RADIATION CROSSLINKING OF POLY(VINYL CHLORIDE) ENHANCED BY A TETRAFUNCTIONAL COAGENT

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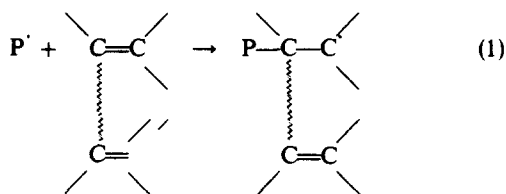Centro di Studio per la Fisica delle Macromolecole del C.N.R., Bologna, Italy

Abstract—Irradiations were carried out with mixtures of poly(vinyl chloride) and a solvent capable of preventing the polymer from discoloration, such as tetrahydrofuran or cyclohexanone, both in the absence and in the presence of a tetrafunctional monomer (ethyleneglycol dimethacrylate) acting as a coagent for enhanced crosslinking. Comparison of the results enabled formulation of a reaction scheme based on an early depletion of the free coagent molecules via polymerization. In the early stages, the PVC macromolecules, whenever dissociated into free radicals, initiate a chain addition of coagent molecules resulting in the formation of complex macromolecules with a number of pendant C=C groups. All the latter macromolecules, because of their high susceptibility to radical attack, grow rapidly and eventually become part of the gel portion. In the late stages, radical addition to pendant C=C groups in the gel network still occurs effectively but the addition steps are very few and there may be only one such step before radical deactivation. Hence, there is small consumption of double bonds; further, the PVC macromolecules, once homolytically dissociated, are directly incorporated into the gel. An interesting consequence is that no crosslinked macromolecules remain in the sol portion. The influence of the solvent is discussed.
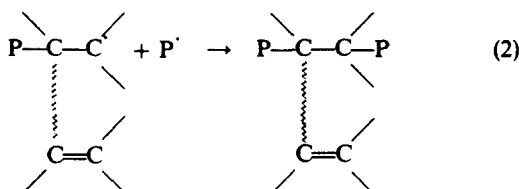
INTRODUCTION

Radiation-crosslinking of polymeric material is of increasing commercial importance, because of the superior properties, especially with regard to high temperature applications, imparted by a high level of crosslinking. It is common practice industrially to add to the material monomers with two or more ethylenic bonds, and in some cases monomers with one acetylenic bond [1], to enhance the radiation crosslinking yield [2]. These monomers, denoted coagents or promoters, are generally employed in small proportions around 5% [3], although for poly(vinyl chloride) (PVC) far larger amounts are reported [4, 5].

The enhanced crosslinking can be produced in various ways. The simplest action of coagents is the following reaction with a polymer radical produced by radiolysis:

$$P^{\cdot} + \quad \begin{matrix} \backslash \\ \end{matrix} C{=}C \begin{matrix} / \\ \backslash \end{matrix} \rightarrow P{-}C{-}C \qquad (1)$$

(I)

$$P{-}C{-}C \quad + P^{\cdot} \rightarrow P{-}C{-}C{-}P \qquad (2)$$

where I represents a tetrafunctional monomer and P˙ a macroradical resulting from the cleavage of C–C and C–X bonds, X being hydrogen, halogen, etc.

As a result, two macroradicals join through a coagent double bond, with formation of a new macromolecule with a pendant double bond. When the latter also reacts in turn according to Eqns (1) and (2), one notes that four macroradicals give rise to one instead of two macromolecules [6].

A more effective mechanism for coagent action can be formulated if reaction (1) is followed, at least partially, by hydrogen atom abstraction [7]:

$$P{-}C{-}C^{\cdot} + PH \rightarrow P{-}C{-}C{-}H + P^{\cdot} \qquad (3)$$
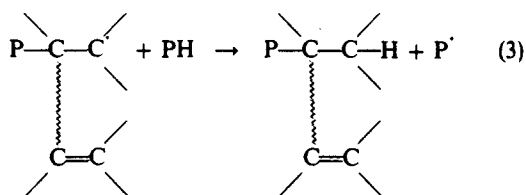
where PH is a normal macromolecule.

The occurrence of the same reactions with the second double bond leads to a crosslink with conservation of the radical site. In other words, the crosslinking proceeds via a chain reaction. A similar reaction scheme can be written when the monomer with two ethylenic bonds is replaced by an acetylenic compound [1].

Another reason for enhanced crosslinking can be envisaged if reaction (1) is so fast that the macroradical P˙ is prevented from undergoing reactions which might lead to chain scissions and/or degradation of other type [7]. Finally, ill-defined mechanisms involving interactions of the coagents with ionic active centres have also been postulated [2].

Among the polymers for which radiation crosslinking is of concern, PVC is one of the most important. However, there is a drawback due to the dehydrochlorination leading to discoloration during radiation exposure of PVC [8, 9]. This reaction always accompanies crosslinking and chain scission reactions and, moreover, becomes significant at a much earlier stage. Whenever irradiation is carried out with mixtures of PVC and solvents, crosslinking and chain scission take place without polymer discoloration [10–13]. In particular, solvents of the class of cyclic ethers have been patented as stabilizers against deleterious effects of radiation [14].

For the action of the latter solvents, a mechanism was formulated [13] thus:

$$P^{\cdot} + CH_2\!\!-\!\!CH_2 \;\rightarrow\; PH + CH_2\!\!-\!\!CH_2 \qquad (4)$$
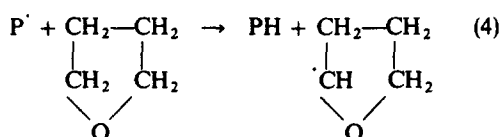
followed by successive hydrogen abstraction from the tetrahydrofuran (THF) radical by another P' macroradical, resulting in the formation of a double bond in the solvent molecule. A similar reaction has been postulated [15] also for ketones, such as cyclohexanone (CX), which have particularly labile hydrogens at the α position to the carbonyl group.

The disappearance of macroradicals P' should lead to suppression not only of dehydrochlorination but also of crosslinking. Since with THF the latter reaction does occur to a large extent, another explanation was advanced by other authors [11]. THF undergoes a ring opening followed by addition to two macroradicals P' in a fashion similar to reactions (1) and (2).

In the present work investigations have been carried out on the irradiation of PVC mixtures with THF and CX in the presence of small amounts of ethyleneglycol dimethacrylate (EGDM).

EXPERIMENTAL

Material

PVCSICRON 548 ($\overline{M}_w = 130{,}000$, $\overline{M}_n = 53{,}000$) was provided by Montedison S.p.A. THF (RP, C. Erba product) was refluxed over NaOH and distilled under N_2 immediately prior to use. CX (RP, C. Erba product) was purified by distillation under N_2 at reduced pressure (b.p. $70°/40$ mm Hg). Methanol (Rudipont) was distilled prior to use. EGDM (Sartomer SR 206) was used as received.

Procedure

Liquid EGDM (0.05 or 0.10 g) was added to 1 g PVC powder, and homogeneously dispersed. The mixture was sinterized into a thin disc by means of a Buehler Ltd laboratory press at 100° under a pressure of ~250 atm for 10 min. The disc was cut into narrow strips, which were introduced in a pyrex glass vial containing 1 g solvent. Before appreciable swelling took place, the vial was degassed by repeated freezing-thawing cycles and flame-sealed under 10^{-5} mm Hg vacuum. A similar procedure was adopted with the samples with no EGDM added. All the vials were stored at room temperature overnight to allow preliminary swelling of the polymer and then heated at ~110° for 30 min so that homogeneous and transparent mixtures were obtained. These conditions were chosen because longer periods and higher heating temperatures

gave rise to bubbles. The vials were irradiated with ^{60}Co γ-rays for various times at a fixed dose rate, determined by means of a Fricke dosimeter, using $G(Fe^{3+}) = 15.5$. After irradiation, each vial was broken and its contents were Soxhlet extracted for two days with THF. The insoluble polymer portion (gel) was washed with excess methanol, vacuum dried and weighed. The soluble fraction (sol) was recovered from the solution first through concentration by solvent evaporation and then by precipitation with methanol, followed by vacuum drying and weighing.

i.r. Analysis was performed by means of a Perkin–Elmer IR 580 Spectrophotometer on the polymer samples incorporated into KBr pellets after thorough grinding at liquid N_2 temperature. Carboxylic groups and C=C groups were determined, the former from the ratio of the peak at 1730 cm^{-1} to that at 630 cm^{-1}, and the latter from the ratio of the peak at 1640 cm^{-1} to that at 630 cm^{-1}. The absorption at 630 cm^{-1}, due to C–Cl stretching, is used as internal standard to allow for changes in sample thickness. Calibration curves were obtained using EGDM/PVC mixtures of various compositions. For both groups the plots of absorbance ratio vs. EGDM percentage appeared satisfactorily linear over the range investigated.

Measurements of light scattering were made on the sol fractions in THF solution with a Sofica photogoniodiffusometer, adopting a procedure described previously [16], and of gel permeation chromatography (GPC) with a Waters Associates instrument, using four columns, designated 10^6, 10^5, 10^4 and 10^3, in combination. Chlorine analyses were made on the samples by the Schröninger method.

RESULTS AND DISCUSSION

Radiations were carried out with PVC/THF mixtures at a constant dose rate of 0.205 Mrad/hr up to various post-gel doses. Even with the maximum dose of 12 Mrad, no discoloration was observed in the recovered dried samples in agreement with previous findings [10–13].

The gel weight fractions, g, for the various doses are reported in Table 1 together with some $\overline{M}_w$ values for the sol fractions and some chlorine analyses for both fractions.

It can be seen that the chlorine weight percentages, determined rather imprecisely, are always somewhat lower than the theoretical value of 56.7, indicating that the irradiated samples no longer consist entirely of VC units, a fact already found by previous authors [11]. Chemically-bonded molecules of solvent, as previously advanced [11], or replacement of chlorine by hydrogen atoms through the radiolysis cleavage of C–Cl bonds followed by reaction (4) of the macroradical P' [13], might be the explanation. In any case, these small changes in composition are such as not to

Table 1. Radiation runs with mixtures of PVC/THF in the weight ratio 1:1

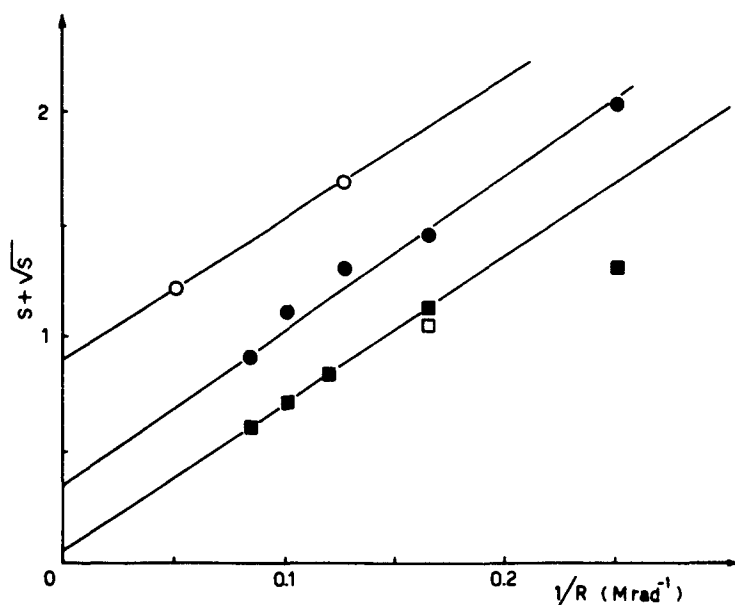| Dose (Mrad)	g	Gel fraction		Sol fraction		
		% Cl	% VC units	% Cl	% VC units	$\overline{M}_w$
4.1	Trace					
6.0	0.361					
7.6	0.465	56.2	98.8			558,000
9.8	0.575	54.3	95.3	56.1	98.7	
12.3	0.688	54.7	96.2			457,000

Fig. 1. Values of $s + \sqrt{s}$ as a function of reciprocal doses for mixtures: PVC/THF, 1:1 (●); PVC/THF/EGDM, 1:1:0.05 (■); and PVC/CX/EGDM, 1:1:0.05 (○). The point (□) refers to a mixture PVC/THF/EGDM, 1:1:0.10.

affect appreciably the determined values of the gel and sol weight fractions, i.e. g and s, respectively.

The values of $s + \sqrt{s}$ are plotted vs the reciprocal dose in Fig. 1. A straight line can be satisfactorily traced through the data points, in agreement with the equation of Charlesby–Pinner [17], valid for irradiation of polymers with most probable MWD:

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{1}{q_0 P_n R} \qquad (5)$$

where p_0 and q_0 are the values per unit dose of the density of chain scissions and the density of cross-linked units, respectively.

From the intercept and the slope, the values of $p_0 = 7.3 \cdot 10^{-5}\,\mathrm{Mrad}^{-1}$ and $q_0 = 18.3 \cdot 10^{-5}\,\mathrm{Mrad}^{-1}$ were obtained. These led to $G_s = 0.55$ and $G_c = 0.70$,

as the number of main chain scissions and the number of crosslinks per 100 eV of energy absorbed by the PVC/THF mixture. The gel point dose is 4 Mrad. It is interesting to compare this value with that of 2.5 Mrad, found previously in an investigation in the pre-gel region with 12% PVC solutions in THF [12]. The faster crosslinking with a more dilute solution seems to point to active participation of the intermediates of radiolysis of THF, which is not easy to explain. Regarding the $\overline{M}_w$ values of the sol, they appear to be rather high and decreasing with increasing dose as expected [17].

Analogous irradiation runs were carried out with PVC/THF mixtures containing 5 phr EGDM and the found g values are reported in Table 2. The Table also shows the value for a run with 10 phr EGDM, which seems to indicate a rather small increase in the co-

Table 2. Radiation runs with mixtures PVC/THF/EGDM in the weight ratio 1:1:0.05

| Dose (Mrad) | g^* | | Gel fraction | | | | | | Sol fraction | | |
		% Cl	% VC units	% EGDM units calc.†	% EGDM units (i.r.)‡	% EGDM units (i.r.)§	% Cl	% VC units	% EGDM units (i.r.)‡	$\overline{M}_w$
1.0	Trace						55.0	96.8	2.5	1,560,000
2.2	0.202	48.6	85.5	24.1	7.0	3.8	54.9	96.7	1.0	703,000
4.1	0.438	48.0	84.4	10.9	9.6	3.2		~0		
6.0	0.555	48.1	84.7	8.6	9.2	2.9				
8.3	0.710	50.6	89.1	6.7	6.4			~0		82,000
9.8	0.765	47.9	84.3	6.2	6.4	3.0	55.1	96.9		79,000**
12.3	0.814	50.2	88.4	5.8	5.0	1.5				90,000
6.0††	0.601	46.1	81.1	15.1	9.5					

* Ratio of the weight of insoluble fraction to (the initial amount of PVC + amount of EGDM).
† Ratio of initial amount of EGDM to amount of gel.
‡ Relative to ester group absorption.
§ Hypothetical percentages of unreacted EGDM units derived from C=C absorption.
** By GPC measurement.
†† Mixture of PVC/THF/EGDM (1:1:0.10).

agent crosslinking efficiency over this concentration range.

From these data it appears that Eqn (5) is no longer valid. Plotting in Fig. 1 the $(s + \sqrt{s})$ values as a function of reciprocal doses, only the points for the higher doses can be considered to lie satisfactorily on a straight line, while large deviations are shown by the values at 4.1 Mrad, also plotted in Fig. 1, and the values at 2.2 and 1.0 Mrad, not reported. In particular, the last dose value corresponds to the gel point, as compared with the value of 3 Mrad, which is found by extrapolating the linear region of the plot. This discrepancy undoubtedly points to a crosslinking process of PVC in the presence of EGDM proceeding along lines different from those postulated for the derivation of Eqn (5).

To gain more insight into the mechanism of the coagent action, other measurements have been carried out and the data are reported in Table 2.

The chlorine weight percentages in the gel fractions indicate an appreciably lower content of VC units than in the gel fractions of the samples irradiated in the absence of EGDM, while there is no appreciable difference in percentage when the sol fractions are concerned. This result can be explained by assuming that, upon irradiation, EGDM becomes all chemically-bonded to the gel portion. Weight percentages of EGDM units calculated on this assumption are shown in column 5 of Table 2. Indeed, starting with the sample at 4.1 Mrad, by addition of the values of columns 4 and 5, the wt % of foreign units present in the samples approach those for the runs without EGDM and are similarly independent of dose.

Support for the above assumption was obtained by i.r. analysis. The measurements of the ratio of the peak at $1730\,\text{cm}^{-1}$ to that at $630\,\text{cm}^{-1}$ permitted estimation of the EGDM percentages in the gel, reported in column 6 of Table 2. As can be seen, the agreement with the calculated values is good, if the run performed with 10 phr EGDM is excepted. Moreover, it should be noted that i.r. analysis of the sol fractions did not reveal any ester group absorption. These considerations do not apply to the early stages of the gel region where it might be expected that EGDM is shared between the sol and gel fractions and, in part, is still ungrafted.

From the ratio of the $1640\,\text{cm}^{-1}$ (weak) peak to the $630\,\text{cm}^{-1}$ peak a rough determination of the fraction of residual unsaturation of EGDM incorporated into the gel could be made. Since the calibration curve was derived for mixtures of PVC and EGDM monomer, the i.r. measurements gave hypothetical wt % of EGDM with both ethylenic bonds unreacted. Dividing these percentages (column 7 of Table 2) by those of column 5 or column 6, one obtains residual unsaturation fractions somewhat less than 1/2 and little dependent on dose. Thus, it can be inferred that the EGDM molecules react all with one double bond and in part with both double bonds in a comparatively rapid fashion during the pre-gel region and the first part of the post-gel region, while consumption of residual double bonds proceeds very slowly thereafter.

Moreover, the yield of the reacted double bonds per 100 eV energy absorbed, averaged over the irradiation period up to 4 Mrad, should be larger than the value calculated for the case corresponding

to all the EGDM reacted with only one double bond. This calculation gives G(double bonds saturated) > 30 and undoubtedly considerably larger values would be obtained for irradiation stopped at lower doses. Therefore, it should be concluded that initially EGDM undergoes addition polymerization resulting in the formation of chains of a certain length.

Finally, some light-scattering measurements were carried out on the sol fractions. As shown by Table 2, after the gel point the $\overline{M}_w$ values decrease drastically from the very high values attained and become lower than that of the untreated polymer, at variance with the case without EGDM, where the decrease of $\overline{M}_w$ occurs to a much smaller extent. From such results, it can be inferred that in the later stages of irradiation only macromolecules which have undergone no crosslinking remain in the sol portion.

Further evidence in line with this assertion was obtained by GPC analysis of the sol fraction of the 9.8 Mrad sample. In fact, the chromatogram, reported in Fig. 2 together with that for the untreated PVC, shows no tail in the high molecular weight region, commonly observed [12] in polymers subjected to crosslinking. Additional information can be gained by comparing the two chromatograms of Fig. 2. It appears that the sol fraction has maintained the most probable MWD with only a slight shift to lower molecular weights with respect to the untreated polymer. This result can be plausibly accounted for by postulating not only the removal from the sol fraction of the macromolecules initially involved in the crosslinking reaction but also the occurrence of chain scissions at random along the linear macromolecules left unreacted.

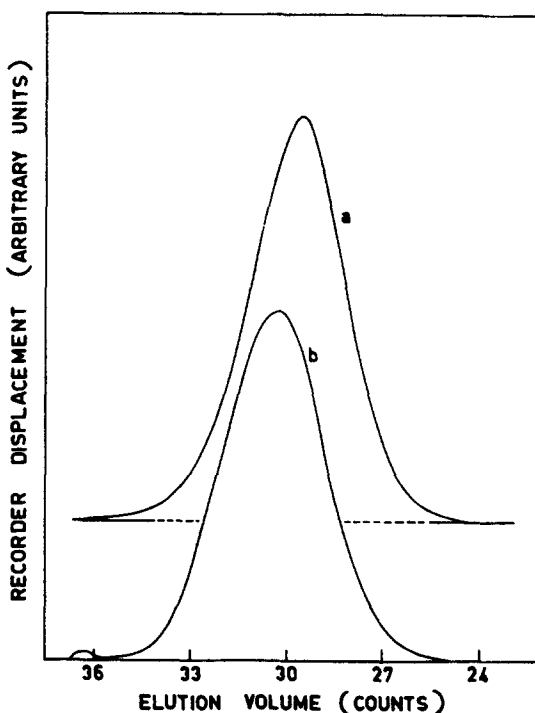From the above picture the general patterns of the

Fig. 2. Gel permeation chromatographs of: original PVC (a) sol fraction relative to PVC/THF/EGDM (1:1:0.05) sample irradiated at 9.8 Mrad (b).

coagent action can be assumed to resemble those described by Salmon and Loan for systems with a much larger coagent proportion with respect to PVC and in the absence of solvent [4]. Upon irradiation the macroradicals and the other small radicals produced by radiolysis initiate the polymerization of the coagent molecules. Thus, reactions (1) and (2) should be replaced by the over-all reaction

$$2P^{\cdot} + n \overset{\diagdown}{\underset{\diagup}{C}}{=}\overset{\diagup}{\underset{\diagdown}{C}} \;\rightarrow\; P{-}(C{-}C)_n{-}P \quad (6)$$

(II)
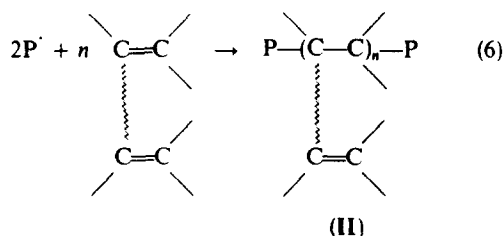
with n being initially rather large but decreasing steadily as the irradiation goes on. Obviously, macromolecules of type II with one or both polymeric substituents P replaced by small groups are also formed. Chains grafted to PVC macromolecules and homopolymer chains are produced in the former case and in the latter case, respectively.

All these types of macromolecules, which have a number of pendant C=C groups, will readily add, through one of the double bonds at least, to subsequently growing macroradicals to give rise to very large complex macromolecules. The latter, being even more susceptible to radical attack, will react still more readily. Thus, all macromolecules of type II are bound to grow rapidly and eventually to become part of the insoluble polymer portion at an early stage.

Because of polymerization, a comparatively rapid consumption of double bonds takes place. However, the chain reaction involves mostly the double bonds of mobile free coagent molecules and only to a small extent the pendant C=C group. This results in a rather early depletion of the free coagent molecules, while a great amount of unsaturation remains in the system as pendant C=C groups attached to complex molecules of type II and, later on, to the gel network. Owing to the restricted mobility of the pendant C=C groups, radical addition is no longer a chain reaction; only single steps, such as reaction (1), will take place before radical deactivation.

Also in these late stages, and not only when the double bonds are mobile and numerous, radical addition to double bonds largely prevails over other reactions which the macroradicals might undergo.

Consequently, for those PVC macromolecules which happen to be dissociated radiolytically, the fate by far most probable is to become part of the gel portion. In the earlier stages the macroradicals P' firstly become part of complex molecules of type II and then of the insoluble polymer portion. In the later stages, as soon as the PVC macromolecules are transformed into radicals, the latter react with pendant C=C groups and are directly incorporated into the gel, without passing through any intermediate steps of growth.

In this way, only original macromolecules will remain in the sol portion, in accordance with the molecular weight determinations. For the fact that the $\overline{M}_w$ values were lower than that of the original polymer, it can be reasonably supposed that some macroradicals can escape addition to double bonds and produce chain scissions. In this context it is interesting to note that no peculiar function is to be attributed to THF, apart from that of acting either as a solvent or as a swelling agent.

In order to obtain some information on this point, two runs were carried out with PVC/CX mixtures in weight proportion 1:1 at 8 and 20 Mrad, respectively. No discolouration was observed in the samples as in the mixtures with THF. Even at these high doses no gel was observed, in agreement with previous investigations on the CX behaviour [10]. Determination of $\overline{M}_w$ gave for the lower dose a value of 1.2×10^6, suggesting a proximity to the gel point if the theoretically derived [17] linear relationship between reciprocal $\overline{M}_w$ and dose is valid. However, with the higher dose, there was an increase in $\overline{M}_w$ up to 3.5×10^6 but no gel was formed. This anomaly deserves further consideration and more experimental data are desirable.

Conversely, irradiation at the same dose rates in the presence of 5 phr EGDM brought about formation of gel. Data analogous to those derived for the THF mixtures are collected in Table 3, and the related $(s + \sqrt{s})$ values are plotted vs reciprocal dose in Fig. 1.

These results, although referring to only two runs, suggest that the mechanism proposed for the THF mixtures might well operate with the CX mixtures but with considerable difference in the crosslinking efficiency. This can be accounted for by assuming that CX is much more susceptible to hydrogen abstraction by radicals than THF and, hence, such reaction is largely competitive with the radical addition to double bonds. Accordingly, the production of gel is retarded, owing to the slowing down of the formation of type II macromolecules of Eqn (6) and also because of the shorter coagent chains grafted. Another conse-

Table 3. Radiation runs with PVC/CX/EGDM mixtures in the weight ratio 1:1:0.05

Dose (Mrad)	g^*	% Cl	% VC units	Gel fraction % EGDM units calc.†	% EGDM units i.r.‡	% EGDM units i.r.§	Sol fraction $\overline{M}_w$
8	0.238	34.5	60.8	20.0	15.7	4.2	
20	0.517	48.5	85.3	9.2	7.0	1.0	115,000

* Ratio of the weight of insoluble fraction to (the initial amount of PVC + amount of EGDM).
† Ratio of initial amount of EGDM to amount of gel.
‡ Relative to ester group absorption.
§ Hypothetical percentages of unreacted EGDM units derived from C=C absorption.

quence is that a larger proportion of the C=C groups is saturated with small-sized substituents, so that it is more likely that coagent single molecules or oligomers remain ungrafted, in accordance with the lower EGDM content determined in the gel by i.r. than that calculated (see columns 5 and 6 of Table 3).

An important point is that the i.r. analysis do not show any appreciable contribution from a carbonyl group absorption to be attributed to chemically-bonded CX molecules. Hence, it should be considered that the radicals originating from CX by hydrogen abstraction neither add to double bonds nor combine with macroradicals. Perhaps, a second hydrogen abstraction with formation of a CX derivative having an ethylenic bond might occur, as already reported for THF [13].

Clearly for the elucidation of the role of CX, and also of THF, more detailed information on the composition of the irradiated systems is needed. At any rate, it does not seem that the solvent stabilizing action against PVC discoloration consists in repairing the broken bonds of the macromolecules via hydrogen atom transfer, i.e. Eqn (4) since the latter reaction would also compete effectively with the crosslinking process, an effect which can be readily admitted for CX but not for THF.

As to the EGDM action, two final considerations could be made. At high irradiation doses, the polymer changes appear to be described satisfactorily by Eqn (5) although the reaction scheme formulated here in the presence of EGDM is considerably different from that on which the equation is based.

The present results support the view that the reaction scheme, implying an early consumption of the coagent via polymerization, is valid not only for PVC systems in which the coagent is present in high proportions and heterogeneously dispersed [4, 5, 18] but also for systems containing low concentrations of homogeneously dissolved coagent. Moreover, bearing in mind that an early free-monomer depletion was recently [19] observed in the enhanced crosslinking of

polyethylene with a small amount of coagent, the scheme might be of general validity.

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