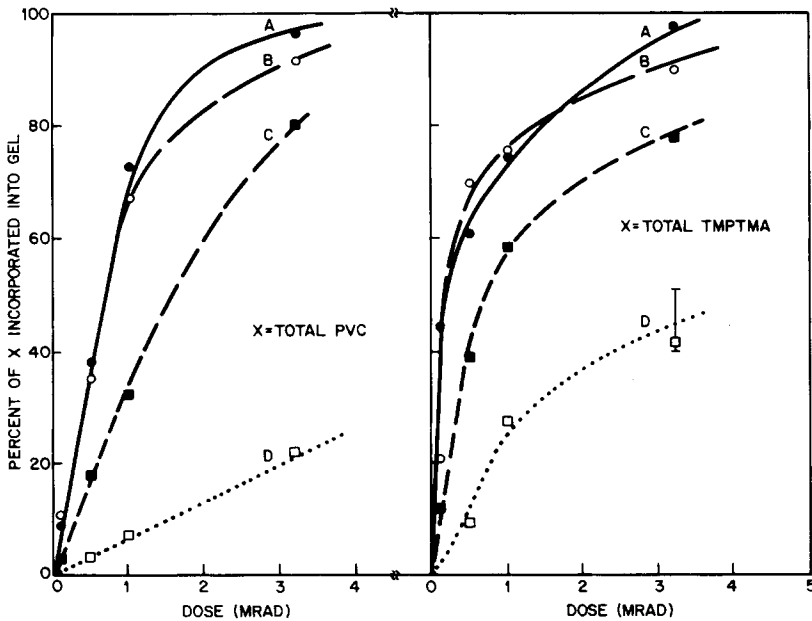


Fig. 6. Percent PVC and TMPTMA incorporated into the gel vs. radiation dose. Symbols as in Figure 1.

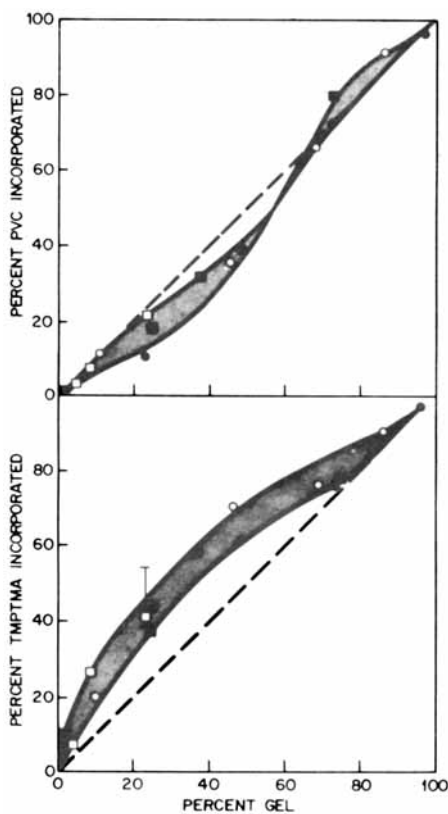


Fig. 7. Percent PVC and TMPTMA incorporated into the gel vs. percent gel. Symbols as in Figure 1.

is consumed, a compensating trend occurs, and the PVC molecules are bound onto the TMPTMA-rich network.

## DISCUSSION

Blends originally prepared with nominal PVC:TMPTMA ratios of 1:1, 2:1, 4:1, and 10:1 were found to have compositions in Table I after blending and compression molding. As more TMPTMA was added, the PVC began to be saturated. For example, migration of the monomer to the surface and subsequent removal by surface contact (e.g., molding, blending, and handling) reduced the TMPTMA percentage in blend A from 50% to 41%. After blend preparation, the molecular weight of the PVC component increased by 5–15%. Blend A, richest in TMPTMA, showed the largest change with the molecular weight of the PVC ( $\bar{M}_w$  in Fig. 4) increasing from 160,000 to 190,000 g/mol. This may be interpreted as small amounts of PVC crosslinked via TMPTMA grafts. These reactions were thermally initiated during processing.

Upon irradiation free radicals were produced in both the TMPTMA monomer and the PVC. The TMPTMA 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.<sup>9,10</sup>



During irradiation of pure PVC, these radicals would initiate dehydrochlorination and small amounts of main chain scission and crosslinking. The radiation chemical yields for pure PVC are  $G(\text{HCl}) = 13$ ,  $G(\text{crosslinking}) \approx 0.3$ ,  $G(\text{scission}) \approx 0.2$  at  $25^\circ\text{C}$ .<sup>9-11</sup> The dehydrochlorination proceeds via a chain reaction to produce conjugated double bonds. These unsaturated structures absorb in the UV-visible wavelengths, thereby producing discoloration in the PVC. In the blends, the PVC radicals will be scavenged by the TMPTMA molecules producing graft copolymers and inhibiting discoloration. Eventually, the graft sites will become the points from which the PVC main chain will be covalently bound into the crosslinked matrix. There exists a competition for the TMPTMA molecules between homopolymerization and the grafting pathways.

The composition range covered by the blends A–D shows the major aspects of this competition. The initial rate of gelation was approximately proportional to the TMPTMA concentration, reflecting the dominance of the rapid TMPTMA polymerization reactions. With the TMPTMA being consumed, the grafting and crosslinking reactions involving PVC molecules become increasingly more important at the later stages of gelation. It is *not* a two-step sequence in which monomer polymerization is complete before the onset of PVC incorporation. Such a two-step process has been observed in a related system, PVC–tetraethyleneglycoldimethacrylate blends.<sup>3,12</sup> In our system only preferences exist for one reaction over another, and the balance moves from TMPTMA incorporation to PVC incorporation as gelation proceeds.

TMPTMA-rich blends (A,B) have gel fractions that are initially heavily biased towards TMPTMA while TMPTMA-poor blends (C,D) have a much weaker bias (Fig. 5). The differences arise from the role of grafting reactions. The high concentration of TMPTMA in blends A and B favors rapid homopolymerization into a TMPTMA network with PVC bound subsequently. In blends C and D the lower concentrations of TMPTMA allow grafting reactions to compete with the homopolymerization with the result that *soluble* graft copolymers of PVC–TMPTMA are found (Fig. 4). In the TMPTMA-rich blends, these graft copolymers would rapidly be bound into the network via TMPTMA polymerization reactions.

Degradation reactions begin to become important at high doses and with TMPTMA-poor blends. Dehydrochlorination occurs since the free radicals are no longer being scavenged by the TMPTMA molecules. The free radicals formed by C–H and C–Cl bond cleavage are the precursors to dehydrochlorination which produces conjugated double bonds. These polyene structures are observed as (1) a discoloration of the blend and (2) an increase in UV absorption (seen in Fig. 3).

## CONCLUSION

The molecular crosslinking mechanism presented in Paper I of this study<sup>5</sup> has been extended and found to be consistent over a wide range of blend compositions. The kinetics of gelation have been described in terms of grafting, scavenging, and polymerization reactions undergone by the PVC and TMPTMA molecules in the blend.

### References

1. S. H. Pinner, *Nature*, **183**, 1108 (1959).
2. A. A. Miller, *Ind. Eng. Chem.*, **51**, 1271 (1959).
3. W. A. Salmon and L. D. Loan, *J. Appl. Polym. Sci.*, **16**, 671 (1972).
4. V. I. Dakin, Z. S. Egorova, and V. L. Karpov, *Plast. Massy*, **1979**, 40-2; *Chem. Abstr.* **91**, 75220j (1979).
5. T. N. Bowmer, D. D. Davis, T. K. Kwei, and W. I. Vroom, *J. Appl. Polym. Sci.*, **26**, 3669 (1981).
6. M. Y. Hellman, T. N. Bowmer, and G. N. Taylor, *Am. Chem. Soc., Org. Coat. Plast. Chem. Prepr.*, **45**, 126 (1981).
7. V. F. Gaylor, H. L. James, and J. P. Herdering, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1575 (1975).
8. M. Ezrin and M. Brown, Abstracts of Paper of Amer. Chem. Soc., ANAL 73-P73, Sept. 1979.
9. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.
10. M. Dole, *Radiation Chemistry of Macromolecules*, Academic, New York, 1973.
11. A. Charlesby, *Atomic Radiation and Polymers*, Pergamon, New York, 1960.
12. H. E. Bair, M. Matsuo, W. A. Salmon, and T. K. Kwei, *Macromolecules*, **5**, 114 (1972).

Received January 6, 1983

Accepted January 14, 1983