

# Radiation-Induced Crosslinking in Polymer–Polyfunctional Monomer Systems

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## SYNOPSIS

The dose dependence of crosslinking yields was determined for irradiated compositions of poly(vinyl chloride) and polyethylene with an allylic polyfunctional monomer (PFM). Therewith, the notion of the differential crosslinking yield  $G_c^*$  was used. The dose dependence of  $G_c^*$  has a maximum for the investigated systems. The current consumption of allylic groups and PFM molecules was determined. In the investigated systems, the process of network formation proceeds through chain crosslinking of graft chains of poly-PFM.

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## INTRODUCTION

Radiation crosslinking of polymers is the basis for a series of radiation–chemical technologies.<sup>1</sup> There is an important need for sensitization to, or promotion of, the radiation crosslinking of polymers, i.e., for an increase of radiation–chemical crosslinking yield.<sup>2</sup> There are several reasons why promotion of crosslinking is needed: The first is to decrease processing costs for the radiation crosslinking of polymers.<sup>3</sup> The second is to increase the crosslinking yield and to decrease the modification dose to reduce the contribution of adverse processes, e.g., radiation dehydrochlorination in poly(vinyl chloride).<sup>4</sup> The third is to promote the crosslinking of polymers, which otherwise degrade [e.g., polyisobutylene, poly(methyl methacrylate)]. It is possible to satisfy these needs by the use of polyfunctional monomers (PFM) as promoters of the radiation crosslinking of polymers.<sup>2</sup> It has been assumed that radiation crosslinking in “polymer–PFM” systems is a stepwise process.<sup>5,6</sup> However the mechanism of promoting by PFM has not been investigated in any great detail. In the present work, the radiation crosslinking in polymer–allylic PFM systems was investigated on the basis of the differential (current) radiation–chemical crosslinking yield.

## BACKGROUND

Radiation crosslinking is nonlinear and dose-dependent in all polymers in the total dose region. Actually, radiation crosslinking can take place by means of first-order or second-order reactions.<sup>7</sup> Respectively, the proportion of units crosslinked

$$q = 1 - \exp(-CR) \quad (1)$$

or

$$q = CR(1 + CR)^{-1} \quad (2)$$

where  $q$  = the proportion of units crosslinked,  $R$  = the dose, and  $C$  = a constant.

The principal equation of the theory of radiation crosslinking of polymers, elaborated by Charlesby,<sup>8</sup> is

$$q = q_0R = CR \quad (3)$$

where  $q_0$  = the proportion of monomer units crosslinked per unit radiation dose. Equation (3) is linear and this equation is a particular case of the general eqs. (1) and (2) at  $CR \ll 1$ .

According to eqs. (1) and (2), the crosslinking density of polymers, i.e., the value  $q$ , is nonlinearly dependent on the dose in the general case. However, some factors can increase the probability of the

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nonlinear dose dependence of  $q$  even at  $CR \ll 1$ , e.g., the following factors:

- Noninert mediums;
- Presence of additives;
- Nonhomogeneous polymeric structure, e.g., in copolymers;
- Formation or consumption of the reactive groups in polymers.

The equations of ref. 8 are often used for calculation of the radiation-chemical yield of crosslinking  $G_c$ , namely, on the basis of  $q_0$ :

$$G_c = kq_0/w \quad (4)$$

where  $G_c$  = the radiation-chemical yield of crosslinking (crosslinked units per 100 eV),  $w$  = the molecular weight of one unit, and  $k = 0.96 \times 10^4$  if dose  $R$  is in MGy. However, in the published work,<sup>8</sup> only the linear dose dependence of  $q$  is considered and the value of  $q_0$  is taken as a constant, i.e.,  $q_0$  is dose-independent. Hence, the equations of Ref. 8 are not suitable for the research of radiation crosslinking in polymeric systems with the dose-dependent  $G_c$ . For this purpose, it is advisable to use the so-called differential radiation crosslinking yield  $G_c^*$ .

The value of  $G_c^*$  is calculated on a basis of the differential parameter  $q_0^*$ :

$$G_c^* = kq_0^*/w \quad (5)$$

where  $w$  = the molecular weight of one unit and  $k = 0.96 \times 10^4$ . The parameter

$$q_0^* = \frac{dq}{dR} \quad (6)$$

where  $q$  = the proportion of units crosslinked and  $R$  = dose.

In practice, it is convenient to use the following procedure for the calculation of  $q_0^*$  and  $G_c^*$ : The dose dependence of  $q$  or the characteristic, proportional to  $q$  (e.g., concentration of crosslinked units  $n_c$ ), is determined. Therewith, for a determination of  $q$ , it is possible to use corresponding equations of Ref. 8, relating the parameter  $q$  and experimental characteristics. If the dose dependence of  $q$  is nonlinear, then it is possible to approximate this dependence by means of a broken line with the constant dose step  $\Delta R$ , e.g.,  $\Delta R = 10$  kGy. For every dose step, the corresponding change of  $q$  is determined, i.e.,  $\Delta q$ . Therewith,

$$(q_0^*)_i = (\Delta q)_i / \Delta R \quad (7)$$

where index "i" corresponds to the  $i$ -th step on the dose axis ( $i = 1, 2 \dots N$ ). For every  $(q_0^*)_i$ , the value  $(G_c^*)_i$  is calculated according to eq. (5). After that, the dose dependence of  $G_c^*$  is plotted; therewith, the doses, corresponding to the  $i$  steps, are used.

## EXPERIMENTAL

### Materials

Poly(vinyl chloride) (PVC) with number-average molecular weight,  $\bar{M}_n$ , equal to 50,000 and low-density polyethylene (PE) with  $\bar{M}_n$  equal to 30,000 were used. The degree of crystallinity was equal to  $\sim 10\%$  for PVC and  $\sim 50\%$  for PE. The allylic PFM, namely, triallyl isocyanurate (TAIC), was purified by recrystallization and had a melting point of 23°C. Specimens of a mixture of the polymer and PFM were formed into slabs by compression molding. The formed samples were heated at 110°C during 0.5 h for a decrease of the orientation effect.

### Irradiation

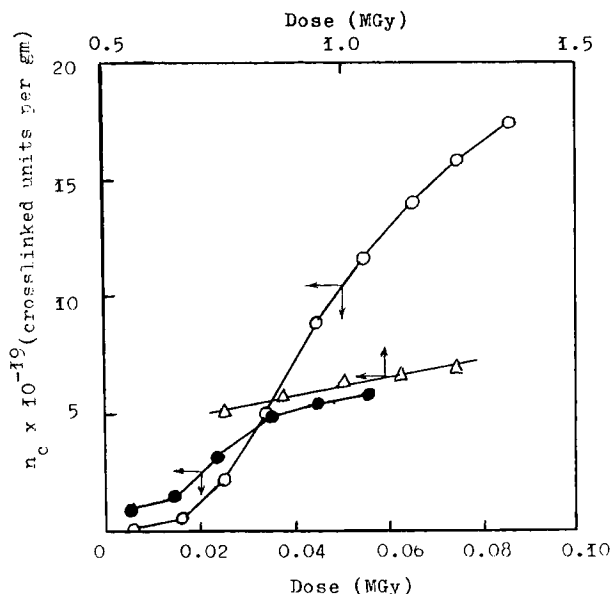
The samples were irradiated by  $^{60}\text{Co}$   $\gamma$ -rays under vacuum ( $10^{-3}$  Torr) at  $\sim 30^\circ\text{C}$  with the dose rate  $\sim 5$  Gy/s. The posteffect was absent in irradiated samples of the polymer-PFM systems.

### Analysis

The gel fraction of irradiated samples on the basis of PVC was determined by the method of solvent extraction in tetrahydrofuran ( $\sim 30$  h at the boiling point of the solvent). The PVC content in the gel was calculated on the basis of determination of PVC content in the sol by the weight method after the PVC isolation.

The equilibrium volume swelling ratio  $V$  was determined for the irradiated samples using dilatometry; therewith, the equations of Ref. 9 were used. The value  $V$  was used for a calculation of the crosslinked units concentration  $n_c$ . The conditions of the  $V$  determination were as follows: cyclohexanone at 25°C for samples on a basis of PVC and *o*-xylene at 80°C for samples on the basis of PE. The minimum value of  $n_c$  conformed to the beginning of the formation of the continuous system of elastic, active network chains<sup>10,11</sup> in irradiated samples.

The content of double bonds of PFM was determined by IR spectroscopy at the frequency 3090



**Figure 1** Dose dependence of the crosslinked units concentration,  $n_c$ , for ( $\Delta$ ) PVC, ( $\bullet$ ) PVC-13% TAIC, and ( $\circ$ ) PVC-23% TAIC.

$\text{cm}^{-1}$  (frequencies of internal standard are 2817 and 765  $\text{cm}^{-1}$ ) in the samples on a basis of PVC. The determination of the concentration of free PFM molecules in PVC-allylic PFM systems was made by GL chromatography after extraction by hexane.

On a basis of the dose dependence of the crosslinked units concentration  $n_c$ , the current (differential) crosslinking yield  $G_c^*$  was calculated. For this purpose, estimations were made by measuring the increments in the crosslinked units' concentration from experimental observations made at intervals of about 10 kGy. The current yield  $G_c^*$  was determined for every interval. In an analogous manner, the current (differential) yield of the double bond decrease,  $G_{-db}^*$ , and the current yield of the free PFM molecules decrease,  $G_{-pfm}^*$ , were determined.

From the values of  $G_c^*$ ,  $G_{-db}^*$ , and  $G_{-pfm}^*$ , the parameters  $n$  and  $m$  were calculated. The parameter  $n$  is the ratio of the current consumption of allylic groups to the current consumption of PFM molecules;  $n = G_{-db}^*/G_{-pfm}^*$ . Parameter  $m$  is the ratio of the current consumption of PFM molecules to the PVC crosslinking yield;  $m = G_{-pfm}^*/G_c^*$ .

## RESULTS AND DISCUSSION

The dose dependence of the crosslinked units concentration  $n_c$  was determined for polymer-PFM systems. The dose dependence of  $n_c$  for polymers without additives was determined for comparison.

Therewith, the value  $n_c$  is proportional to the parameter  $q$ , i.e.:

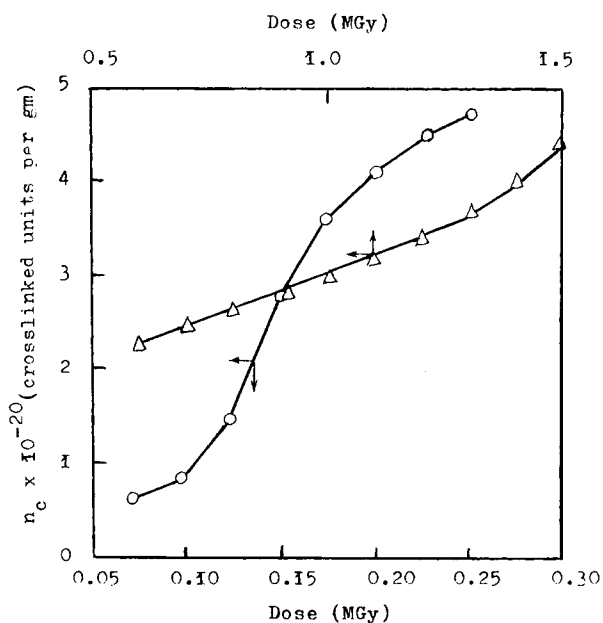
$$n_c = qN_A/w \quad (8)$$

where  $q$  = the proportion of units crosslinked,  $N_A$  = Avogadro's number, and  $w$  = the molecular weight of one unit. The results are shown in Figures 1 and 2.

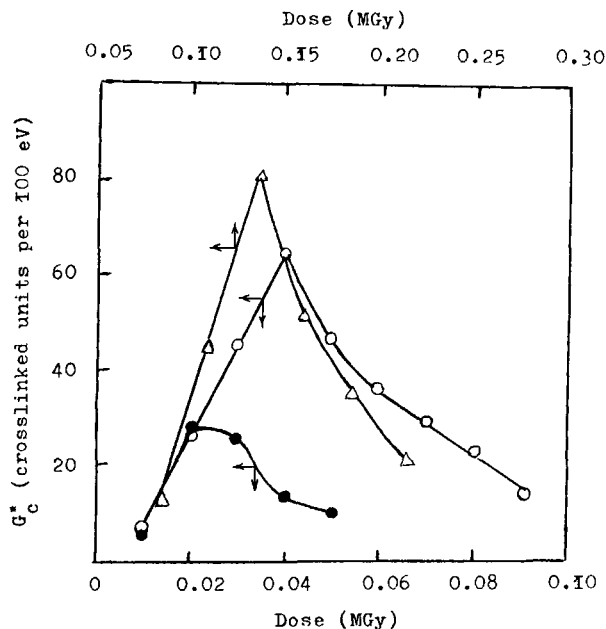
The value of  $n_c$  for polymer-PFM systems is nonlinearly dependent on dose; namely, this dependence has an S-resembling form. For polymers without additives, the dose dependence of  $n_c$  is, in general, linear. In the case of PE, a departure from linearity at large doses is, apparently, a result of the accumulation of reactive double bonds. The radiation-chemical yield of crosslinking  $G_c$ , calculated for polymers without additives, was equal to  $\sim 3$  for PE and  $\sim 0.7$  for PVC (crosslinked units per 100 eV). These values are near the known data.<sup>12,13</sup>

The results for irradiated polymer-PFM systems were processed on the basis of the differential crosslinking yield,  $G_c^*$ . The results are shown in Figure 3. The dose dependencies of  $G_c^*$  have maxima. The location of the maxima on the dose axis depends on the PFM content and the type of polymer. Therewith, the value of  $(G_c^*)_{\text{max}}$  is equal to 30-80 crosslinked units per 100 eV. This large value of  $(G_c^*)_{\text{max}}$  can take place only as a result of the chain process of crosslinking.

We shall analyze the dose dependence of  $G_c^*$  for systems on the basis of PVC using the results of



**Figure 2** Dose dependence of the crosslinked units concentration,  $n_c$ , for ( $\Delta$ ) PE and ( $\circ$ ) PE-6% TAIC.



**Figure 3** Dose dependence of the differential crosslinking yield,  $G_c^*$ , for (●) PVC-13% TAIC, (○) PVC-23% TAIC, and (△) PE-6% TAIC.

additional research, i.e., parameters  $n$  and  $m$ . Dependent on dose  $R$  and the degree of conversion of PFM double bonds, the values of parameters  $G_c^*$ ,  $n$ , and  $m$  change in mutual correlation. Parameter  $n$  is associated with the structure (branching) of poly-PFM chains formed at dose  $R$ , and parameter  $m$  is associated with the average degree of polymerization of poly-PFM chains formed at dose  $R$ .

In Figure 4, the dependencies for the PVC-23% TAIC system are shown. The maximum  $G_c^*$  corresponds to maximum  $n$  and, approximately, to the minimum  $m$  (Fig. 4). The analogous dependencies were obtained for the PVC-13% TAIC and PVC-13% diallyl sebacate (DAS) systems.<sup>14</sup> In the case of the PVC-13% TAIC system, the maxima of  $G_c^*$  and  $n$  are displaced to the region of lesser doses, and in the case of the PVC-13% DAS system, the maxima of  $G_c^*$  and  $n$  are displaced to the region of larger doses in comparison with the PVC-23% TAIC system.<sup>14</sup>

It is possible to assume the following mechanism of network formation in irradiated PVC-PFM systems: The first stage is the formation of crosslinks as the graft chains of poly-PFM with the "hanging" reactive double bonds ( $n \sim 1$ ,  $m \sim 7-8$ ,  $G_c^* \sim 5-7$ ). It is possible to consider this structure as the semifinished product (SF product). The second stage is the transition to the three-dimensional network as a result of the joining of SF products through the "hanging" double bonds and the molecules of PFM ( $n \rightarrow 3$ ,  $m \rightarrow 1-2$ ,  $G_c^* \rightarrow 30-60$ ). This stage

is the chain process of crosslinking. The third stage is the transition to reactions of residual double bonds and PFM molecules ( $n \rightarrow 1-2$ ,  $m \rightarrow 2-3$ ,  $G_c^* \rightarrow 10-13$ ). Apparently, this mechanism takes place also in the case of irradiation of the PE-PFM system.

The second stage may be interpreted in terms of the theory of chain network formation.<sup>8</sup> On the basis of this theory, the characteristic parameter of this process is the so-called amplification factor  $i$ :

$$i = (a)^{-1} \quad (9)$$

where  $a$  = the number of links resulting from each initiation:

$$(G_c)_{\text{chain}} = (G_c)_{\text{nonchain}}/i \quad (10)$$

where  $(G_c)_{\text{chain}}$  = the radiation-chemical yield for the chain process of crosslinking and  $(G_c)_{\text{nonchain}}$  = the radiation-chemical yield for the nonchain process of crosslinking.

For the PVC-TAIC and PE-TAIC systems,

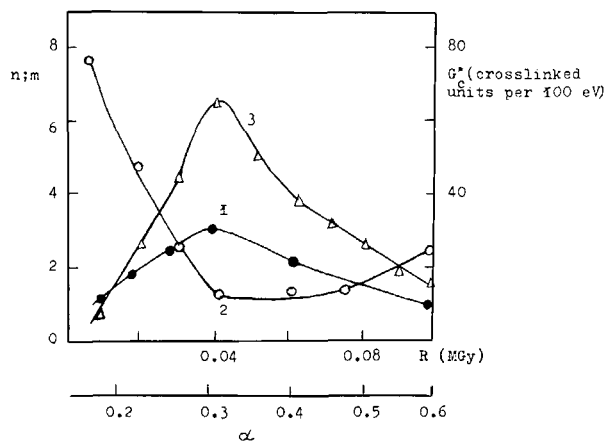
polymer + PFM  $\rightarrow$  SFP  $\rightarrow$  chain process

$$G_c^* \sim 5-12 \quad (G_c^*)_{\text{max}} \sim 30-80$$

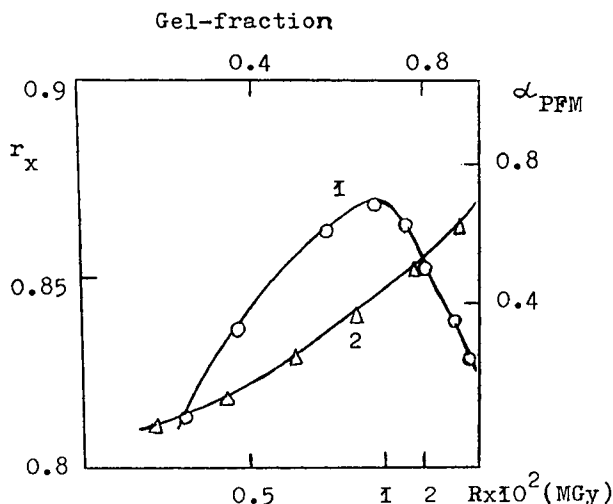
Therewith, the value  $i \approx 0.1-0.15$ .

Evidence of this mechanism is the dose dependence of the PVC part in the gel,  $r_x$ . The maximum value of the PVC part is at a dose corresponding to the SF product stage (Fig. 5). At larger doses, the value of  $r_x$  decreases because of the joining of residual PFM molecules to the gel.

We compared results for systems based on PVC and PE (Fig. 3). The local concentration of PFM in



**Figure 4** Parameters  $n$  (1),  $m$  (2), and  $G_c^*$  (3) in dependence on dose  $R$  and conversion degree of double bonds  $\alpha$  for the irradiated PVC-23% TAIC system.



**Figure 5** Dose dependencies of (1) the PVC part,  $r_x$ , and (2) the PFM part,  $\alpha_{\text{PFM}}$ , in a gel for the irradiated PVC-23% TAIC system.

noncrystalline regions of PE samples is equal to  $\sim 12\%$ , i.e., this concentration is larger than the average content of PFM (6%), because the PFM molecules do not penetrate into the crystalline regions. In the case of systems based on PVC, the local concentration of PFM is near the average content of PFM, because the degree of crystallinity of PVC is small.

The value of  $(G_c^*)_{\text{max}}$  in the case of the system PE-6% TAIC is larger than in the case of the PVC-13% TAIC system. The value of  $(G_c^*)_{\text{max}}$  depends on two parameters, namely, the crosslinking yield corresponding to the SF product stage and the amplification factor  $i$ . The amplification factors for the PE-6% TAIC and PVC-13% TAIC systems are close together, namely,  $\sim 0.15$ . However, the differential yield of crosslinking, corresponding to the SF product stage, in the case of the PE-6% TAIC system, is larger than in the case of the PVC-13% TAIC system (Fig. 3), i.e., a number of crosslinks with reactive "hanging" double bonds is larger. This is possible if the degree of polymerization of graft chains is decreased. Hence, this is a cause of the large value of  $(G_c^*)_{\text{max}}$  for systems based on PE in comparison with systems based on PVC.

## CONCLUSION

The radiation-induced crosslinking process in the PVC-PFM and PE-PFM systems was investigated on the basis of the notion of the differential yield of crosslinking,  $G_c^*$ . In the general case, network for-

mation in the polymer-PFM systems evolves in a stepwise fashion as the dose is increased.

- Formation of crosslinks as the short branched graft chains of poly-PFM; this is the SF product stage. During this stage, the chain polymerization of PFM takes place, but the chain crosslinking does not.
- Formation of a three-dimensional network by the SF product joining with free PFM molecules; the chain crosslinking takes place during this stage.
- Reactions of residual double bonds; during this stage, part of nonchain crosslinking occurs.

The maximum value of the differential crosslinking yield,  $(G_c^*)_{\text{max}}$ , depends, apparently, on the differential crosslinking yield on the SF product stage and the amplification factor  $i$ .

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