

The Radiation Crosslinking of Poly(vinyl Chloride) with Trimethylolpropane Trimethacrylate. I. Dose Dependence and the Effects of Thermal Treatment

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Synopsis

The radiation crosslinking of poly(vinyl chloride), PVC, with trimethylolpropane trimethacrylate, TMPTMA, has been examined. The polyfunctional TMPTMA undergoes rapid polymerization incorporating the PVC into a three-dimensional network. The kinetics and mechanism of these crosslinking reactions were studied with particular reference to dose dependence and thermal treatment. The gel was rapidly formed with a TMPTMA polymerization rate greater than that of the PVC grafting reaction. Only 30–40% of the available bonds were used in the initial polymerization. The remaining 60–70% of the double bonds predominantly react in the final stages of crosslinking (80–100% gelation). The macroscopic properties (e.g., solubility, glass transition temperatures, mechanical characteristics, etc.) of the PVC–TMPTMA blend are discussed in terms of the molecular crosslinking mechanism. The effect of thermal treatment, during and after irradiation, on the reaction rates and mechanism is examined.

INTRODUCTION

The manufacture of large quantities of wire and cable insulation is based on the radiation crosslinking of poly(vinyl chloride), PVC, in the presence of polyfunctional monomeric additives. Upon irradiation, the monomer is crosslinked into a three-dimensional network into which the PVC is incorporated via grafting reactions. This produces an insulation that has both heat resistance and abrasion resistance, advantages that ordinary plasticized PVC does not have.

Polyfunctional monomers that have been shown to act as crosslinking sensitizers for PVC include allyl esters,¹ dimethacrylates,^{2,3} trimethacrylates,³ triallyl isocyanurate,⁴ divinylbenzene,² and triacrylates.³ The polyfunctional methacrylates and acrylates were found to have the greatest sensitivity.

Previous studies^{3,5–8} on blends of PVC with tetraethylene glycol dimethacrylate have examined the radiation-induced crosslinking reaction in terms of viscoelastic and calorimetric properties as well as the macroscopic morphology of the blends. Other investigations^{9–12} have considered the commercial application for wire and cable insulation, using mixtures of PVC with monomer plus a variety of secondary additives—nonreactive plasticizers, stabilizers, and other filler materials. To understand the fundamental chemistry in these PVC–monomer systems, it is desirable to study as simple a mixture as possible, that is, a mixture containing none (or minimal quantities) of the secondary additives. The previous studies on the PVC–tetraethylene glycol dimethacrylate system concentrated on one composition and one irradiation temperature. For a fuller understanding of the kinetics and mechanism of the crosslinking process, an investigation over a broader range of reaction conditions is preferred, e.g., varying the blend composition and irradiation temperature.

This present study will report on the system of PVC and trimethylolpropane trimethacrylate, i.e., $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{—O—CO—CCH}_3\text{=CH}_2)_3$. We will consider the kinetics of crosslinking as a function of irradiation temperature, irradiation dose, and thermal treatment. The interrelationship between the chemical reaction and the physical properties of the system will be discussed.

EXPERIMENTAL

Trimethylolpropane trimethacrylate (TMPTMA) from Ware Chemical Corp. and poly(vinyl chloride)— $M_n \approx 65,000$, $\bar{M}_w \approx 150,000$ —from Goodrich Co. were used. The monomer, together with a thermal stabilizer, was added gradually to the PVC in a high-speed blender at 60–70°C. These powders were roll milled to ensure complete mixing and then compression molded in a press at 150–160°C for 2.5 min to give sheets 60 to 250 μm thick. The composition of the blend was 37% TMPTMA and 63% PVC by weight. The composition was confirmed by GPC analysis and elemental analysis of the mixture.

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 3.0 Mrad. Irradiations were carried out under nitrogen atmosphere at temperatures from –30 to +125°C using an aluminum chamber 12.5 cm in diameter, Figure 1. The chamber is heated by a disc heater inserted into a cavity in the base. A Honeywell temperature controller regulates the temperature to $\pm 0.5^\circ\text{C}$. The nitrogen gas flows through the heated cavity and then into the sample chamber. An aluminum foil window allows the electron beam to pass unattenuated while maintaining the inert atmosphere.

The gel content was determined by Soxhlet extraction (15–20 h) with tetra-

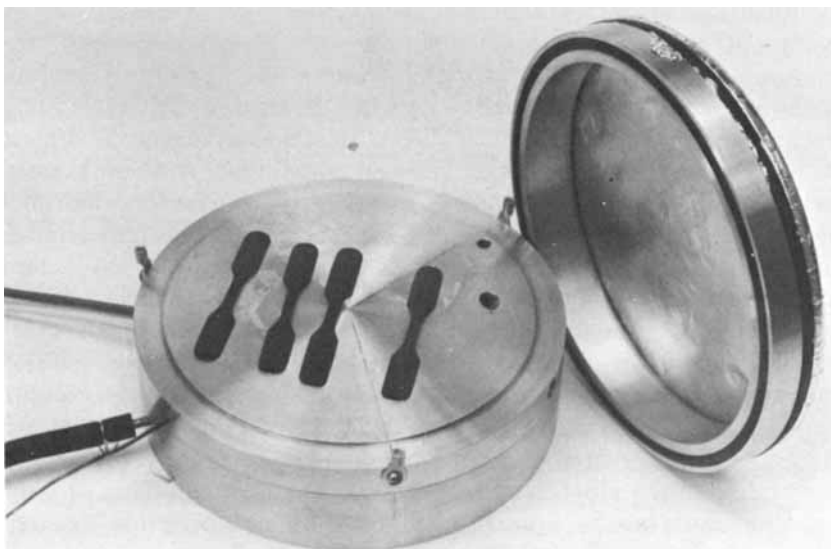


Fig. 1. Irradiation chamber showing thermocouple wire, nitrogen feed line, and heater leads entering from the left. The open lid shows (1) the entry and exit holes for the nitrogen from the heated cavity in the base, (2) four tensile specimens (Neoprene) in irradiation position.

hydrofuran; the insoluble material remaining (dried to constant weight) was defined as the gel content for the sample.

Unsaturation was analyzed by infrared spectroscopy of the blends using the ratio of the absorbance at 1630 cm^{-1} to that at 690 cm^{-1} and to that at 360 cm^{-1} . The 1630 cm^{-1} resonance arises from the C=C stretching mode, while the 690 and the 360 cm^{-1} resonances are from C—Cl stretching and bending modes, respectively.^{13,14} Using the absorbances at 690 and 360 cm^{-1} for internal reference avoids any effects of thickness variations across the films.

Elemental analysis was performed on the gel portion of the irradiated blends to determine the extent of PVC incorporation into the crosslinked structure.

The glass transitions and changes in specific heat, ΔC_p , of the samples were studied by differential scanning calorimetry, using a du Pont 990 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$.

Mechanical properties were evaluated by (1) tensile measurements—strength, modulus, and elongation—and (2) dynamic viscoelastic measurements—dynamic modulus and loss tangent. ASTM Test Method D638 employing type V specimens was used for the tensile measurements.¹⁵ Measurements of the dynamic viscoelastic properties were made with a direct-reading dynamic viscoelastometer from Toyo Measurement Instrument Co., Rheovibron DDV-II-C at a frequency of 110 Hz and a heating rate of $\frac{2}{3}\text{--}1^\circ\text{C}/\text{min}$. The viscoelastomer was semiautomated (via a HP 9825 programmable calculator) as per the method of Kenyon et al.¹⁶

Gel permeation chromatograms of the solute portion of the irradiated blends were obtained on a Waters chromatograph (model 2442) using μ -Styragel columns with tetrahydrofuran as solvent.

RESULTS

Figure 2 shows the formation of gel as a function of dose for the range of irradiation temperatures. The incipient gel dose at room temperature was found to be less than 0.01 Mrad , after which the gel content rose smoothly toward 100% conversion. As the irradiation temperature rose, the reaction rate increased rapidly, with 100% conversion occurring after 0.25 Mrad at 120°C .

Figure 3 shows the residual double bonds vs. percentage gel. Up until 70–80% gelation, only 20–30% of the available double bonds have been utilized. The consumption rate of double bonds accelerated as the last 20–30% of the blend was incorporated into the crosslinked matrix. The consumption rate equals the rate of double bond decrease per percent gel formed. At high conversion (close to 100%), the unreacted double bonds of the trifunctional monomer continued to be depleted by crosslinking and/or grafting reactions. The effect of changing the irradiation temperature is observed by considering the percent double bonds at 50% gelation. As the temperature increases from 9 to 41°C , the percent of residual double bonds decreases from 86 to 62%; more double bonds have reacted at the higher temperature of irradiation for the same percentage gelation.

Figure 4(a) shows the percentage of the gel which is PVC vs. the percent gel (i.e., extent of reaction). Figure 4(b) plots the percent PVC incorporated in the gel [(PVC in gel/PVC in initial blend) $\times 100$] vs. the percent gel. These relationships are seen to be temperature independent, with data from all irradiation temperatures depending only on the extent of reaction (percent gel). One may

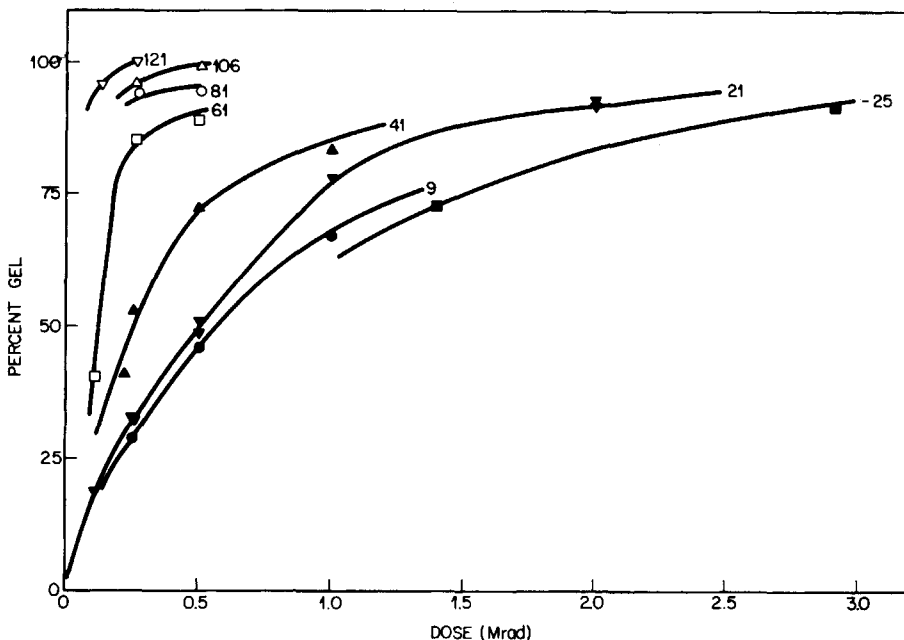


Fig. 2. Percent gel vs. dose: (■) -25 to -30°C ; (●) 9 – 10°C ; (▽) 20 – 22°C ; (Δ) 41°C ; (□) 61°C ; (○) 80 – 83°C ; (△) 104 – 108°C ; (▽) $120.5 \pm 0.5^{\circ}\text{C}$ = irradiation temperature.

view the crosslinking process to be comprised of two primary reactions: (1) polymerizations of TMPTMA and (2) crosslinking of PVC. As the temperature of irradiation increases, the rate of gel formation increases (Fig. 2), but the ratio of the rates for the two reactions above does not change significantly with temperature. Initially, TMPTMA is incorporated into the gel in preference to PVC; e.g., in the initial blend, PVC/TMPTMA = 1.7; in the gel after 0.1 Mrad, PVC/poly(TMPTMA) = 0.45. As the irradiation continues and TMPTMA is exhausted, reaction (2) above will become the dominant process, bringing the PVC/poly(TMPTMA) ratio in the gel toward 1.7.

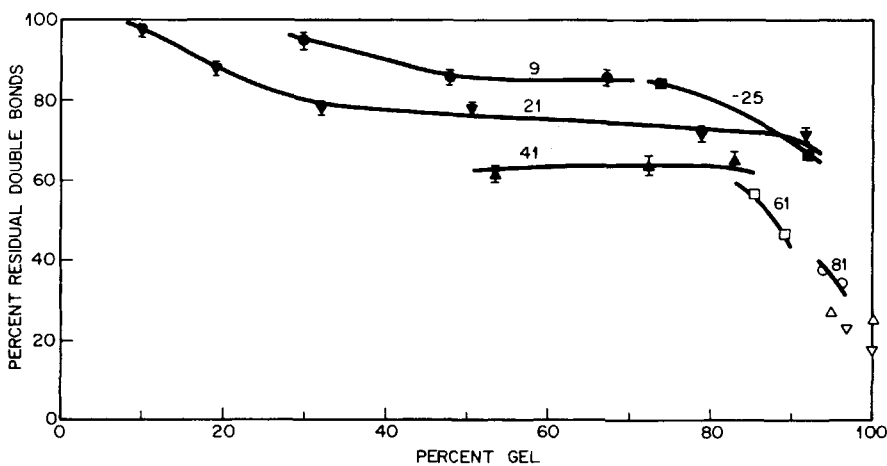


Fig. 3. Residual double bonds vs. percent gel. Symbols as in Fig. 2.

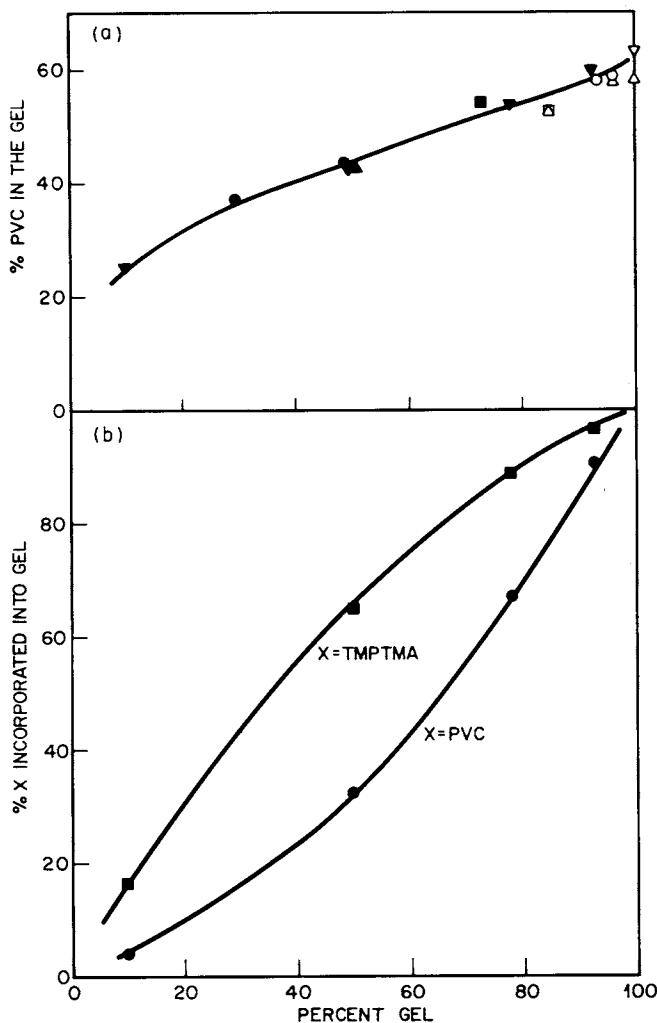


Fig. 4. (a) Percent PVC in gel vs. percent gel. Symbols as in Fig. 2. (b) Percent initial component incorporated in the gel vs percent gel: (■) TMPTMA; (●) PVC. Data points for 20–22°C irradiations shown.

The basic difference between different temperatures of irradiation is in the reaction rates of the second and third double bonds of the trifunctional TMPTMA. This may be seen from the lower double bond contents as the temperature of irradiation increases—noted above in discussion of Figure 3. At 50% gelation, the PVC/poly(TMPTMA) ratio in the gel is the same for irradiations at 10–40°C, Figure 4(a), but at the lower temperature the double bond content is higher, 85% vs. 62%. The lower double-bond content implies a higher crosslinking density.

The differential scanning calorimetry (DSC) profiles are shown in Figure 5 for the initial components, their blended mixture, and a sample of poly(TMPTMA). The addition of the TMPTMA monomer to PVC resulted in a two-phase mixture—a PVC-rich phase with $T_g \approx +50^\circ\text{C}$ and a monomer-rich phase with $T_g \approx -8^\circ\text{C}$. The monomer acted as a plasticizer on the PVC, re-

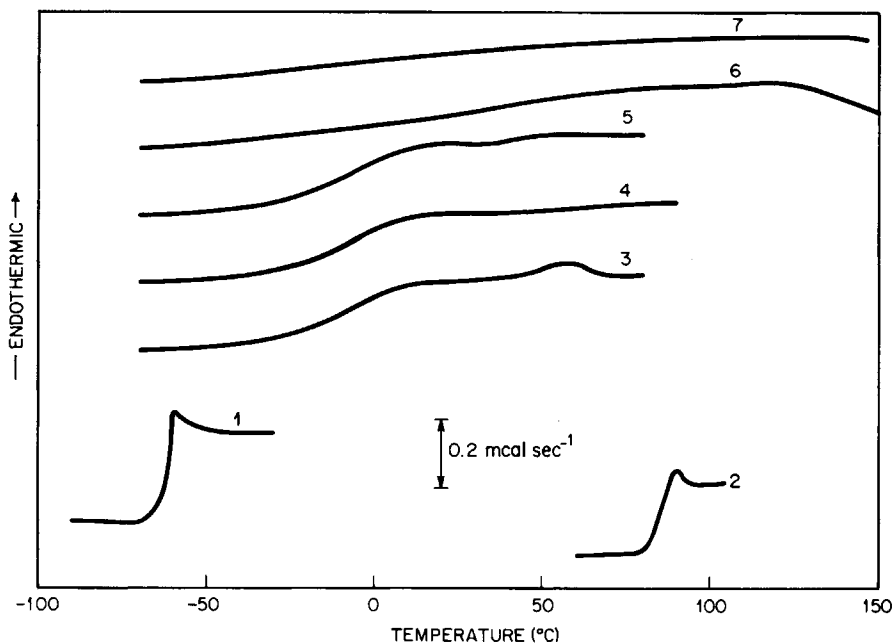


Fig. 5. DSC profiles for (1) TMPTMA, (2) PVC, (3) initial blend, (4) No. (3) quenched from 80°C, (5) No. (3) quenched from 80°C plus 44 h at room temperature, (6) TMPTMA irradiated to 2 Mrad \rightarrow poly(TMPTMA), and (7) No. (6) quenched from 150°C.

ducing the T_g from that of pure PVC, $T_g \approx 85^\circ\text{C}$. Poly(TMPTMA), being a crosslinked matrix, showed no sharp transitions in the DSC profile; but at high temperatures ($>120^\circ\text{C}$), an exothermic peak was observed arising from the polymerization of residual monomer.

Upon irradiation (at room temperature), four features of the DSC profiles were of note, Figure 6. Firstly, the monomer-rich phase transition monotonically increased from -8°C at 0 Mrad to $+80^\circ\text{C}$ after 2 Mrad. Secondly, the PVC-rich phase transition (at 50°C) was unaffected until high conversion ($>90\%$ gel), whereupon the transition began decreasing in magnitude. The transition still remained at approximately 50°C . Thirdly, at 100% conversion (trace 8, Fig. 6), the transition initially assigned to the monomer-rich phase has reached a $T_g \approx 95^\circ\text{C}$ and the PVC-rich phase transition has disappeared. One now has this single transition ($T_g \approx 95^\circ\text{C}$) representing all the PVC, which is all crosslinked into the matrix. Lastly, the exothermic transition at $110\text{--}120^\circ\text{C}$ decreased in magnitude as the dose increased. This is consistent with this exothermic transition arising from polymerization of residual (monomer) double bonds.

As the temperature of irradiation was raised, the crosslinking reaction rate increased. Therefore, the changes noted above concerning the shifts in the transition temperatures and the reduction in the exothermic transition occurred at a more rapid rate (Figure 7).

The mechanical properties of this system are shown in Figures 8 and 9. Figure 8 shows the tensile parameters of the blends—ultimate strength, elongation, work to rupture—for irradiations at room temperature. The corresponding viscoelastic properties obtained from the dynamic mechanical measurements are shown in Figure 9—dynamic modulus, loss tangent, and transition temperature vs. dose.

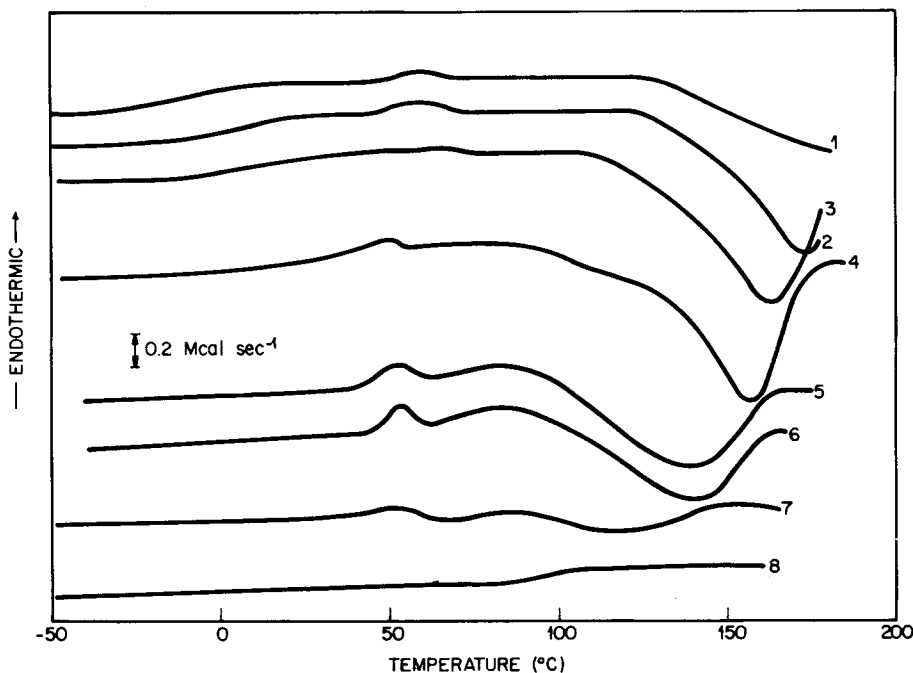


Fig. 6. DSC profiles for irradiated samples. Irradiations at room temperature: (1) 0.0 Mrad; (2) 0.05 Mrad; (3) 0.1 Mrad; (4) 0.25 Mrad; (5) 0.5 Mrad; (6) 1.0 Mrad; (7) 2.0 Mrad; (8) No. (7) after quenching from 165°C.

Upon preparation of the mixtures, the PVC becomes plasticized by the low-molecular-weight monomer. This was reflected in (1) lower ultimate strength and (2) pronounced elongation compared with the pure molded PVC. After 2 Mrad (93% gel), the ultimate strength has increased to 9000 psi—compare pure PVC value at 5700 psi—and the elongation has dropped to 70% from the initial value of 250%. The elongation decreased linearly with increasing gel content (Fig. 10), but the ultimate strength increased exponentially. The initial crosslinks produce a rapid increase in ultimate strength, but the residual monomer molecules still unreacted maintains a plasticizing effect (responsible for the elongation).

The energy (or work) to rupture was determined by measuring the area under the stress-strain curve. This shows the transition from a weak, but flexible, plasticized PVC to a strong, but brittle, crosslinked matrix having similar energy-to-rupture values. At 30–35% gel, there was a maximum in the energy-to-rupture value, which coincided with 50% of the monomer (Fig. 3) having been crosslinked. Thereby at this dose, one has the combination of strength (from crosslinking) and flexibility (from residual monomer) to give the maximum observed in Figure 8.

Considering the dynamic mechanical properties (Fig. 9), similar trends were observed with respect to (1) the PVC plasticization by the monomer and (2) the effects of irradiation. In unirradiated blends, the addition of TMPTMA to the PVC lowers the transition temperature [peak in loss tangent profile—Fig. 9(b)] from 115 to 41°C and decreases the dynamic modulus [Fig. 9(a)]. In addition, the β -transition peak of PVC at $\sim -10^\circ\text{C}$ in the loss tangent profile is eliminated

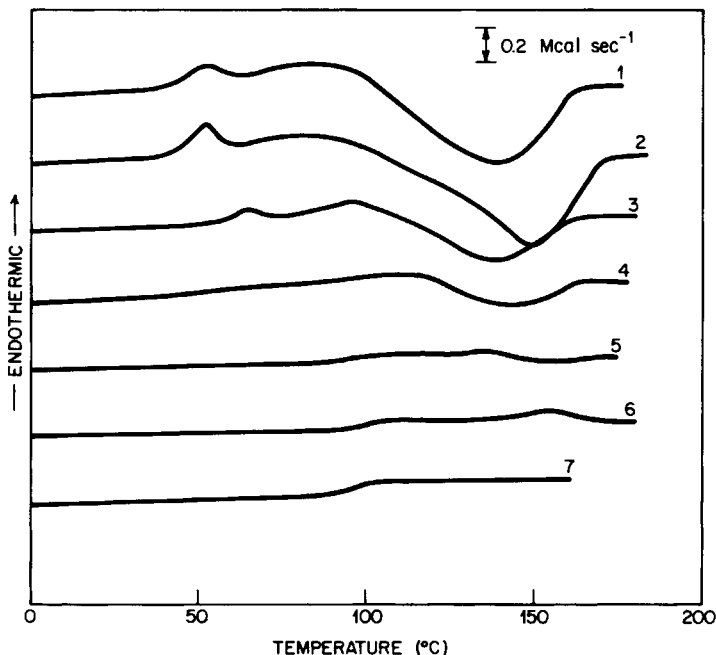


Fig. 7. DSC profiles showing effect of temperature of irradiation, 0.5 Mrad: (1) 9–10°C; (2) 21°C; (3) 41°C; (4) 61°C; (5) 82°C; (6) 100°C; (7) repeat of (6) after cooling from 180°C.

by the introduction of monomer [Fig. 9(b)]. Upon irradiation, the dynamic modulus increases [Figs. 9(a) and 9(c)], the transition temperature rises toward T^* for PVC [Figs. 9(b) and 9(c)], and the β -transition peak is restored—effects consistent with the loss of plasticizing monomer and the formation of a cross-linked network.

The transition temperature T^* is the temperature at which the maximum change in molecular motion is occurring for the test conditions. As the frequency of the applied stress approaches zero, T^* will approach T_g . Therefore, T^* is a measure of the mobility of the polymer chains.

Figure 11 shows the tensile modulus and the dynamic modulus (relative to pure PVC) at 25°C—both reflecting the rapid change in these mechanical characteristics after the initial crosslinks are formed, followed by a more gradual alteration in modulus.

T^* and dynamic modulus may be plotted against percent gel, i.e., the extent of reaction [Fig. 9(c)]. T^* increases almost linearly with percent gel, while tensile elongation decreases linearly with percent gel (Fig. 10). Both T^* and elongation are measures of the mobility of the polymer chains. However, the dynamic strength is strongly dependent on the initial (~20%) crosslinks.

The increase in dynamic modulus that occurs at ~100°C is produced by thermally induced crosslinking of residual monomer. One also notes the decreasing magnitude of the effect with increasing dose, which agrees with the DSC results showing exothermic transitions from the same process. This thermal curing effect will be discussed later. The dynamic modulus curves reflect the decreasing extent of plasticization of the PVC molecules as the monomer reacts. Also, the PVC molecules are becoming incorporated (and therefore less mobile) into the crosslinked matrix.

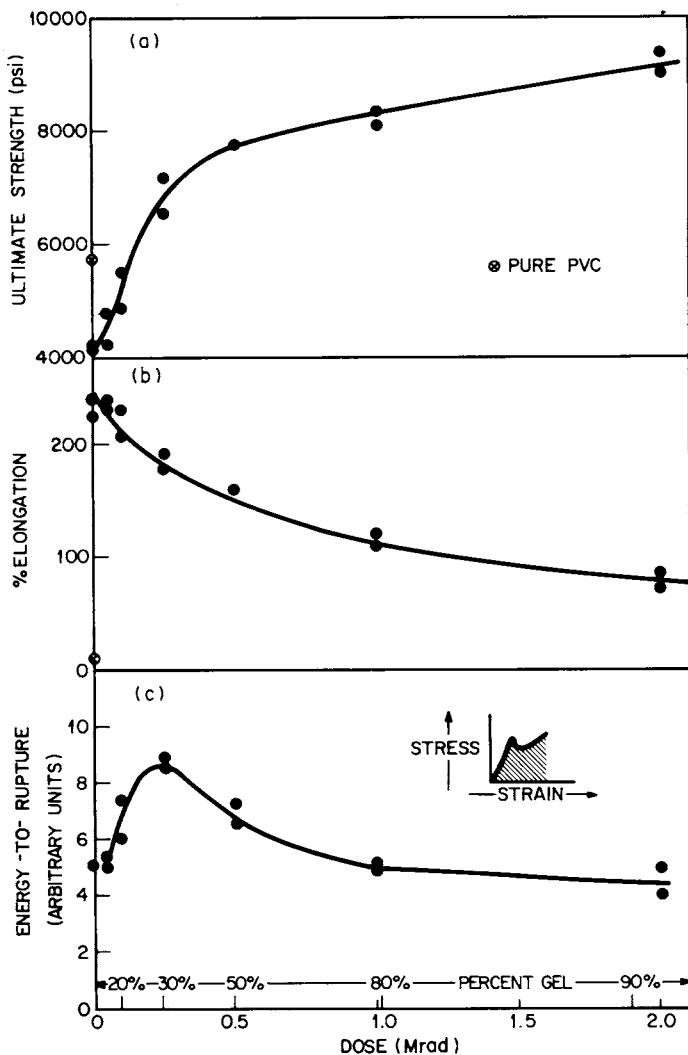
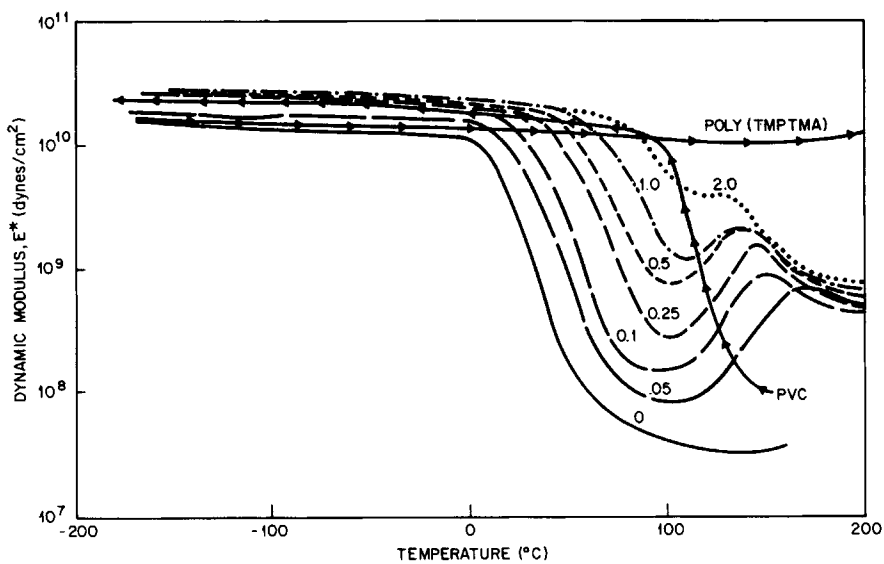


Fig. 8. Tensile properties vs. dose; ultimate strength (a), percent elongation (b), and energy to rupture (c). Irradiations at room temperature.

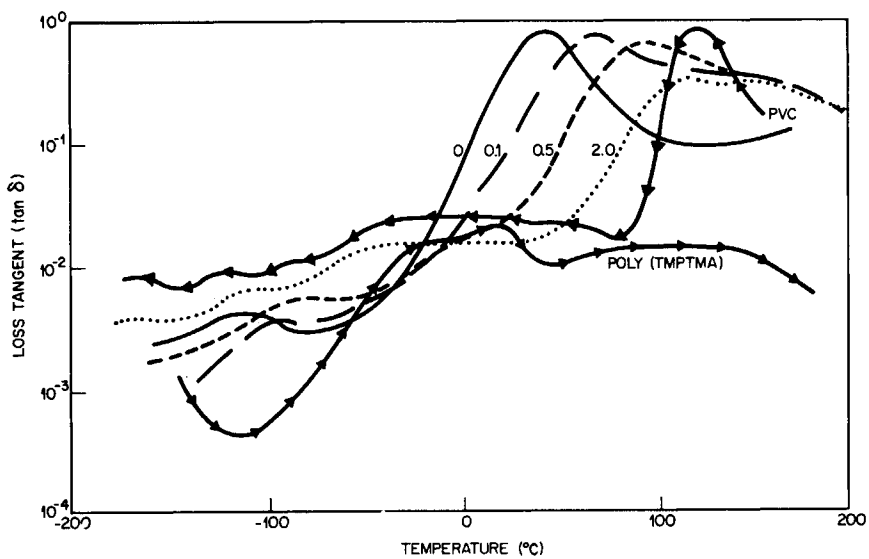
Also plotted in Figures 9(a) and 9(b) are the results for pure poly(TMPTMA) and pure PVC. The crosslinked network of poly(TMPTMA) has little or no features in the dynamic modulus or loss tangent profiles (i.e., no glass transition), maintaining a high modulus and a low loss tangent across the temperature range. In contrast, PVC passes through a transition (at 115°C) to a mobile phase with low modulus. The irradiation blend falls intermediate between the behavior of pure poly(TMPTMA) and pure PVC at high temperatures, Figure 9(a).

THERMAL TREATMENT

The effect of thermal treatment, particularly postirradiation heating, has been noted above in the DSC and viscoelastic results. As the temperature was increased during these tests, postirradiation polymerization reactions resulted.



(a)



(b)

Fig. 9. Dynamic viscoelastic measurements for samples irradiated at room temperature. The dose (in Mrad) is written adjacent to the appropriate trace in (a) and (b). The traces for pure PVC and pure poly(TMPTMA) are also shown for comparison: (a) dynamic or complex modulus E^* vs. temperature, (b) loss tangent ($\tan \delta$) vs. temperature; (c) low-temperature (-165°C) dynamic modulus and the transition temperature (T^*) vs. percent gel and dose.

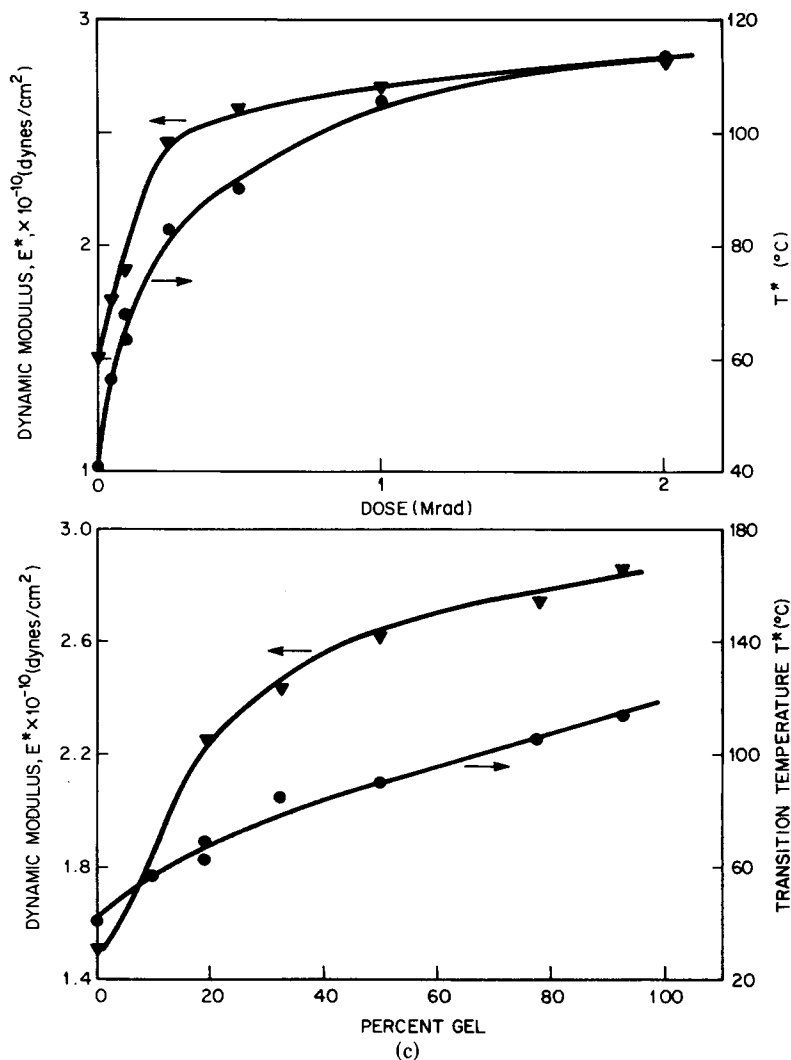


Fig. 9. (Continued from previous page.)

For example, there is an increase in dynamic modulus above $\sim 100^\circ\text{C}$ [Fig. 9(a)] and an exothermic transition in the DSC profile (Fig. 6). To investigate this effect in a controlled manner, experiments were performed in which samples were heated at constant temperature for a prescribed period—in contrast to the increasing temperature conditions in the DSC and viscoelastic experiments. Figures 12 and 13(a) show the effects of thermal treatment for unirradiated and irradiated samples, respectively. Figure 12 plots percent gel vs. time at a prescribed temperature for the unirradiated blend. The gelation rate increases rapidly above 100°C .

Figure 13(a) represents the thermal effects on the irradiated samples. The data are displayed as percent gel vs. dose for the irradiated samples which have been subjected to postirradiation heating at 80, 104, and 124°C (for 30 min). The period of 30 min had a small effect on the unirradiated samples ($<5\%$ gelation). However, the preirradiated samples underwent further crosslinking to a significant extent (up to 50% further gelation occurred).

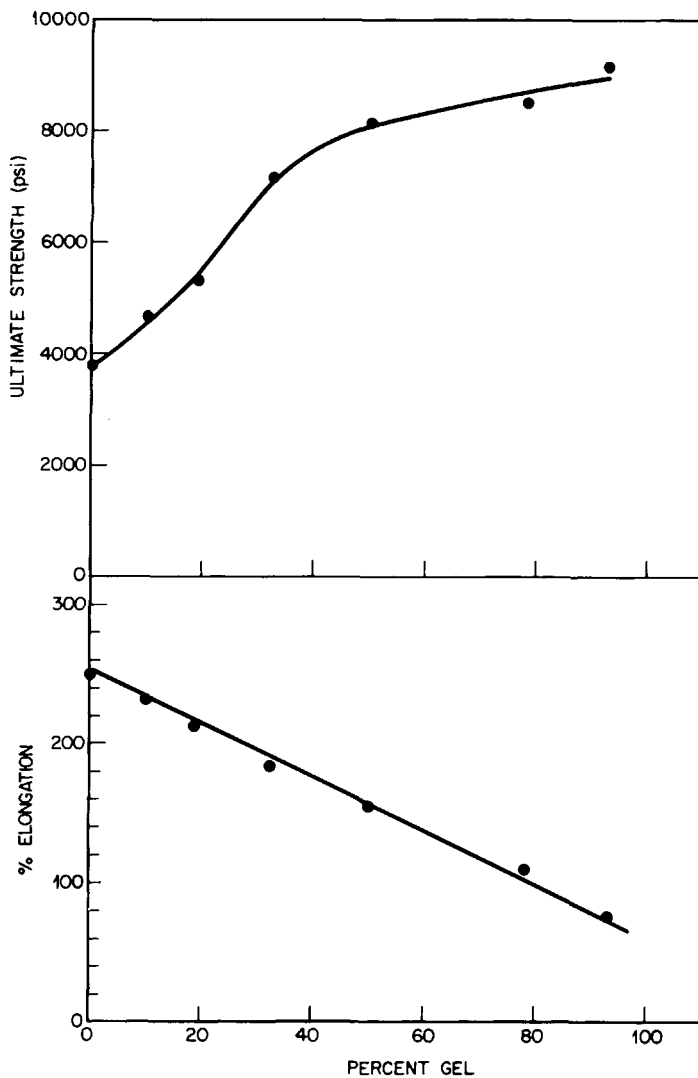


Fig. 10. Tensile properties—(a) ultimate strength and (b) percent elongation—vs. percent gel.

For the irradiated samples, treatment at 80°C produced only 5–10% additional polymerization, irrespective of the dose [Fig. 13(a)]. At 100°C and above, the postpolymerization rate becomes significant, correlating with the increase in dynamic modulus which was observed to begin at ~100°C [Fig. 9(a)]. The postirradiation thermal reaction may be followed in the DSC profiles [Figs. 13(b) and 13(c)], with the reduction of the exothermic (monomer) transition and the advance toward the single transition at ~95°C for the fully crosslinked matrix.

The dynamic modulus curves also show that the thermal reaction (postirradiation) brings the irradiated blends to a similar product—note the convergence of the curves in Figure 9(a) after postirradiation polymerization.

However, the thermally induced polymerization after irradiation does not produce exactly the product as irradiation would produce (Table I). Although

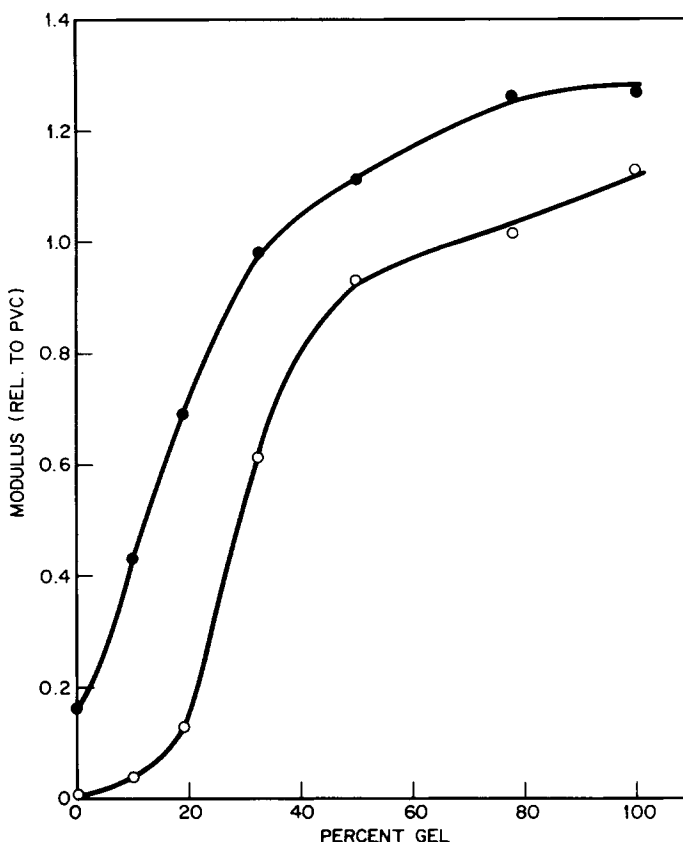


Fig. 11. Dynamic (●) and tensile (○) modulus vs. percent gel—modulus measured at 25°C.

TABLE I
Mechanical Properties after Postirradiation Heating

Dose, Mrad	Postirradiation heating		Percent gel	Tensile properties		
	Temperature, °C	Time, min		Strength, psi	Elongation to break, %	Work to break
0.25	—	—	32.5	6850	180	8.5
0.25	80 ± 1	30	43	6950	87	3.0
0.39	—	—	43	7500	163	7.6
0.25	104 ± 2	30	65	8500	53	2.4
0.75	—	—	65	8100	128	5.7
0.25	124 ± 1	30	91	9000	24	1.0
1.5	—	—	91	8700	93	4.6

the samples on postirradiation show an increase in tensile strength and a decrease in elongation, as expected; the magnitude of the elongation drops to a low value of 24% (Table I). The sample has become brittle—similar to pure poly-(TMPTMA) and pure PVC.

The initiating species for this polymerization will primarily be methacrylate-type free radicals. Figure 14 shows the electron spin resonance spectra of a sample irradiated to 0.3 Mrad at room temperature. One observes the well-

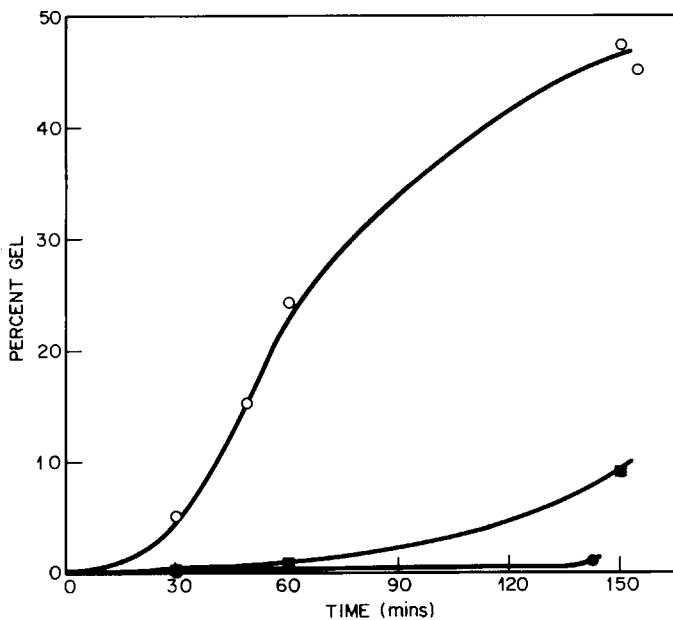


Fig. 12. Percent gel produced after heating unirradiated samples to 80°C (●), 100°C (■), and 124°C (○).

known methacrylate-type radical⁶ and possibly a broader and minor component arising from PVC degradation.

A related effect is the difference that was observed between double bond content for samples irradiated at different temperatures (Fig. 3). Table II details this effect. Irradiations to the same gel content at different temperatures yielded products of different double bond content, tensile strength, elongation, and energy-to-rupture values.

Irradiations at the higher temperatures promoted the reaction of more than one of the double bonds in the trifunctional monomer. This will result in a higher crosslinking density (the poly(TMPTMA/PVC ratio in the gel being unchanged) and therefore a more brittle (lower elongation) product.

Gel Permeation Chromatography

The soluble fractions of the irradiated blends were examined with GPC, resulting in the profiles shown in Figure 15. As the irradiation proceeds, the amounts of TMPTMA and (soluble) PVC were depleted due to incorporation into the gel, and the GPC peak areas reduce in size. From these area measurements, one can determine percent gel data, which were found to be in agreement with the Soxhlet extraction results (Fig. 2).

The decrease in average molecular weight of the extractable PVC—note peak position in profiles—implies that the larger molecules are preferentially incorporated into the matrix. The larger molecules have a greater degree of polymerization than the smaller molecules and hence have a greater probability of attachment as predicted by the statistical theory of crosslinking.¹⁷

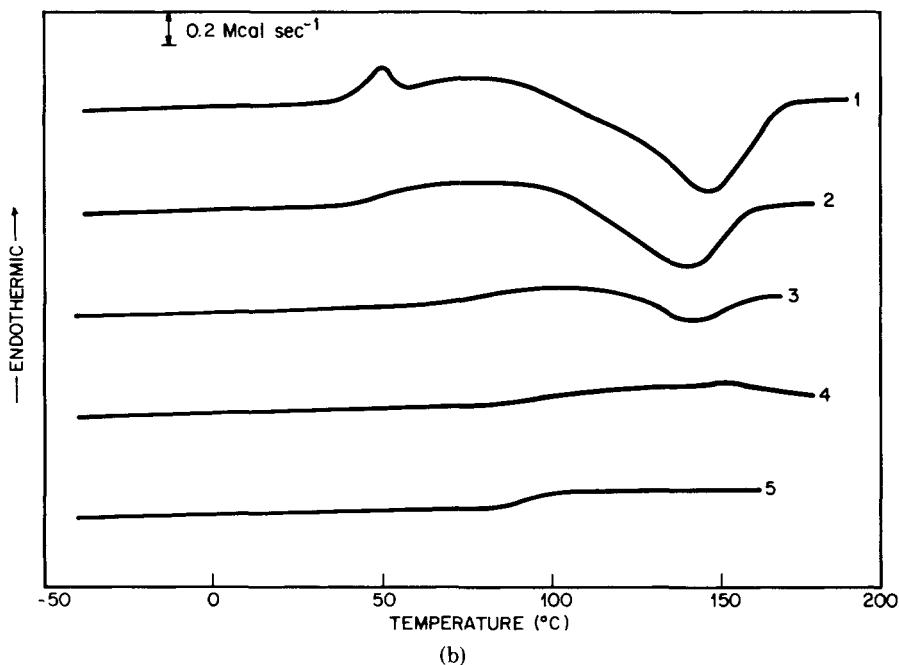
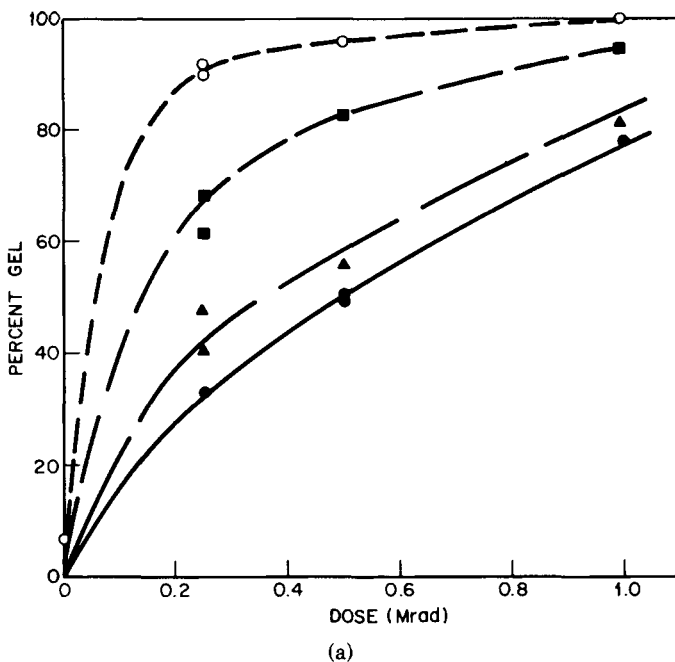


Fig. 13. Postirradiation thermal treatment: (a) percent gel vs. dose for samples before (●) and after 30 min of postirradiation heating at 82.5 (▲), 104 (■), or 124°C (○); (b) DSC profiles for sample irradiated at room temperature to 0.5 Mrad plus (1) no heating, (2) 30 min at 83°C, (3) 30 min at 104°C, (4) 30 min at 125°C, (5) obtained after quenching the sample used in profile (1) or (2) from 170°C; (c) DSC profiles for sample irradiated to 1.0 Mrad at room temperature plus (1) no heating, (2) 30 min at 83°C, (3) 30 min at 103°C, (4) 40 min at 103°C, (5) 60 min at 103°C, (6) 30 min at 124°C, (7) obtained by reheating sample from run No. (1) above. Reheating after (5) or (6) produces the trace shown as solid circles.

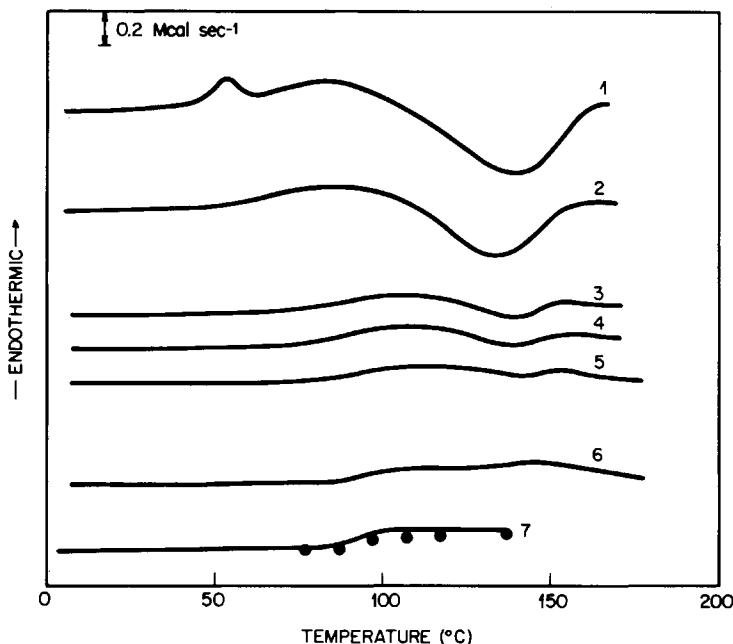


Fig. 13. (Continued from previous page.)

DISCUSSION

Irradiation of pure PVC produces mainly dehydrochlorination and polyene formation (discoloration).¹⁷⁻¹⁹ Scission and crosslinking play a minor role, with $G(\text{crosslinking}) = 0.3$ and $G(\text{scission}) = 0.2$ compared with $G(\text{HCl}) = 13$, for irradiations at room temperature under an inert atmosphere.^{17,19} The irradiation environment will influence this distribution of degradative pathways, with oxygen enhancing scission, for example. Polyfunctional materials are well known to enhance crosslinking and reduce discoloration of PVC.^{1-4,20}

For the PVC-TMPTMA system under consideration, the crosslinking processes are chemically complex. Not only does one have an additive which is consumed during irradiation by reacting with itself and the PVC, but also the blend has at least two phases, possibly more.⁵

The Charlesby-Pinner relationship between soluble fraction (s) and dose (r), used to obtain radiation chemical yields of crosslinking and scission, is not applicable in this case. A plot of $s + s^{1/2}$ vs. $1/r$ (Charlesby-Pinner plot) shows large curvature (concave toward the $1/r$ axis), from which one may infer that the crosslinking efficiency decreases with dose. The interpretation of the slopes

TABLE II
Mechanical Properties and Irradiation Temperature

Dose, Mrad	Temperature, °C	Percent gel	Percent residual double bonds	Tensile		
				Strength, psi	Elongation to break, %	Work to rupture
0.36	21	41	78	7700	170	7.8
0.22	42	41	63	7100	120	4.6
0.1	61	40	~58	7500	101	3.5

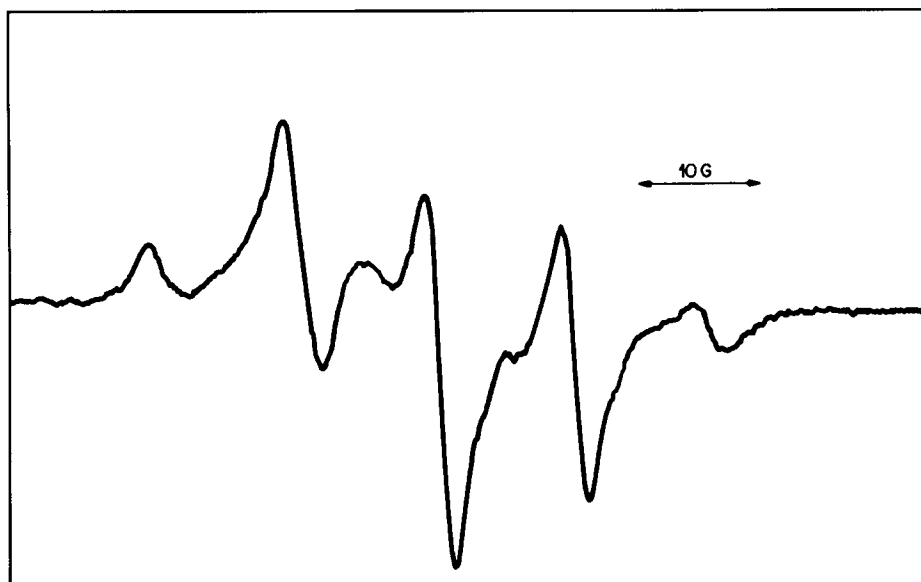


Fig. 14. ESR spectrum from blend irradiated to 0.3 Mrad at room temperature.

and intercepts of this plot in terms of radiation chemical yields is, however, not meaningful. The complexity of this two-component system forbids such interpretation.

Young's modulus may be used to determine an average distance between crosslinks²¹:

$$E = \frac{3R\rho T}{M_c}$$

where R is gas constant, ρ is density (1.26 g/cc for our blend), T is temperature (K), E is Young's modulus ($\approx E^* \cos \delta$), and M_c is distance between crosslinks (or entanglements) in terms of number-average molecular weight. The theory is based on rubbers above their glass transitions. So, using extrapolated values of the high-temperature dynamic modulus (150–180°C), one can calculate M_c

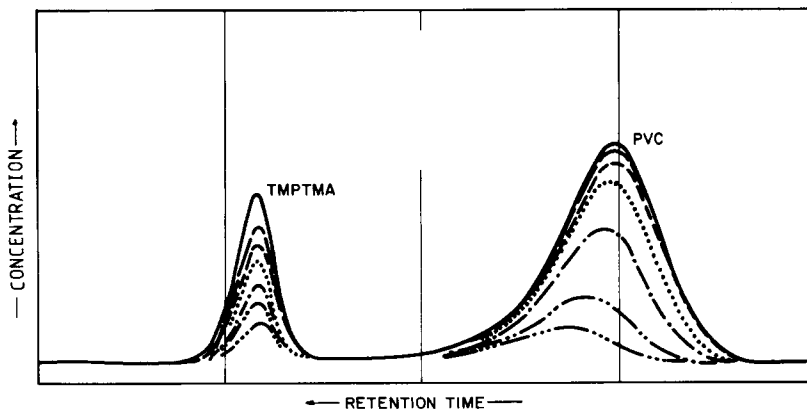


Fig. 15. GPC traces for soluble fractions of the irradiated blends: (—) 0.0 Mrad; (---) 0.05 Mrad; (·····) 0.1 Mrad; (-·-·-) 0.25 Mrad; (- - -) 0.5 Mrad; (- · · · -) 1.0 Mrad; (- · · · ·) 2.0 Mrad.

values for our blends. Extrapolation was required to subtract the postirradiation effects (Fig. 9). The results are shown in Figure 16. The initial M_c values of ~ 4500 represents the distance between the entanglements of the PVC molecules. This value is higher than the pure PVC entanglement value of ~ 3000 , since the TMPTMA initially acts as a filler and/or plasticizer. This dilution of the PVC concentration will reduce the number of entanglements. Upon irradiation, the distance between the crosslinks and/or entanglements rapidly drops until at 90–95% gel one has $M_c = 200$ –250. The magnitude of the number has limited meaning, since the crosslinks are not random. Although the PVC grafting reaction will occur randomly, the trifunctional nature of the TMPTMA will produce local regions of high crosslinking density at the TMPTMA-rich sites. Localization of crosslinking bonds has been reported in PVC–allyl polyfunctional compounds by Egorova et al.²² The value of $M_c = 200$ –250 is therefore an average distance, apparently influenced greatly by the trifunctional TMPTMA crosslinking points.

Upon irradiation, the TMPTMA monomer polymerizes incorporating the PVC molecules into a network. In addition to the methacrylate-propagating radicals, radicals are formed (by irradiation or abstraction reactions) on the PVC chains. These PVC radicals are scavenged by the TMPTMA, thus initiating graft polymerization and further crosslinking. In pure PVC, these radicals would initiate degradation reactions to produce HCl and polyenes, indicated by discoloration of the PVC. The PVC–TMPTMA blends showed no significant increase (<5%) in visible absorption (400–800 nm) upon irradiation at room temperature. For irradiations at temperatures greater than 80°C, discoloration becomes noticeable. At these high temperatures, the dehydrochlorination reaction begins to compete effectively with the TMPTMA grafting reactions for the PVC radicals (particularly when the TMPTMA concentration is depleted at high percentage gel).

Polymerization of the TMPTMA is initially preferred to the incorporation

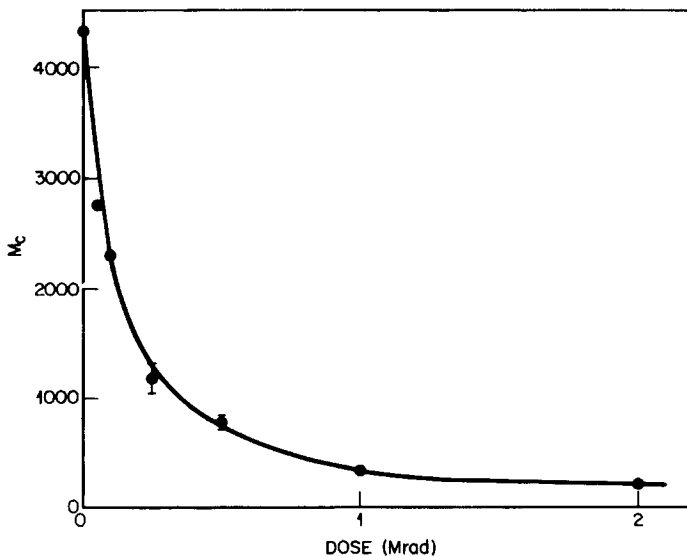


Fig. 16. Crosslinking index M_c vs. dose. $M_c = 3R\rho T/E$.

of the PVC into the gel; but as the TMPTMA is consumed, the PVC grafting reactions become favored. The final stage involves the residual double bonds of the TMPTMA slowly reacting to increase the crosslinking density—not all three double bonds are used initially in forming the matrix. It is of mechanistic interest to compare the sequence of events with that in the tetraethylene glycol dimethacrylate (TEGDM)–PVC system. The initial preference for TMPTMA polymerization over PVC grafting is not as biased as in the TEGDM–PVC case, where the TEGDM polymerization was complete before significant amounts of PVC has been grafted^{3,5} to the matrix. In the TEGDM–PVC case, the two double bonds per monomer were used in sequence. The first double bond was used during the initial (and rapid) polymerization, and the second double bond was used primarily in the grafting reactions of the PVC.³ With the trifunctional TMPTMA, the first one or two double bonds are used in forming a matrix incorporating ~90% of the TMPTMA and the PVC. There is no distinct two-step process in formation of the matrix here as there was in the TEGDM–PVC case. In the final stages (95 to 100% gelation), the TEGDM–PVC system undergoes minor changes,³ whereas the TMPTMA–PVC case is undergoing further reactions as the second and third double bonds are reacting to increase the crosslinking density.

CONCLUSIONS

This study has examined the radiation crosslinking of PVC–TMPTMA blends, describing the properties (mechanical properties, solubility, etc.) in terms of the molecular processes that have occurred.

The thermal treatment of the sample, not only during irradiation but also after irradiation, has been demonstrated to play an important role in determining the reaction extent and mechanical properties of the final product.

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