IRRADIATION OF POLY (VINYL CHLORIDE) IN VARIOUS MEDIA

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The radiolysis of poly (vinyl) chloride (PVC) in chloroform, carbon tetrachloride and dimethyl formamide was studied in air. A few samples without solvents were also studied under similar conditions to serve as blanks. A continuous decrease in intrinsic viscosity was noted in blank samples. Samples irradiated in carbon tetrachloride showed decrease in intrinsic viscosity upto 3.5 megarads. On further irradiation an increase was noted. In chloroform the intrinsic viscosity first increased gradually up to 5 megarads and later on the increase was very fast. Colour development in samples irradiated alone and in solvents was observed and this was attributed to conjugated structures. Thermal gravimetric study revealed better heat resistance in samples irradiated in chloroform and in carbon tetrachloride, the former being more thermally stable than the latter at lower dosages.

INTRODUCTION

The effect of radiation on PVC in the solid state has been reported in the literature [1-4]. It leads to cross-linking or degradation as well as to other chemical changes depending upon irradiation conditions. The first report by Wippler [4] on the radiolysis of PVC in solution has shown that the degree of crosslinking depends on the nature of solvent, being negligible in cyclohexanone and very high in dimethyl formamide.

A more detailed study on the subject was carried out in tetrahydrofuran solution [5]. Shinohara and Takamatsu [6] studied PVC as powder and thin film in water. The cross-linking yield was found to be much higher than while irradiating the dry polymer. Shinohara and Takamatsu assumed that the observed increase in cross-linking might have been due to indirect action on the polymer molecule involving $\overset{\bullet}{H}$ atoms and $\overset{\bullet}{OH}$ radicals. The chemical changes in the polymer irradiated in solution may result either (a) from the direct action of radiation (b) or, via the indirect action of the solvent on the polymer. The combined effects of (a) and (b) may extend the application of the polymer. In the present work, a systematic study of the radiolysis of PVC in dry state and in chlorinated solvents has been, therefore, carried out to investigate the accompanying changes in the polymer produced by the combined effects of (a) and (b).

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EXPERIMENTAL

Commercial PVC (BDH, mol.wt. 100,000) was used as received. The solvents, tetrahydrofuran (THF), carbon tetrachloride, chloroform, and dimethyl formamide (DMF), were of A.R. grade from Merck, Germany.

Irradiation of PVC. Irradiation of PVC was carried out in AECL Gamma beam ^{60}Co source at PINSTECH at 25° in the presence of air. The dosimetry in each case was performed by means of Fricke dosimeter (ferrous sulphate [7]. About 0.5 g of PVC was taken in a test tube and suspended in 5 ml of the solvent. It was then irradiated at dose rate of (i) 0.323 megarad/hr and (ii) 0.92 megarad/hr. PVC without solvent was also irradiated under similar conditions to serve as the blank. After irradiation the solvent was removed from the sample and then dried in the vacuum oven at 50°.

CHARACTERIZATION

Viscosity measurements of the irradiated samples were carried out in a Ubbelohde Viscometer at $303\pm0.02^{\circ}$ using THF as the solvent. The specific viscosity, ηsp, of a solution is given by the relationship.

$$\eta sp = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} ,$$

where

η = viscosity of the solution
η_0 = viscosity of the solvent
t = flow time for solution
t_0 = flow time for solvent

The intrinsic viscosity $[\eta]$ was obtained by extrapolating a graph of $\eta sp/C$ against concentration to zero concentration. Using Mark and Houwink's equation $[\eta] = KM^a$, molecular weights were calculated, with values for the constants, $K = 219 \times 10^{-5}$ and $a = 0.54$ [8].

Thermal gravimetric thermograms for the irradiated and non-irradiated PVC samples were obtained using the thermal gravimetric analysis (TGA) method with Stanton Model TG-750. About 6.0 mg of each sample was run in an inert atmosphere (argon) flowing at 50 ml/min at a normal heating rate of 10°/min from 0 to 600°.

Optical density (OD) spectra were recorded in solution of THF using a Beckmann Ultraviolet Spectrophotometer.

RESULTS AND DISCUSSION

Figs. 1-3 give viscosity evaluation at different dosages for PVC irradiated alone and in the presence of CCl_4 and $CHCl_3$ at a dose rate of 0.323 megarad/hr. Our results indicates a regular decrease in $[\eta]$ for PVC, however, in $CHCl_3$ a gradual increase in $[\eta]$ is observed at lower dosages (upto 5 megarads) and above this dose the increase is very fast. In CCl_4 the $[\eta]$ decreases gradually. After 4 megarad the decrease is slow and it goes up as compared to PVC irradiated alone (Fig. 4). The decrease in $[\eta]$ may
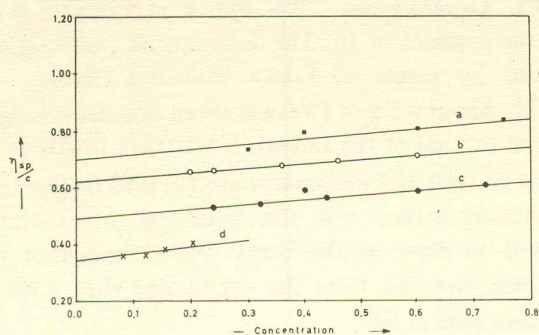
correspond to degradation. The decrease in $[\eta]$ does not always serve as the decisive test of polymer degradation, since this decrease may also be due to the main chain fracture resulting in cross-linking. The increase in $[\eta]$ corresponds to cross-linking.

Molecular weight changes of PVC irradiated alone, in CCl_4 and in $CHCl_3$ are shown in Fig. 5. Irradiated PVC alone indicates decrease in molecular weight and this corresponds to degradation. In $CHCl_3$ the molecular weight increases due to cross-linking. PVC irradiated in CCl_4 indicates decrease in molecular weight at lower

Fig. 3. Intrinsic viscosity evaluation of PVC irradiated in $CHCl_3$ at (a) 2.0, (b) 4.0, (c) 5.0, (d) 7.0, (e) 9.0 megarads.

Fig. 1. Intrinsic viscosity evaluation of PVC irradiated at (a) 1.0, (b) 3.0, (c) 5.0, (d) 9.0 megarads.

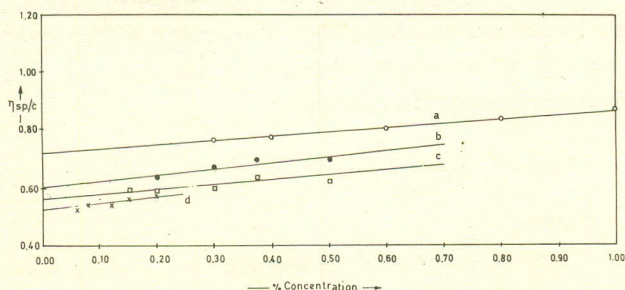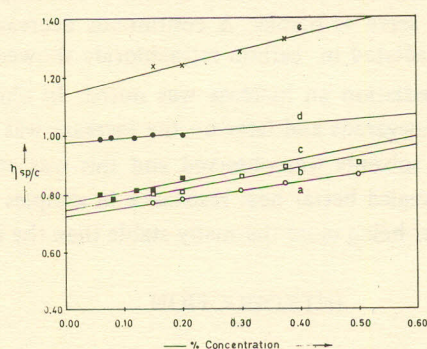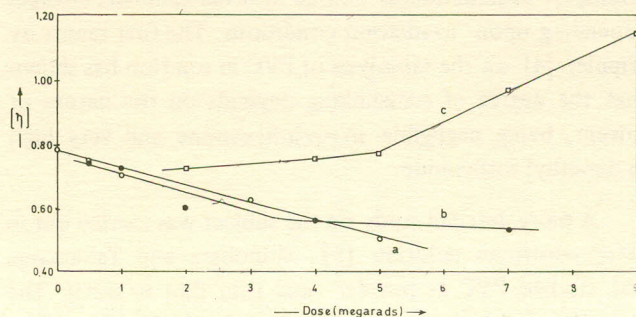Fig. 4. Plot showing the effect of gamma dose on the intrinsic viscosity of PVC irradiated (a) as such, (b) in CCl_4, (c) in $CHCl_3$.
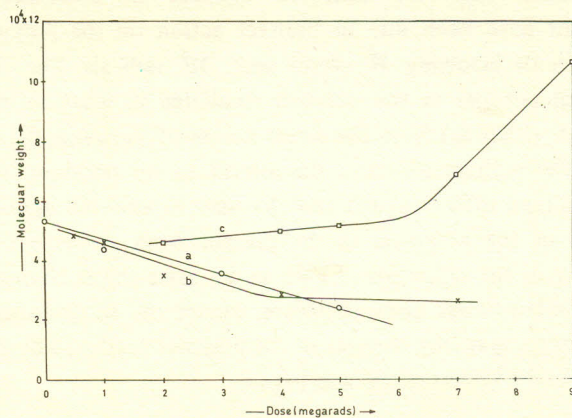

Fig. 2. Intrinsic viscosity evaluation of PVC irradiated in CCl_4 at (a) 1.0, (b) 2.0, (c) 4.0, (d) 7.0 megarads.

Fig. 5. Plot showing the effect of gamma dose on the molecular weight of PVC irradiated (a) as such, (b) in CCl_4, (c) in $CHCl_3$.

dosages. The molecular weight increases at higher dosages and this increase corresponds to cross-linking.

The solubility of the polymer in $CHCl_3$ gradually decreases after 12 megarads. The polymer irradiated alone and in CCl_4 remains soluble at higher dosages (upto 30 megarads). In CCl_4 the colour developed in PVC at a faster rate then when irradiated alone or in $CHCl_3$, the least being observed in the latter case. The development of the colour on irradiation is attributed to the formation of conjugated polyene structures resulting from the dehydro-chlorination of the polymer. Optical spectrum of unirradiated PVC in THF did not show) any maxima in the region of 295-450 nm (Fig. 6). Optical spectra of various samples
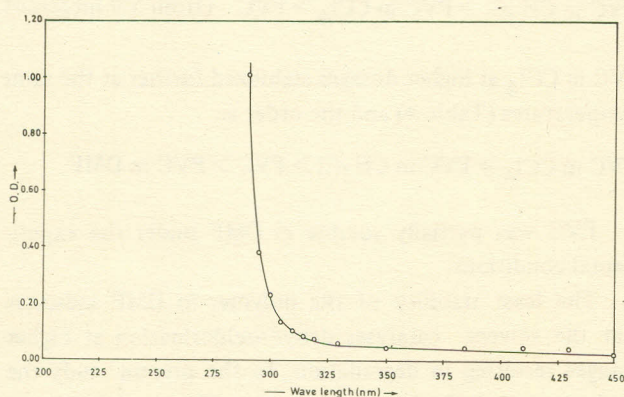
are presented in Figs. 7-9. The maxima in the region of 295-335 nm were obtained and the colour intensity was the

Fig. 9. Optical spectra of PVC irradiated in $CHCl_3$ to various dosages.

highest in the samples irradiated in CCl_4 (Fig. 8) and the least in $CHCl_3$ (Fig. 9). It was found that the intensity of the colour increases with the dose. The absorption in the region of 250-295 nm may be due to cross-linked structures.

Our results indicate that the samples irradiated to various dosages undergo not only elimination but also cross-linking reactions. Such structural changes may influence the thermal behaviour of the polymer. Tables 1-3 present percentage weight loss data for PVC irradiated alone, in CCl_4 and in $CHCl_3$ for various dosages at a

Fig. 6. Optical spectrum of PVC in THF.

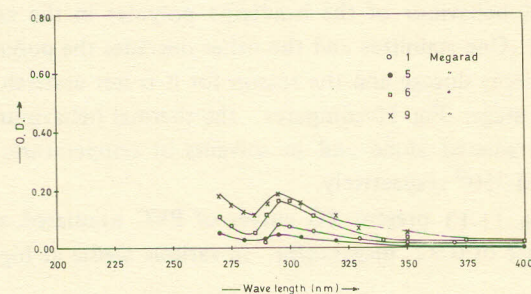
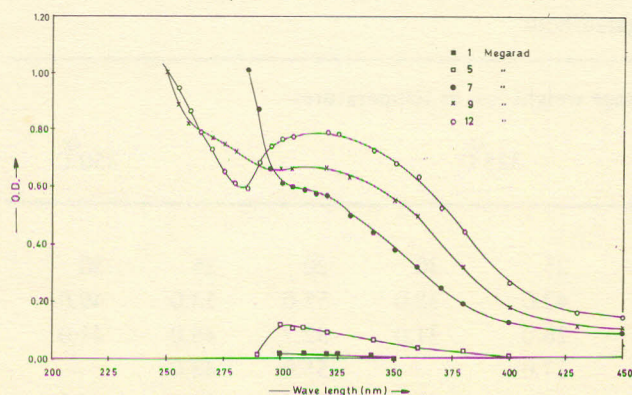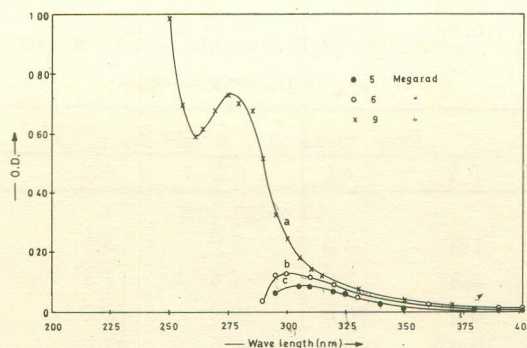Fig. 7. Optical spectra of PVC. irradiated to various dosages.

Fig. 8. Optical spectra of PVC irradiated in CCl_4 to various dosages.

Table 1. Percentage Weight loss data for PVC irradiated at different dosages

Temp. (°C)	Dose magarad / Weight loss (%)					
	0	1.0	5.0	6.0	7.5	9.0
200	—	—	—	no weight loss	—	—
230	,,	,,	,,	,,	0.3	0.5
250	,,	,,	,,	,,	1.9	2.0
277	1.0	1.2	2.0	3.0	4.0	4.2
295	3.0	3.5	5.0	6.0	7.0	7.5
300	4.0	6.8	7.0	7.0	8.0	10.0
325	23.0	24.0	24.0	29.0	30.0	33.0
350	45.0	45.0	45.0	46.0	47.0	47.2
375	53.0	54.0	55.0	56.0	56.3	56.8
425	61.0	61.5	62.8	62.6	61.8	62.0
450	62.5	62.7	63.0	63.0	63.2	62.8
500	63.5	63.2	64.5	64.5	65.0	68.0
550	71.5	74.5	74.0	74.0	74.0	74.5
600	79.5	78.8	77.0	79.0	77.2	77.4

dose rate of 0.323 megarad/hr. PVC irradiated upto 6 megarads is thermally stable at 250°. Above this PVC undergoes steady degradation (Table 1). Our results are in agreement with Lawton's findings [1]. In CCl_4, the polymer is thermally stable at 258° upto 9 megarad (Table 2). At higher temperatures the polymer degrades upto 4 megarads and it stabilizes at alone this dose. In CH_3Cl, the polymer is thermally stable at 100°. At higher temperatures, the polymer first stabilizes upto 6 megarads and above this it degrades (Table 3). The results agree with U.V. observations, i.e. the samples undergo both degradation and cross-linking. The termal stability of PVC at 300-350° in various media is in the following order:

PVC in $CHCl_3$ > PVC > PVC in CCl_4 (upto 5 megarads).

PVC in CH_3Cl > PVC in CCl_4 > PVC   (from 5-9 megarad).

PVC in CCl_4 at higher dosages stabilized further at the same temperatures (Table 4) and the order is:

PVC in CCl_4 > PVC in CH_3Cl > PVC > PVC in DMF.

PVC was partially soluble in DMF under the experimental conditions.

The least stability of the polymer in DMF indicates that the solvent catalyses dehydrochlorination at higher dosages resulting in degradation. In the present study the mechanism is difficult to understand. The results indicate that the solvents, CCl_4 and $CHCl_3$, do not affect the thermal behaviour of the irradiated polymer in the same manner. One stabilizes and the other degrades the polymer at the same dosage and the reason for it is not understood at this stage. Fig. 10 compares the thermal behaviour of PVC irradiated alone and in solvents at temperatures of 325 and 350° respectively.

Fig. 11-13 present TG curves of PVC irradiated at a dose rate of 0.92 megarad/hr. in various media at higher

Table 2: Percentage weight loss data for PVC irradiated in CCl_4 at different dosages

Temp. °C	Dose megarad / weight loss (0%)				
	0.5	4.0	6.0	8.0	9.0
258	no weight loss				
280	1.0	4.0	3.9	3.5	3.0
300	4.0	8.0	7.8	7.5	6.0
325	29.0	30.0	28.0	20.0	17.0
350	49.0	46.0	45.0	43.0	39.0
400	60.0	61.0	60.0	59.5	59.8
450	62.8	63.2	62.8	61.7	61.5
500	64.0	64.7	64.0	63.5	63.4
550	74.0	75.7	74.5	73.0	71.0
600	78.0	78.7	78.0	76.5	74.5

Table 3: Percentage weight loss data for PVC irradiated in $CHCl_3$ at different dosages

Temp. °C	Dose megarad / % weight loss						
	1.0	2.0	5.0	6.0	8.0	9.0	12.0
100	no weight loss						
133	1.4	1.3	1.2	1.1	1.8	2.0	2.1
200	1.5	1.5	1.5	1.4	3.0	4.8	7.5
258	1.75	2.0	2.0	2.0	3.2	5.0	9.0
300	5.1	6.0	6.0	6.0	7.5	9.0	15.0
325	14.0	14.0	14.0	13.0	15.0	16.0	27.0
350	43.0	40.0	37.0	33.0	40.0	42.1	44.0
400	62.0	61.5	61.0	59.5	58.5	61.0	63.0
450	65.2	65.0	64.0	62.5	64.0	64.5	65.6
500	65.5	66.0	65.3	64.0	65.0	66.0	66.5

Table 4: Percentage weight loss for PVC irradiated in different media. Dose rates 0.92 megarad/hour

Medium	Percentage weight loss at temperatures								
	300 °C			325 °C			350 °C		
Dose (megarad)	20	25	30	20	25	30	20	25	30
PVC alone	31.0	21.0	18.5	49.0	42.0	38.0	55.0	53.0	49.0
CCl_4	14.5	10.5	9.5	37.5	26.0	21.0	52.7	45.0	41.0
$CHCl_3$	20.2	14.0	—	33.0	27.0	—	55.0	48.0	—
DMF	52.0	51.5	51.0	54.5	54.0	53.0	56.5	56.0	55.0

dosages. In DMF, the polymer is the least stable upto 350° and above this the polymer stabilizes. There are two distinct stages of weight loss. The first stage of weight loss corresponds to elimination reaction. The second stage of weight loss is due to the decomposition of the ethylenic structures.
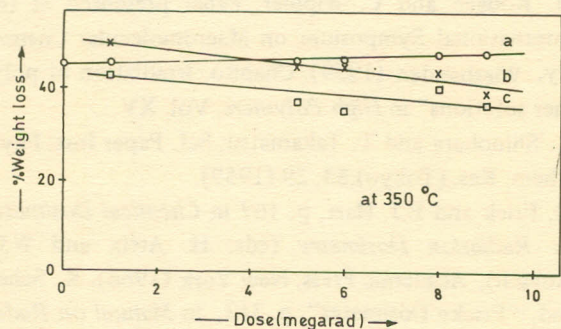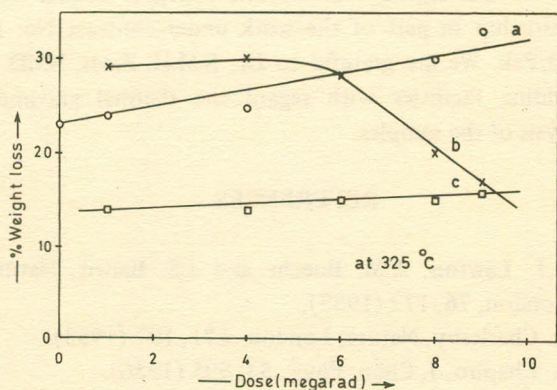

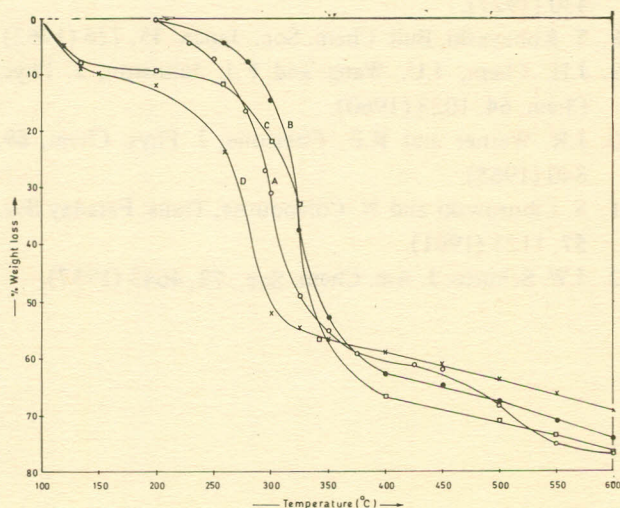Fig. 10. Percentage weight loss of PVC irradiated (a) as such, (b) in CCl_4, (c) in $CHCl_3$.

Fig. 11. TG curves of PVC irradiated at 20.0 megarads (a) as such (b) in CCl_4, (c) in $CHCl_3$, (d) in DMF.
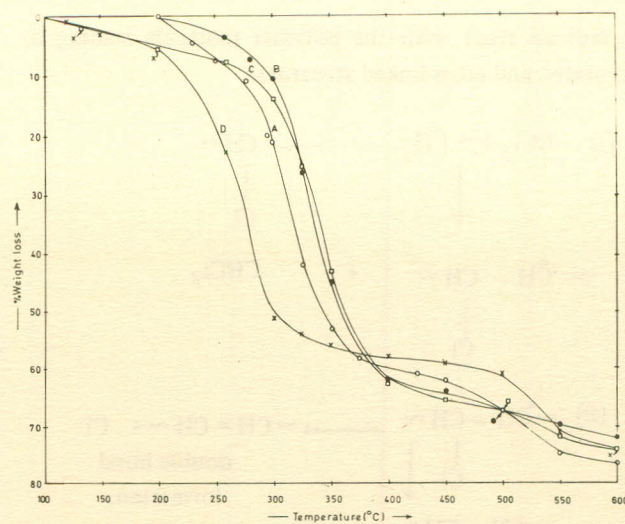

Fig. 12. TG curves of PVC irradiated at 25.0 megarads (a) as such (b) in CCl_4, (c) in $CHCl_3$, (d) in THF.
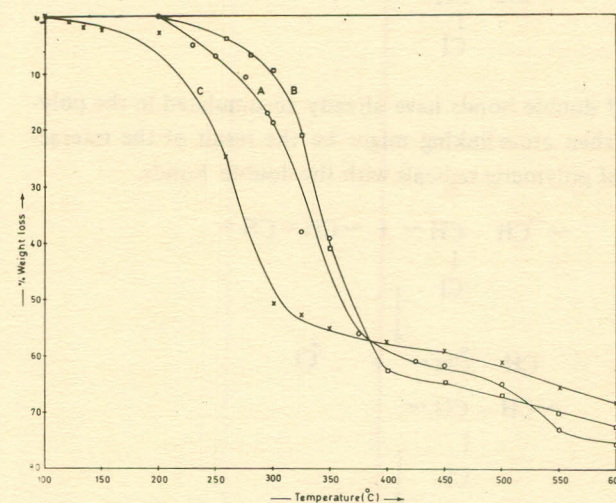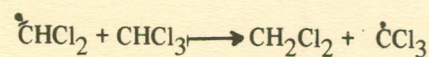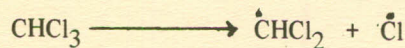

Fig. 13. TG curves of PVC irradiated at 30.0 megarads (a) as such (b) in CCl_4, (c) in DMF.
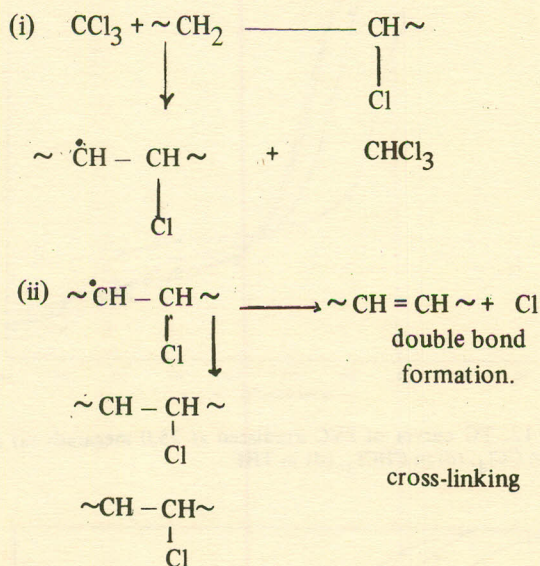
MECHANISM

Based on these observations the following mechanism is suggested. The solvents, CCl_4, $CHCl_3$ readily yield free radicals [9-12].
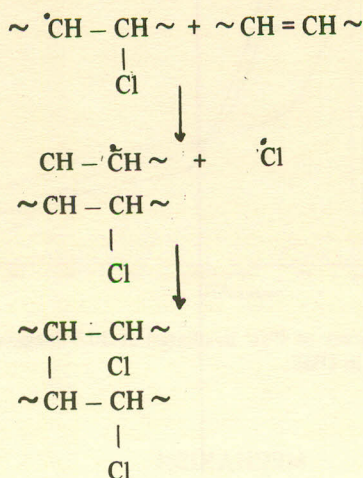
$$CHCl_3 \longrightarrow \overset{\bullet}{C}HCl_2 + \overset{\bullet}{C}l$$

$$\overset{\bullet}{C}HCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \overset{\bullet}{C}Cl_3$$

$$CCl_4 \longrightarrow \overset{\bullet}{C}l + \overset{\bullet}{C}Cl_3$$

The radicals react with the polymer molecule leading to unsaturated and cross-linked structures.

(i)

$$CCl_3 + \sim CH_2 \longrightarrow CH \sim$$
$$|$$
$$Cl$$

$$\downarrow$$

$$\sim \overset{\bullet}{C}H - CH \sim \quad + \quad CHCl_3$$
$$|$$
$$Cl$$

(ii)

$$\sim \overset{\bullet}{C}H - CH \sim \longrightarrow \sim CH = CH \sim + \ Cl$$
$$|$$
$$Cl \ \downarrow \qquad \qquad \text{double bond}$$
$$\qquad \qquad \qquad \text{formation.}$$

$$\sim CH - CH \sim$$
$$|$$
$$Cl$$

$$\qquad \qquad \qquad \text{cross-linking}$$

$$\sim CH - CH \sim$$
$$|$$
$$Cl$$

If double bonds have already accumulated in the polymer, then cross-linking might be the result of the interaction of polymeric radicals with the double bonds.

$$\sim \overset{\bullet}{C}H - CH \sim + \sim CH = CH \sim$$
$$|$$
$$Cl$$

$$\downarrow$$

$$CH - \overset{\bullet}{C}H \sim + \ \overset{\bullet}{C}l$$
$$\sim CH - CH \sim$$
$$|$$
$$Cl \ \downarrow$$

$$\sim CH - CH \sim$$
$$| \quad Cl$$
$$\sim CH - CH \sim$$
$$|$$
$$Cl$$

The cross-linking process may occur via the main chain fracture if hydrogen mobility along the chain is permitted. The two radicals formed due to chain scission combine to form a cross-link. (This cross-link differs from the conventional cross-link in that the molecular weight decreases on irradiation and the polymer remains soluble).

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