

# Gamma Irradiation of Polypropylene Fibers in the Presence of Carbon Tetrachloride

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## Synopsis

Polypropylene (PP) fibers have been irradiated with  $^{60}\text{Co}$   $\gamma$  rays in the presence of carbon tetrachloride, in the absence of oxygen. Irradiations have been carried out between dose rates of 0.078 and 0.664 Mrad/hr, and the effects of absorbed dose and temperature on the C—Cl formation in the PP fibers have been investigated.  $G(\text{C—Cl})$  values were higher at lower dose rate.  $G(\text{HCl})$  values were found to be much higher than the  $G(\text{C—Cl})$  values, and IR absorption studied indicated increasing unsaturation with increasing dose. The number average molecular weights ( $\bar{M}_n$ ) were evaluated from intrinsic viscosity measurements in decalin at 408 K and the  $\bar{M}_n$  values decreased with increasing dose and temperature.  $G(\text{scission}) - G(\text{crosslinking})$  values were calculated and it was found that the  $G_s - G_x$  values are higher at lower doses and higher dose rates. The thermal characteristics of the irradiated fibers were investigated by thermogravimetry (TG) analysis in air or argon and with differential scanning calorimetric (DSC) studies. The TG data indicated slightly less thermal stability for the modified fibers both in air as well as argon. The DSC data indicated very little change in the melting points of the samples, the melting points being around  $444 \pm 2$  K.

## INTRODUCTION

Polyolefins like polyethylene, polypropylene, and polyisoprene have been chlorinated using chlorine in the presence of high-energy radiation, either in solution or in suspension.<sup>1-4</sup> Klaus and Herbert<sup>5</sup> have reviewed the properties and applications of these modified polymers. The high  $G$  value for chlorination ( $\sim 10^5$ ) of these polymers results in high chlorine content even at low absorbed doses with a nonuniform distribution of C—Cl bonds, as the chlorination takes place preferentially at the outer surface. Low chlorine content with a homogeneous distribution may be desirable for the fibers to be used for grafting with other vinyl monomers. These modified fibers can have fire retardancy.

In recent years, attempts have been made to modify the polymers using  $\gamma$  radiation in the presence of carbon tetrachloride or chloroform. Tagawa et al.<sup>6</sup> have observed that, when  $\gamma$  rays and vapors of chloroform or carbon tetrachloride are used on polypropylene, there is an enhanced scission. Varma, Sharma, and Varma<sup>7</sup> have irradiated polyvinyl alcohol in the presence of chloroform or carbon tetrachloride in order to modify the polymer. The objective of the present study is to find suitable conditions for introducing a few C—Cl bonds in each polypropylene molecule. Carbon tetrachloride has been used as the chlorinating agent in the presence of  $^{60}\text{Co}$   $\gamma$  radiation. Properties of the modified polypropylene fibers are presented here.

## EXPERIMENTAL

### Materials

Polypropylene (PP) fiber, type S, supplied by the M/s Monte Catini Edison Group through the spinning of isotactic polypropylene, was used.

### Chemicals

All other chemicals used were of BDH AnalaR grade.

### Sample Preparation and Irradiation

PP fiber (350 mg), dried at  $\sim 343$  K in a vacuum oven for 24 hr, was taken in a thick pyrex glass tube of  $\sim 15$ -ml capacity. Exactly 4 ml of carbon tetrachloride was added so that the fibers were immersed completely. The tube having a constriction and a standard B-14 cone was attached to a vacuum manifold. Repeated freeze-pump-thaw cycles using liquid nitrogen removed the dissolved oxygen in the system. The vacuum sealed sample was kept at 353 K for about 18 hr for complete swelling of the fiber. Three different " $\gamma$  chambers" having  $^{60}\text{Co}$  of different activity were used to get different dose rates. The dose rates were measured using a Fricke dosimeter, and the absorbed doses were calculated after making corrections for electron density changes. The sample tubes were kept in a Dewar flask with ethylene glycol at the required temperature during irradiation and the temperature was maintained within  $\pm 2$  K.

### Determination of HCl, CCl, and CCl<sub>3</sub> Yields

The irradiated ampoule, cooled to 77 K, was broken under a known volume of triply distilled water. Under these conditions the HCl liberated in the system was quantitatively estimated by following the change in pH. From the known weight of the PP fibers, the HCl yield in  $\mu\text{mole/g}$  was calculated.

The PP fiber was washed with methanol, pressed between filter papers, and dried in a vacuum oven to a constant weight. The chlorine content of the fiber was determined by the oxygen flask method.<sup>8</sup>

The CCl<sub>3</sub> group in the PP was converted to —COOH group by successive treatments with 0.1N sodium hydroxide at 313 K for 12 hr and 1N hydrochloric acid. The fiber was dried after repeated washings with hot triply distilled water. The free —COOH in the PP was estimated by reacting a known amount with dilute carbon dioxide free sodium hydroxide solution and following the pH. A control experiment was performed with an identical amount of unmodified PP.

### Determination of Unsaturation

The PP fibers were brominated in the absence of air in sealed ampoules by contacting them with bromine vapor, following the method of Szweczyk et al.<sup>9,10</sup> The bromine content of the polymer was determined by the standard neutron activation analysis, using the 35.3 hr Br-82 isotope activity.<sup>11</sup>

### Molecular Weight Determinations

The number average molecular weights ( $\bar{M}_n$ ) of the PP fibers were determined from the intrinsic viscosity measurements of 0.1% (w/v) polymer solution in decalin at 408 K.<sup>12</sup> The solution contained 1% of 2,6-diterbutyl *p*-cresol as a stabilizer. Equation (1) was employed in the following calculation:

$$[\eta] = 1.38 \times 10^{-4} \bar{M}_n^{0.8} \quad (1)$$

### IR, TG, and DSC Measurements

Infrared (IR) absorption measurements were carried out using a Perkin-Elmer model 577 IR spectrophotometer. The thermogravimetric (TG) analysis of control PP and modified PP fibers were carried out in a microthermo balance built in this laboratory, with a temperature rise of 5°/min in atmospheres of argon and air. The differential scanning calorimetry (DSC) runs were taken on a Perkin-Elmer DSC-1B.

### RESULTS

Figures 1 and 2 show the variation in the yields of CCl and HCl in  $\mu\text{mol/g}$  of fiber at two different dose rates, 0.078 and 0.664 Mrad/hr (curves A and B). The HCl and CCl *G* values (calculated on the basis of dose absorbed in the PP fiber part only) show a decrease at higher dose rate for the same absorbed dose. The average *G* values have been calculated and are given in Table I. It should be noted that the HCl yield is higher than that of CCl by almost an order.

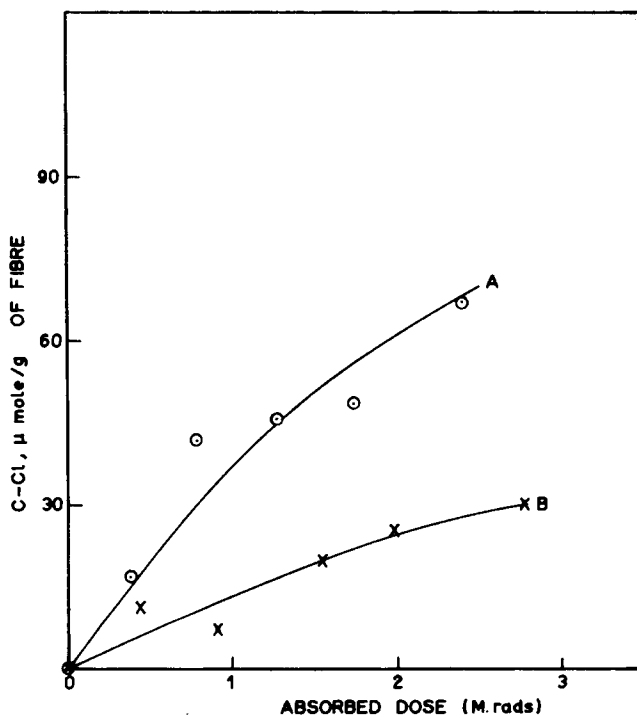


Fig. 1. Variation of C—Cl yield with absorbed dose in  $\gamma$ -irradiated PP +  $\text{CCl}_4$ . (A) 0.078 Mrad/hr; (B) 0.664 Mrad/hr.

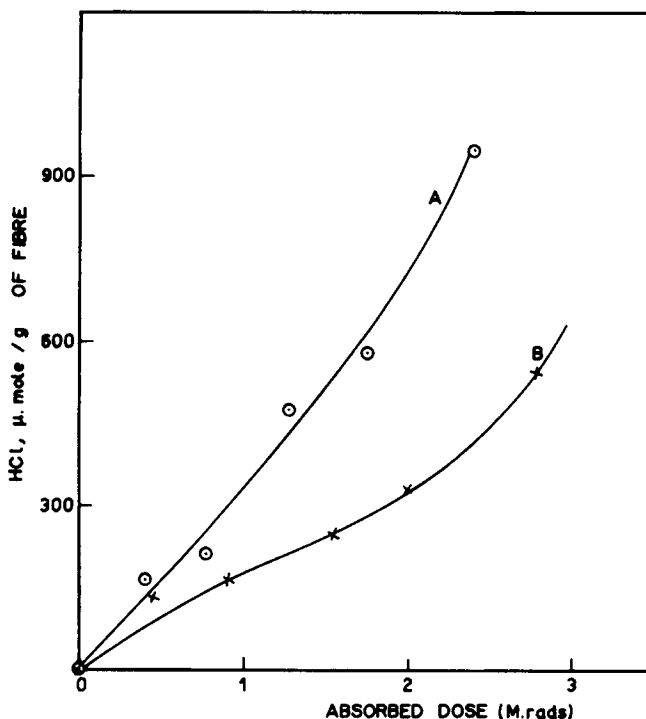


Fig. 2. Dependence of HCl yield with absorbed dose in PP + CCl<sub>4</sub> with  $\gamma$  rays. (A) 0.078 Mrad/hr; (B) 0.664 Mrad/hr.

The CCl yield includes the part belonging to CCl<sub>3</sub> groups. The CCl<sub>3</sub> content for the PP fiber irradiated to a total dose of 2.4 Mrad at a dose rate of 0.078 Mrad/hr was determined to be  $\sim 0.59 \mu\text{mole/g}$ , whereas the total CCl was found to be  $67 \mu\text{mole/g}$ . This indicates that the chlorine content of the polymer is almost due to the substitution of an H atom with a Cl atom.

It has been estimated that the CCl<sub>4</sub> present in the swollen phase is only 0.93 g/g, even though the heterogeneous system contains 19 g/g of CCl<sub>4</sub>-to-PP ratio.

Table II summarizes the effect of temperature on the HCl and CCl yields for a constant absorbed dose and dose rate. It is observed that the yields do not change significantly in the temperature range 283–343 K. It can be presumed that the experimental variation of  $G(\text{C—Cl})$  and  $G(\text{HCl})$  values might be due to the variation in the ratio of the amount of crystallites to the amorphous portion in the fiber, since the reaction is supposed to occur predominantly in the amorphous portion of the fiber. At 355 K, however, the system becomes homogeneous and the  $G(\text{CCl})$  value increases by an order of magnitude.

TABLE I  
Dose Rate Effects on Yields in  $\gamma$ -Irradiated PP-CCl<sub>4</sub> System

Dose rate, Krad/hr	Temp. K	C—Cl yield, mole/g rad	HCl yield, mole/g rad	$G_{\text{C—Cl}}$ *	$G_{\text{HCl}}$
78	303	$40 \times 10^{-12}$	$315 \times 10^{-12}$	28.6	304
664	303	$14 \times 10^{-12}$	$220 \times 10^{-12}$	13.5	212

TABLE II  
Effect of Temperature on  $G$  Values in  $\gamma$ -Irradiated  $\text{CCl}_4$ -PP System<sup>a</sup>

Temp., K	Absorbed dose, Mrads	$G_{\text{C-Cl}}$	$G_{\text{HCl}}$
283	0.73	25	73
303	0.75	32	85
325	0.77	20	102
343	0.96	31.5	103
355 <sup>b</sup>	0.75	302	78

<sup>a</sup> Dose rate: 0.258 Mrad/hr.

<sup>b</sup> At this temperature, fiber had gone into solution and system was no longer heterogeneous.

Table III summarizes the bromine contents of different PP samples with the unsaturation yields in  $\mu\text{mole/g}$ . It was found that the unsaturation increases linearly up to a dose of 1 Mrad, in the case of low dose rate (0.078 Mrad/hr) samples. The control PP contained unsaturation to the extent of  $\sim 44 \mu\text{mole/g}$ . The  $G^0$  (unsaturation) calculated at the initial doses ( $\sim 0.75$  Mrad) were 106 and 209 at 0.078 Mrad/hr and 0.664 Mrad/hr, respectively.

### Infrared Absorption Studies

The IR spectra of the cold pressed film of the unirradiated PP as well as the modified ones were used to follow the unsaturation and crystallinity characteristics. The IR spectra indicate strong absorptions with maxima at 1435, 1700, and 992  $\text{cm}^{-1}$ . Figure 3 illustrates the changes in the relative optical densities at 1700  $\text{cm}^{-1}$  compared to that at 1435  $\text{cm}^{-1}$  as a function of the absorbed dose at two dose rates. The broadband with absorption maximum at 1700  $\text{cm}^{-1}$  is attributed to the C=C unsaturation. The 1435  $\text{cm}^{-1}$  absorption band is a common reference band, and the ratio method avoids the necessity of measuring the exact film thickness. The absorption due to unsaturation is found to increase at both the dose rates. Figure 4 shows the changes in absorption at 992  $\text{cm}^{-1}$ , attributed to the interchain interaction in the crystalline region of PP<sup>13-15</sup> as a function of the dose. It was found that there is a complex dependence with

TABLE III  
Unsaturation Yields in  $\gamma$ -Irradiated PP Fibers in Presence of Carbon Tetrachloride

Dose rate, Mrad/hr	Dose, Mrad	Weight % Br	Unsaturation, mole/g	$G$ (unsaturation) <sup>a</sup>
0	0	0.7	43.6	
0.078	0.39	1.21	75.6	
	0.77	2.33	145.6	
	1.27	2.90	181.3	106
	1.74	1.20	75.0	
	2.40	2.82	176.3	
	0.66	0.44	2.35	146.9
0.91		1.05	65.6	
1.55		6.10	381.3	209
2.78		2.40	150.0	

<sup>a</sup>  $G$  values calculated from the initial slope.

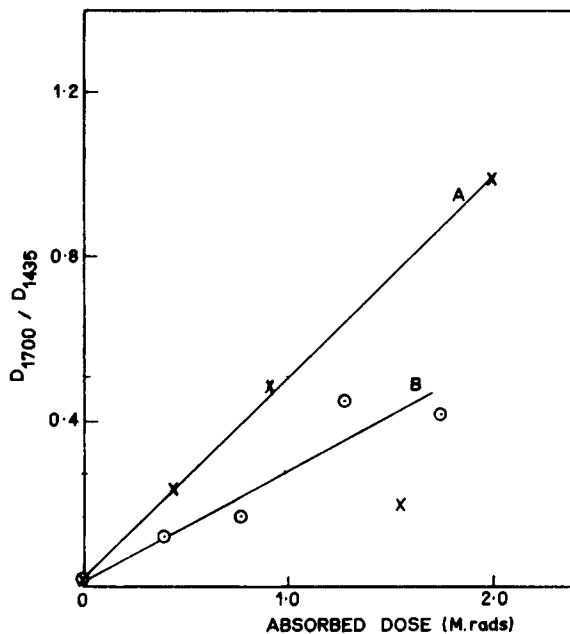


Fig. 3. Change of unsaturation (C=C) with absorbed dose.  $\circ$ , 0.078 Mrad/hr; X, 0.664 Mrad/hr.

increasing dose of this absorption. Below about 1 Mrad, there is a decrease in the interchain interaction at a low dose rate, as contrasted to the higher dose rate where there is an increase.

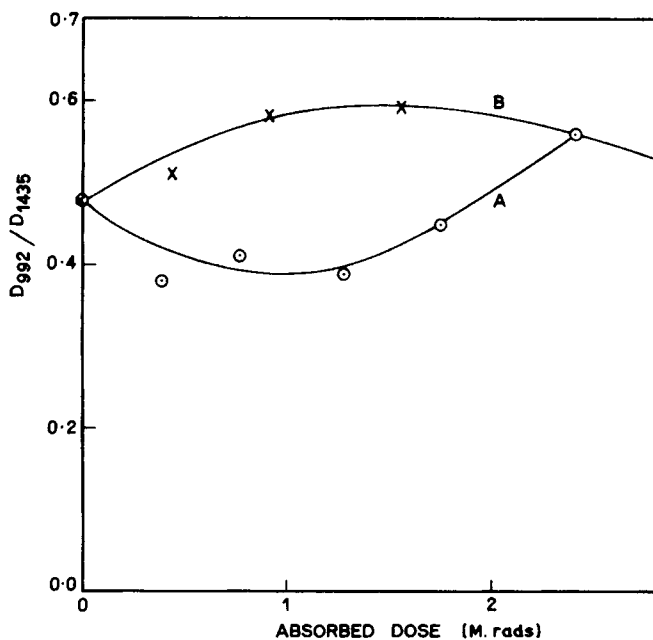


Fig. 4. Change of IR absorption due to interchain interaction in crystallites with dose.  $\circ$ , 0.078 Mrad/hr; X, 0.664 Mrad/hr.

### Molecular Weights

Tables IV and V summarize the  $\overline{M}_n$  values of the different PP fibers. The  $\overline{M}_n$  value of PP has been found to decrease from  $1.23 \times 10^5$  to about half this value even at an absorbed dose of  $\sim 0.5$  Mrad. The sol fraction indicates the soluble part in decalin at 408 K whose molecular weight alone has been indicated. Higher dose rate and higher temperature results in lower molecular weights.

The  $G_s - G_x$  yields were calculated from the  $\overline{M}_n, \overline{M}_n^0$  and absorbed dose using eq. (2):

$$(G_s - G_x) = (1/\overline{M}_n - 1/\overline{M}_n^0) \cdot 1/D(\text{rad}) \cdot 9.652 \times 10^{11} \quad (2)$$

Figure 5 illustrates the variation of  $G_s - G_x$  with dose at two different dose rates. The  $G_s - G_x$  value falls rapidly with increasing dose with a higher  $G_s - G_x$ , at a higher absorbed dose rate.

### Thermal Characteristics

Figures 6 and 7 illustrate the thermal decomposition behavior of the various PP fibers in atmospheres of air and argon, respectively. The control PP starts degrading at 453 and 523 K in air or argon, respectively. The chlorinated samples did not show much variation with absorbed dose in their thermal decomposition in air, where the onset of decomposition occurs 20 K lower than the control. In

TABLE IV  
Molecular Weights of Modified PP Fibers

Dose rate, Krad/hr	Temp., K	Absorbed dose, Mrad	Sol fraction	$\overline{M}_n$ ( $10^5$ )
0	—	0	1.00	1.23
78	303	0.39	0.88	0.63
		0.77	0.72	0.84
		1.27	0.56	0.84
		1.74	0.89	0.55
		2.40	1.00	0.88
260	343	0.54	1.00	0.92
		2.64	1.00	0.72
		0.44	0.96	0.60
		0.91	0.96	0.60
664	303	1.55	0.92	0.47
		1.99	0.89	0.51
		2.78	1.00	0.35

TABLE V  
Effect of Irradiation Temperature on  $\overline{M}_n$  Values (0.26 Mrad/hr  $\sim$  0.75 Mrad)

Irradiation temp.	Sol fraction (in decalin at 408 K)	$\overline{M}_n$ ( $10^5$ )
(control PP)	1.00	1.23
283	1.00	0.90
303	1.00	1.54
325	1.00	0.85
355	0.97	0.35

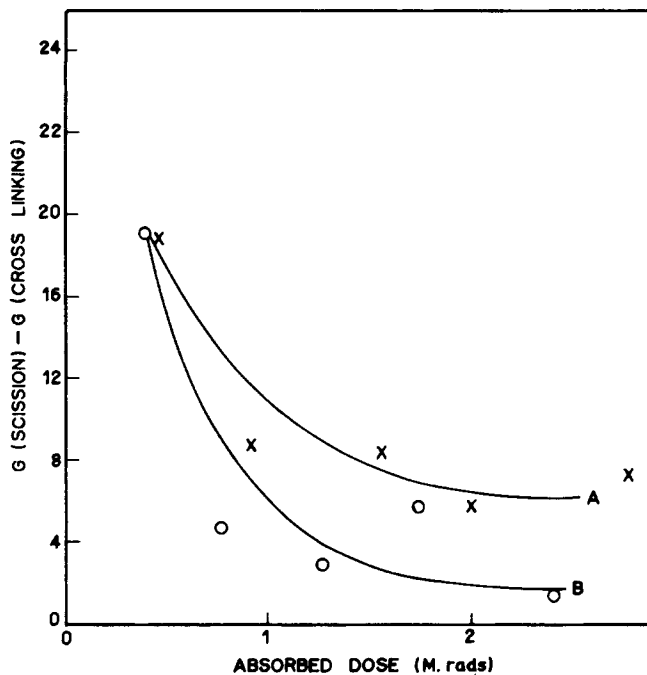


Fig. 5. Variation of scission yield with absorbed dose. O, 0.078 Mrad/hr; X, 0.664 Mrad/hr.

argon, however, the decomposition starts only at 450 K for these samples. The fiber with a higher absorbed dose shows greater rate of decomposition.

The DSC runs indicated that the melting point peak temperatures were 445

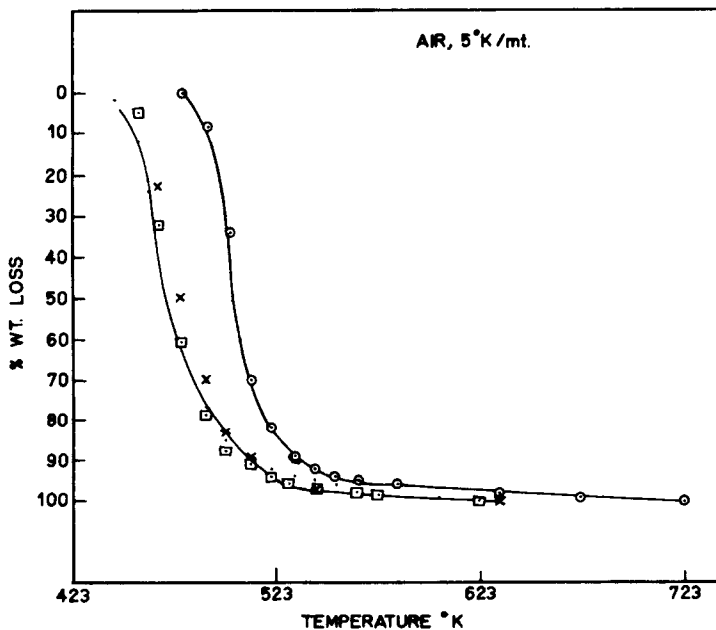


Fig. 6. Thermal degradation behavior of modified PP in air, O, control, □, 0.39 Mrad. ·, 1.37 Mrad; X, 2.4 Mrad.



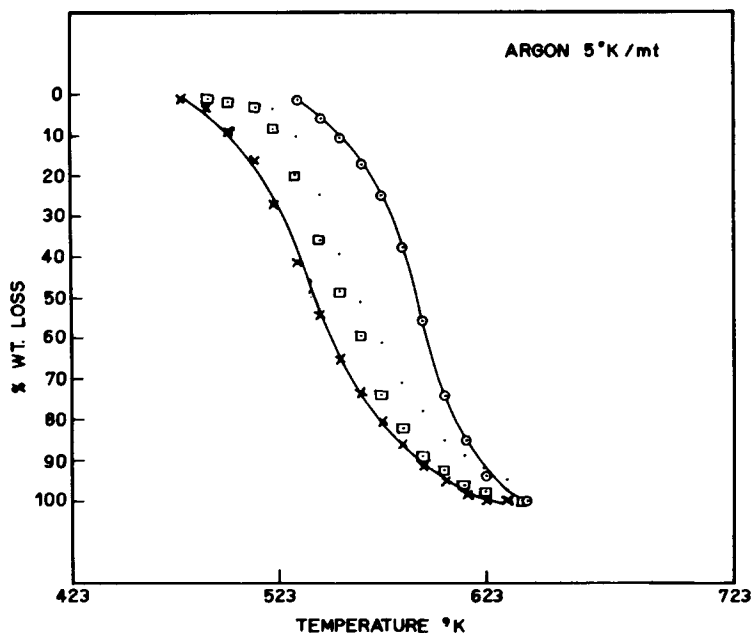


Fig. 7. Thermal degradation in argon atmosphere of modified PP fibers. ○, control; □, 0.39 Mrad, 1.27 Mrad; X, 2.4 Mrad. Argon = 5 K/mt.

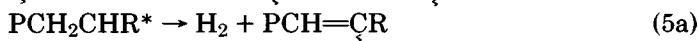
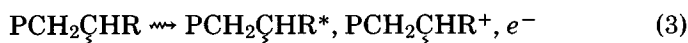
(±1), 442, 444, and 442 K for the control PP and samples irradiated for 0.4, 1.3, and 2.4 Mrads, respectively. This indicates that crystallinity is not very much affected in the modification process.

## DISCUSSION

The PP—CCl<sub>4</sub> system considered in this work is a heterogeneous system with a 19-fold excess of CCl<sub>4</sub>, where the swollen phase contains only 0.93 g of CCl<sub>4</sub>/g of fiber. When this two-phase system is subjected to a radiation field, energy is simultaneously absorbed in both the solid PP phase and the liquid CCl<sub>4</sub> phase. As discussed in the following section, the active species responsible for the CCl yield in PP and HCl production can be generated in both phases and it is difficult to estimate the energy transfer from one phase to the other. In view of this, it is necessary to relate the product yields to the energy absorbed in the PP fiber part directly due to  $\gamma$  irradiation for the system with a definite weight fraction of CCl<sub>4</sub>. The *G* values have been calculated based on the absorbed energy in the PP moiety, neglecting the simultaneous energy absorption in the liquid CCl<sub>4</sub> both in and outside the swollen phase. The possible reactions occurring in the heterogeneous system have been classified into three parts and are discussed next.

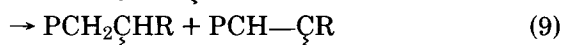
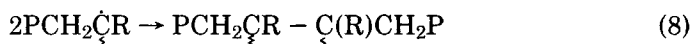
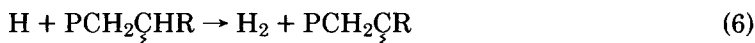
### Direct Energy Absorption in PP (PCH<sub>2</sub>CHR)

Reactions (3)–(5) are postulated giving rise to free radicals:





Reaction (3) describes the direct ionization and excitation processes. Reactions (4), (5a), and (5b) describe the C—H bond cleavage, unimolecular hydrogen elimination, and C—C bond scission of excited PP. Reactions (6)–(9) describe the abstraction, recombination, and disproportionation reactions of the free radicals:



The  $G(R)$  value for pure PP has been found to be 5.2 by Konde and Dole.<sup>16</sup> Kirscher, *et al.*,<sup>17</sup> have found evidence for the disproportionation reaction (9) involving PP radicals.

#### Direct Energy Absorption in CCl<sub>4</sub>

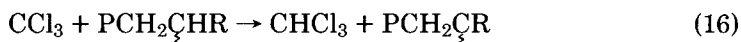
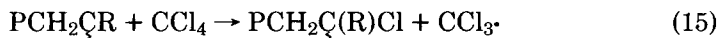
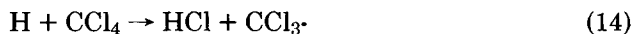
Reactions (10)–(13) can be postulated in this case:



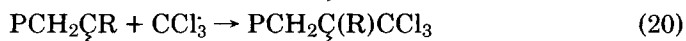
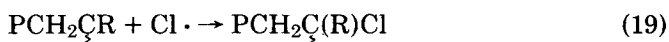
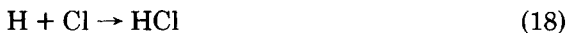
Thus, the products due to energy absorption in carbontetrachloride are dichloroethane and chlorine. In reactions (12) and (13)  $M$  stands for a third body to remove the recombination energy. The  $G$  values for the total radical ( $Cl$  and  $CCl_3$ ) in irradiated liquid  $CCl_4$  have been quoted from 23 to 70 by Cibrowski *et al.*<sup>18</sup> and Minoura and Asao,<sup>19</sup> respectively.

#### Possible Reactions of Active Species in the Mixture

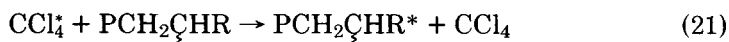
Radical Substrate Reactions:



Radical Radical Reactions:



Energy Transfer:



It can be seen that reactions (15), (19), and (20) result in CCl bond formation with reactions (15), (16), and (17) constituting a chain reaction. The very low amount of ( $\approx 2\%$ ) of  $\text{CCl}_3$  in the polymer indicates that the significant contribution for the CCl yield is due to (15), which is a Cl atom abstraction reaction by polymer backbone radical.

HCl is produced by reactions (14), (17), and (18) and the contribution of reaction (18), which involves the recombination of two radicals, should be quite small in view of the low radical concentration. The mechanism should explain the higher yields of CCl and HCl at lower dose rates and the much higher HCl yields.

Stone and Dyne,<sup>20</sup> have found a small chain reaction giving rise to chlorocyclohexane when homogeneous cyclohexane— $\text{CCl}_4$  mixtures were irradiated with  $\gamma$  rays at a dose rate of 0.5 Mrad/hr. These authors have obtained, however, a low  $G(\text{HCl})$  value ( $\sim 4$ ) and  $G(c\text{-C}_6\text{H}_{11}\text{Cl})$  was  $\sim 25$  and  $G(c\text{-C}_6\text{H}_{11}\text{CCl}_3) = 0.65$ . The PP— $\text{CCl}_4$  system indicates that the  $\text{CCl}_3$  yield is quite small compared to CCl yield.

The high  $G(\text{HCl})$  compared to the low  $G(\text{CCl})$  cannot be explained if reaction (15), where the polymer radical abstracts a Cl atom from  $\text{CCl}_4$ , occurs with a high rate constant, since each HCl results in the production of a polymer radical. The obvious inference is that the reactions (8) and (9), where the polymer radicals undergo addition and disproportionations, respectively, occur with a much higher rate constant. However, these two reactions will be favored at higher dose rates when the radical concentrations are higher, favoring bimolecular reactions. Thus, the HCl formation can be due to reaction (17) involving Cl atoms which have also been produced in the bulk  $\text{CCl}_4$ , present both inside and outside the swollen phase. Since there is a 19-fold excess of  $\text{CCl}_4$  and the  $G$  value calculations have not taken into account the energy absorbed in  $\text{CCl}_4$ , the  $G(\text{HCl})$  values appear to be high. A part of the  $\text{PCH}_2\dot{\text{C}}(\text{R})\text{Cl}$  is due to the radical addition reaction of Cl and  $\text{PCH}_2\dot{\text{C}}\text{R}$  radicals.

At higher dose rates, fewer of the Cl atoms are available for reactions (19) and (17) because of recombination reactions, and thus, the HCl and CCl yields are lower at higher dose rates.

The high  $G$  (unsaturation) values (106 and 209 at low and high dose rates) indicate that they arise due to energy absorption in bulk  $\text{CCl}_4$ . It is to be noted that there is no correspondence between the  $G(\text{HCl})$  and  $G$  (unsaturation) yields, the former being higher at lower dose rates, thus indicating little contribution to dehydrochlorination of chlorinated PP to give unsaturation. If unsaturation arises due to the disproportionation reaction (9) only, then its yield will be higher at higher dose rates, which has been found to be the case. Unsaturation also arises by reaction (5a) involving a unimolecular hydrogen from excited PP produced directly or through the energy transfer reaction (21) from excited  $\text{CCl}_4$ . At higher dose rates, the energy deposition rate is higher resulting in a higher unsaturation.

The IR absorption at  $1700\text{ cm}^{-1}$  shows that the unsaturation increases with increasing dose rate and absorbed dose, in corroboration with the unsaturation estimation by the bromine method.

The 992  $\text{cm}^{-1}$  absorptions indicate that the interchain interactions change with increasing dose in a complex way. At smaller dose rates, because of reduced radical recombination reactions, there is greater probability of chlorine atoms diffusing into the crystalline region resulting in a decreased interchain interaction. The experimental observations from Figure 4 illustrate this point.

### Molecular Weights

In the absence of an idea of the molecular weight distribution of the modified PP fibers and in the presence of an insoluble fraction of the PP in decalin at 408 K, it is difficult to use the  $\overline{M}_n$  values of the sol fraction in the complete description of the system. However, the results indicate certain trends in the  $\overline{M}_n$  values which can be explained. It can be noted that at 2.4 Mrad, the  $\overline{M}_n$  decreases to 75% of its control value at lower dose rates, whereas at higher dose rates it decreases to about 30%. Similarly, the  $G_s - G_x$  values are  $\sim 3$  and  $\sim 9$  (at 1.3 Mrad) at the lower and the higher dose rates, respectively. Reaction (5b) is responsible for a C—C scission and this involves excited PP molecules. It has been seen earlier that higher dose rates result in higher yields of excited species, favoring a higher contribution of [reaction (5b)]. This results in enhanced scission and consequently low  $\overline{M}_n$  values. The crosslinking might be taking place because of reaction (8). From the results shown in Figure 5, it is evident that at  $\sim 0.38$  Mrad, the  $G_s - G_x$  ( $\sim 19$ ) is constant irrespective of the dose rates used, and hence, one can presume that it is mostly scission, since crosslinking needs two radicals within the bond distance. At higher doses, however, it is observed that  $G_s - G_x$  is dependent on the dose rate, the values obtained were lower at 78 Krad/hr than at 664 Krad/hr. These results indicate that the crosslinking is higher at lower dose rates. It appears that the rate determining step for crosslinking is the rate of migration of the radical sites to adjacent positions for crosslinking. Tagawa, et al.<sup>6</sup> have obtained a  $G_s$  value of 1.9 in PP for 20 Mrad of absorbed dose at a dose rate of 1.25 Mrad/hr, which indicates that presence of  $\text{CCl}_4$  enhances the scission yields and crosslinking yields considerably.

### Thermal Characteristics

The degradation of PP in air might be due to oxidative degradation,<sup>21</sup> and thus the onset of decomposition occurs at a lower temperature compared to the argon atmosphere. These results indicate that the modification of PP fiber has resulted in greater susceptibility for thermal degradation at temperatures above  $\sim 450$  K, and the fibers can be used in inert atmospheres up to this temperature without any deleterious effect.

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