The radiation crosslinking of PVC coated wires has been recently established as the first radiation process of big volume. As the radiation crosslinking of PVC is performed in presence of monomeric additives, this process is both a grafting and a crosslinking reaction.

For crosslinking additives, bifunctional esters of methacrylic acid are often used. These monomers exhibit some features which make their use advantageous. Firstly, they are effective plasticizers for PVC, giving good contact with the PVC chains and thus facilitating the grafting reaction. Secondly, they are sensitive to radiation: their free radical yield (G-value) upon irradiation is high. In the classical concept of graft copolymerization this is regarded as a disadvantage. If we use a monomer with a high G-value, the free radicals are generated mainly in the monomer, giving rise to homopolymerization rather than grafting. But, things stand differently with bifunctional monomers like the dimethacrylates. Aso has shown, that in these monomers the second double bond has about 7-5 times less reactivity, because of restricted mobility. The dimethacrylates polymerize therefore mainly in long chains, which are crosslinked at a relatively early stage, but in which a high concentration of pendant double bonds remains, in spite of considerable internal cyclization. The concentration of pendant double bonds does hardly change up till high conversions. Through these pendant double bonds may the poly-dimethacrylate homopolymer form graft copolymer and consequently crosslinks with the matrix polymer.

The crosslinking of PVC in the presence of monomeric additives has been extensively studied by Salmon and Loan.5 50 parts of tetraethylene glycol dimethacrylate has been added to 100 parts of PVC and processed on a mill. The total gel content rises to almost 50% with a dose of only 100,000 rads. But this does not mean, that at this point the PVC has been effectively crosslinked. The crosslinked material consists mainly of poly-tetraethylene glycol dimethacrylate, while only 20% of the PVC is crosslinked. A substantial part of the original unsaturation is yet also present at this stage, in the form of pendant double bonds, leading, in the second stage, to the crosslinking of the greater part of the PVC, in this case of 81% of the original polymer at 5 Mrad.

The taking of good kinetic curves of the polymerization in similar systems presents considerable difficulties. The dilatometer commonly used in chemical kinetics for taking continuous curves from the same sample, is here not applicable. Thus, the scatter between different samples has to be taken into account. In addition, the course of the kinetic curve is expectedly more complicated, than in homogenous kinetics. Therefore, we made use of microcalorimetry and followed the chemical kinetics through the thermokinetic curves.

The microcalorimeter built for this purpose is of the Calvet-type (Fig. 1). It consists of two metallic cylinders situated in a block connected to a water thermostat. The thermal contact between the metallic cylinders and the block is secured through batteries of 120 thermoelements connected in series; any temperature difference between cell and block creates a proportional thermal flux through the wires and, at the same time, a proportional electromotive force. The two cells are connected in opposition. The time constant of the calorimeter is 3 min; as the time scale of the experiments is much longer, the reading of the electromotive force may generally be taken as a measure of the instantaneous rate of polymerization.

The construction of our calorimeter allows the introduction of the thermostated block into a cobalt-source of 500 Ci; for purely thermal measurements without radiation, we made use of a high sensitivity commercial microcalorimeter type Setaram.

Figure 2 shows the thermokinetic curves of the polymerization of methyl methacrylate at 55°C. The rate of polymerization is even in the stationary state steadily increasing, as often in radiation polymerization. One may see in the region of the gel-effect a maximal increase in rate by about 12 times.

If we add PVC powder to the monomer, the increase in rate becomes much more conspicuous, the maximum being about 6 times higher, than in methylmethacrylate homopolymerization. In the mixture with only 20 parts of methylmethacrylate the reaction slows down at a very low conversion. The reason is, that at the comparatively low temperature of the experiment the monomer forms a
glassy mixture with PVC, getting immobilized together with the PVC chains.

For pure ethylene glycol dimethacrylate, the rate of polymerization increases sharply already at a very low conversion (Fig. 3). In fact, as compared with methyl methacrylate, the reaction begins with a much higher rate, but has a longer running out, much longer too, than the samples with PVC plus methylmethacrylate.

The limiting conversion in homopolymerization is generally determined by the glass-forming composition of the polymer-monomer mixture at the given temperature. In the case of ethylene glycol dimethacrylate, the glass-forming composition may be calculated after Kelley and Bueche to be about 75% polymer at 55°C, but the polymerization stops or rather slows strongly down at a much lower conversion. This may be due to the fact, that the first double bond of ethylene glycol dimethacrylate reacts much more rapidly, than the second one. Thus, a conversion of 55% does not mean in the case of a similar monomer, that the reaction mixture contains 55% polymer and 45% monomer. It means rather, that over 80% of the monomer disappeared, and perhaps 30% of the pendant double bonds reacted, roughly half of which formed intramolecular rings and the other half intermolecular crosslinks, while the greater part of the pendant double bonds remained yet intact but reacts further very slowly.

Figure 4 shows the rate of polymerization of ethylene glycol dimethacrylate with PVC powder, initiated by azobis-izo-butyronitrile. After a small peak the beginning of the reaction is strongly delayed. In this case, we have no signal for over 50 hr, but after that we have a sudden, rapid polymerization. If we increase the proportion of the monomer, a part of it does not come into intimate contact with the PVC; this is the reason of such curves with two maxima, as can be seen on Fig. 5.

In radiation initiation at 55°C (Fig. 6), too, we have an inhibition of about 200 min, after which the reaction starts with a high rate. Some accelerating effect of PVC as compared with the pure monomer can be observed although it is not as conspicuous as with methylmethacrylate; the maximal rate is about twofold.

Let us examine now the radiation polymerization reaction inside the processed sheets prepared with PVC and ethylene glycol dimethacrylate monomer, and have a look at the first stage of this reaction. It is during this stage, when the unreacted monomer disappears from the sheets and when the most conspicuous changes in properties occur. Such is the case e.g. after a small radiation dose of 50 krad. Figure 7 shows dielectric depolarization spectra of pressed sheets. The dielectric depolarization is performed by polarizing the samples at 150°C by a high d.c. voltage, cooling at constant rate under tension, then heating at a constant rate, while measuring the current. As can be seen, in the unirradiated sample a high peak appears, corresponding to the PVC plasticized by the free monomer. After only 50 krad or irradiation, the peak corresponding to the glass transition of hard PVC appears, while that corresponding to the phase rich
Radiation crosslinking of PVC

Fig. 4. Polymerization of 50 parts of ethylene glycol dimethacrylate in the presence of 100 parts of PVC powder. Initiator 0.5% azo-bis-izo-butyronitrile. Temperature 50°C.

Fig. 5. Same as Fig. 4 but 110 parts of ethylene glycol dimethacrylate.

Fig. 6. Radiation polymerization of 50 parts of ethylene glycol dimethacrylate in the presence of 100 parts of PVC powder. Dose rate 32 krad/hr, temperature 55°C.
in monomer diminishes. The monomer polymerizes further during the measurement and in the second run only the transition of the hard PVC can be observed together with a high temperature peak.

When using commercial monomers with 50-100 ppm hydroquinone, without additional inhibition, it is generally observed, that the monomer begins to polymerize already during the processing or the storage, before any irradiation. Table 1 shows gel content and residual monomer measurements of roll milled sheets. Milling was performed at 160°C. As can be seen, some monomer disappears by evaporation and by polymerization, already during the milling. After storage a measurable quantity of gel is formed. Upon annealing at a moderately higher temperature, the gel content rises and the residual monomer is further reduced. Notwithstanding the comparatively low amount of monomer left, the sample is still in the very first stage of the crosslinking process.

A sample of the same batch was investigated in the microcalorimeter 16 months after preparation (Fig. 8). Right at the beginning, during the warm-up period, a sharp exotherm was observed, similar e.g. to the so-called fast reaction obtained with rising temperature in acrylonitrile polymerization. A similar course of the reaction with a lower peak was observed with milled sheets prepared 16 months ago from 100 parts of PVC and 20 parts ethylene glycol dimethacrylate (Fig. 9).

The kinetic character of the fast reaction is such, that it must clearly be initiated by a relatively high concentration of trapped free radicals. This could be shown also by ESR. Figure 10 shows the ESR signal of the same milled, unirradiated sheet of 100 parts PVC and 50 parts ethylene glycol dimethacrylate, after storage of 16 months. This is the characteristic so-called 5+4 line spectrum of derivatives of the methacrylic acid in solid or gelled media. The spectrum corresponds to a concentration of $9 \times 10^{-5}$ mol/l. radical. After 60 min at 55°C, the concentration of the radicals falls by over one order of magnitude, (Fig. 11),

![Fig. 7. Dielectric depolarization currents in pressed sheets from 100 parts of PVC and 60 parts of ethylene glycol dimethacrylate. Polarization at 150°C, 5 kV/cm for 30 min. (1) unirradiated, (2) irradiated by 50 krad, first run; (3) irradiated by 50 krad, second run.](image)

![Fig. 8. Polymerization in milled sheet prepared from 100 parts of PVC and 50 parts of ethylene glycol dimethacrylate. Dose rate 32 krad/hr, temperature 55°C. Storage time 16 months.](image)

<table>
<thead>
<tr>
<th>Storage time</th>
<th>48 hr</th>
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<th>16 months 55°C, 60 min</th>
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<td>Annealing no.</td>
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<td>no.</td>
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<tr>
<td>16 months</td>
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<tr>
<td>55°C, 60 min</td>
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<td>16 months</td>
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Table 1. Storage effects in miled sheets from 100 parts of PVC and 50 parts of EGDM
but by further storage for one month at room temperature the concentration increases again to \(6 \times 10^{-7}\) mol/l.

During the fast reaction, about 3% of the initial double bonds is used up. If we assume that all the free radicals react, this corresponds to a chain length of over \(10^3\). This shows, that the fast reaction is a chain polymerization with comparatively long kinetic chains.

The question arises, where these free radicals originate from? It is known, that free radicals are produced during mechanical treatment of PVC and may be produced during milling. But these radicals recombine in the soft sheets and can not survive at room temperature for 16 months. Figure 12 shows the ESR spectrum of a freshly milled sheet of the same composition. Only a peroxy-type singlet may be discerned which is probably present in the other signals as well. The lower curve is the signal of the glass. Similarly, no trace of the methacrylate spectrum can be observed, when the sheets are milled twice for 10 min at 160°C. These samples do not give the fast reaction either.

Thus, it can be concluded, that the frozen-in methacrylate radicals in the unirradiated system must be formed in a thermal polymerization process during storage.

It is also clear, that in unirradiated, or only slightly irradiated soft samples, in which not only the production, but also the termination of free radicals may take place at a reasonable rate, there may be a slow polymerization during the time of storage, but neither can frozen-in free radicals be detected by ESR, nor any fast reaction can be observed.

The glass transition temperatures of the investigated samples were determined by a penetration measurement: a profile of \(2 \text{ mm}^2\) was forced under a load of 0.5 kp/cm\(^2\) into the specimen, while increasing the temperature at a constant rate (Fig. 13). The rigid PVC (1), as well as samples polymerized up till high conversion by radiation, exhibit a glass transition of 80°C. The freshly milled
sample, prepared with 50 parts ethylene glycol dimethacrylate (3), shows a strongly plasticized character, even more so, than the PVC plasticized with 20 parts of dioctyl phthalate (2). But storing for 16 months brings the glass transition temperature of the PVC higher, just to about 40-50°C, where the fast reaction occurs (4). In our experience, high concentration of free radicals in unirradiated, stored samples is found, when the glass temperature of the samples is just above room temperature. These are samples, which were formerly soft, where the free radicals formed during storage immobilized themselves by the polymerization reaction.

Let us go now over to the second stage of the crosslinking reaction. In this stage, above a dose of about 60 krad, there is already practically no monomer in the system. This stage is the reaction of the pendant double bonds with each other and with the PVC. From the calorimetric curves it can be seen, that the disappearance of the double bonds proceeds even in this stage in an efficient chain reaction, although the reaction rate or the average chain length may be several times less, than in the first stage. The glass transition temperature of PVC is in this stage practically the same as that of the hard PVC.

If we irradiate the milled sheets produced from 100 parts PVC and 50 parts ethylene glycol dimethacrylate by say 0.2 Mrad, a high concentration of free radicals of the methacrylate type can be observed. These free radicals decay slowly, but in a curious way. So, e.g. in a sheet irradiated 16 months ago, an appreciable concentration of free methacrylate radicals of several times 10^{-3} mol/l was measured. Then, after further storage of a week at about 35°C, the concentration of free radicals increased by over tenfold! The free radicals seem to play at hide and seek. Obviously, the motion of the pendant double bonds, the generation of the new free radical sites goes on even in these, essentially glassy materials.

If we go now even higher with the dose, the instantaneous rate of disappearance of the double bonds—as witnessed by the calorimetric curves—becomes smaller; the rate is in fact after some hundred thousand rad by two or more orders of magnitude less, than in the first stage. Thus, one may assume, that pendant double bonds react in very short chains or even singly, leaving high concentration of frozen-in free radicals.

Sheets prepared from 100 parts PVC and 50 parts ethylene glycol dimethacrylate were irradiated by high doses of several Mrad. Figure 14 shows the signal of a sample irradiated by 4 Mrad and measured within 24 hr after irradiation. The signal is again of the methacrylate type, but the radical concentration amounts to 5 \times 10^{-3} mol/l, showing the extreme radical trapping capability of these crosslinked glassy systems.

A great part of these radicals has been formed originally on the PVC chains, but became transformed to methacrylate radicals in the course of the polymerization reaction. Upon storage, the radical concentration in these highly irradiated samples diminishes. After one month storage at room temperature, a concentration of 10^{-2} mol/l still remains, but the spectrum shows a strong component of a peroxy-type asymmetric singlet (Fig. 15). After 16 months, radical concentration of several times of 10^{-3} mol/l was measured. At a slightly higher temperature this, too, disappeared, leaving only the asymmetric singlet of comparable concentration.

Let us say now some words about the structure of our system in this final, crosslinking stage.

The monomer units with pendant double bonds may be regarded from the structural point of view as the monofunctional comonomers of ethylene glycol dimethacrylate. The monofunctional analogue of ethylene glycol dimethacrylate is ethylene mono methacrylate mono isobutyrte. The homopolymer of this monomer has
its own glass transition temperature at 2°C. Thus, through copolymerization, it diminishes the glass transition temperature of polyethylene glycol dimethacrylate. Figure 16 shows penetration measurements of a pressed PVC-ethylene glycol dimethacrylate sample without and after irradiation by 200 krad. The T_g of hard PVC appears already at this comparatively low dose; it does not change much even in highly crosslinked materials. The transition at about 110°C may be tentatively ascribed to the “co-graft-co-polymer” of fully and partly reacted ethylene glycol dimethacrylate. Through higher radiation doses, this transition is shifted to higher temperatures, as the pendant double bonds polymerize, and the copolymer is gradually transformed into homo-graft of poly-ethylene glycol dimethacrylate. Extensive phase studies, combined with high sensitivity microcalorimetry and ESR analysis should contribute to the better understanding of this reaction.


Methyl methacrylate: analytical grade, twice vacuum distilled.
Ethylene glycol dimethacrylate: Fluka, stabilized with 60 ppm hydroquinone. For milling and pressing used as such, for other experiments extracted and vacuum distilled.
Milling was performed at 160°C, pressing at 150°C. Monomer and plasticizer concentration given in parts added to 100 parts of PVC.

Acknowledgements—The author is indebted to Dr. P. Hedvig, Mrs. A. Somogyi and Miss E. Takács for their continuous help, to Dr. A. Rockenbauer for the ESR measurements and to Miss Barbo Löfgren for doing some of the experiments.

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