

Radiation Protection of Poly(Vinyl Chloride) by N-Methyl Dithiocarbamate Substitution

TSUTOMU NAKAGAWA,* H. B. HOPFENBERG, and V. STANNETT,
*Department of Chemical Engineering, North Carolina State University,
Raleigh, North Carolina 27607*

Synopsis

The effect of N-methyl dithiocarbamate substitution on the radiation stability of poly(vinyl chloride) (PVC) films was studied. PVC containing between 2 and 11 mole-% N-methyl dithiocarbamate (PMD) was irradiated with γ -rays from a ^{60}Co source at 40°C and the evolved gaseous products were measured and analyzed with a mass spectrometer. The apparent G values for gas evolution for PMD decreased remarkably. For example, a G value of 0.28 was obtained for a PMD which contains 11 mole-% dithiocarbamate group compared with a G value of 10.8 for unmodified poly(vinyl chloride). Furthermore, the mass spectrum of the evolved gas from the same PMD sample (PMD-44) with 10 Mrad irradiation showed no hydrogen chloride to be present. The external protection was studied using polymer-blended films of PVC and PMD-44. The stabilization coefficients for internal protection and external protection in polymer blends were calculated. The ESR spectrum of the irradiated PMD-44 showed a strong anisotropy with high g values which differed significantly from the spectrum of the irradiated PVC. A suggested mechanism for radiation protection of PVC against γ -rays irradiation by the N-methyl dithiocarbamate group is discussed.

INTRODUCTION

The stabilization of polymers by admixing with additives such as anti-oxidants or substituted aromatic compounds has been widely investigated,¹ but comparatively little work has been reported on stabilizing polymers by introducing an additive to provide high energy radiation protection.²⁻⁵ Poly(vinyl chloride), PVC, is well known to be rather unstable to ionizing irradiation, generating gaseous products. Miller⁶ and Lawton⁷ have reported G value for hydrogen chloride and hydrogen gas evolution of 13 and 0.4, respectively, with ionizing irradiation at room temperature under vacuum. The formation of radicals in the polymer chains themselves has been investigated and mechanisms for the degradation of PVC by ionizing radiation have also been presented.⁶⁻¹¹

If (1) the formation of the chlorine radical, which is a carrier for the reaction, is inhibited or (2) the polymer radicals are stabilized, PVC may become a more stable polymer in a high-energy radiation field. According to

* Present address: Industrial Products Research Institute, Shimomaruko Ota-ku, Tokyo, Japan.

Charlesby,¹ the protection of a polymer by a covalently bonded functional group against irradiation is referred to as internal protection, whereas protection of the polymer by admixed additives is referred to as external protection.

One of us has prepared PVC containing N-methyl dithiocarbamate.¹² The present paper deals with the internal and external protection of PVC by N-methyl dithiocarbamate against γ -irradiation.

EXPERIMENTAL

Poly(vinyl chloride), PVC. A commercial PVC ($\bar{D}P \approx 600$), PVC-1, manufactured by Sumitomo Chemical Co., Ltd., and a PVC ($\bar{D}P \approx 1100$), PVC-2, manufactured by Geon Co., were used. The polymers were purified by precipitation with methanol from a dioxane solution followed by drying. The membranes were cast at room temperature from a tetrahydrofuran (THF) solution on glass plates floating on mercury and were removed from the plates after they were quite dry. The membranes were then immersed in methanol for several days and dried under vacuum. The resulting film thickness was about 30 μ .

PVC Containing N-Methyl Dithiocarbamate Group (PMD). Thirteen grams dried sodium N-methyl dithiocarbamate and 9.4 g PVC-1 were dissolved in separate 150-ml aliquots of dimethylformamide (DMF), and then both solutions were mixed in a 500-ml amber-colored flask which was equipped with a mechanical stirrer, an inlet for nitrogen, and a thermometer. During the reaction, the flask was immersed in a constant-temperature bath at 50°C under an atmosphere of nitrogen. The solution was then added dropwise to a stirred solution of methanol-water in a 50:50 volume ratio, and the precipitated polymer was washed with methanol and then dried and stored in dark bottles. The polymer was reprecipitated once from a dioxane solution and washed and dried under vacuum prior to determining the degree of substitution. The degree of substitution was calculated from the nitrogen content. PMD membranes were prepared by the identical technique used for the PVC films. The film thickness was about 40 μ .

PMD-PVC Blend Film. PMD whose degree of substitution was 10.9 and PVC-2 were used for the blend. Each polymer was dissolved in THF separately, and then both solutions were mixed and stirred at room temperature. The films of the blend polymers were prepared with the technique described for PVC film preparation. Film thickness of the blend was about 60 μ .

Measurement of Evolved Gaseous Products Consequent to Irradiation. A 40- to 50-mg film sample was weighed precisely and placed in a 4- to 5-ml sample cell equipped with a small mercury manometer. The prepared film was degassed for several days at 10^{-5} mm Hg pressure until the amount of degassing was negligible and irradiated in a sealed sample cell by γ -rays from a ^{60}Co source at a dose rate of 1.0 Mrad/hr at 40°C. The total dose

ranged between 1 and 35 Mrad. After irradiation, the cell was immersed in a constant temperature bath at 25°C, and the pressure increase was measured by cathetometric observation of the Hg in the manometer. At the final stage of the experiment, the volume of the cell was determined by a mercury displacement technique. In the other runs, 250 mg PVC and 500 mg PMD were put in tubes with a breakable seal, separately, and irradiated under vacuum with 6 Mrad and 10 Mrad, respectively. The evolved gaseous products were analyzed with a CED mass spectrometer.

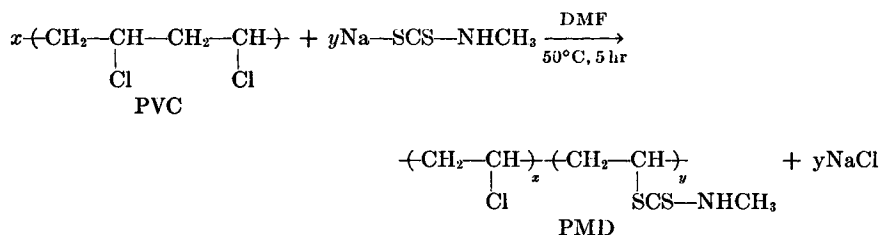
ESR Spectra. Samples of PVC and PMD films were put in the quartz tubes, separately, and irradiated with 9.6 Mrad under vacuum at room temperature at a dose rate of 0.143 Mrad/hr. The irradiated tube was stored in liquid nitrogen immediately, and the ESR spectrum was obtained at -196°C with a Varian ESR spectrometer.

Gel Content. About 50 mg (W_1) of the irradiated membrane was weighed carefully, then immersed in 100 ml of THF for about two days. The insolubilized portion was separated and its weight (W_2) was measured after drying to constant weight. The gel content was calculated as $W_2/W_1 \times 100$.

RESULTS AND DISCUSSION

Preparation of PMD and PMD-PVC Blend Polymer

The reaction between PVC and sodium N-methyl dithiocarbamate in DMF has been reported in detail.¹² The reaction was confirmed by comparison of the synthesis of the corresponding model compound of S-ethyl N-methyl dithiocarbamate:



where $x = 88$ to 89 and $y = 11$ to 12 . The degree of substitution y of the PMD was varied by controlling the reaction time. The results are summarized in Table I. PMD having a degree of substitution between 13 and 15 formed a gel-like product in the reaction mixture. Therefore, PMD-34 or PMD-44 with y value of approximately 11 represented the maximum degree of substitution.

The blended polymers listed in Table II were prepared with varying proportions of PMD-44 and PVC-2 by the technique described in the experimental section.

TABLE I
PVC Containing N-Methyl Dithiocarbamate (PMD)

Polymer	Reaction time, hr	Nitrogen, wt-%	MD ^a in polymer	
			mole-% (y)	weight-%
PMD-31	0.5	0.50	2.3	4.8
PMD-32	2.0	0.97	4.6	9.4
PMD-33	3.0	1.35	6.5	12.9
PMD-34	5.0	2.22	11.2	21.2
PMD-44	5.0	2.17	10.9	20.6

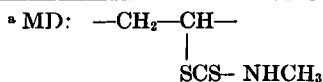
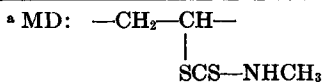


TABLE II
PMD-PVC Blend Polymers

Blend polymer	PMD-44, wt-%	MD ^a polymer, wt-%
PMD/PVC-1	77.3	15.9
PMD/PVC-2	60.5	12.5
PMD/PVC-3	39.5	8.1
PMD/PVC-4	21.8	4.5



Internal Protection of PVC by N-Methyl Dithiocarbamate

The amount of gaseous products evolved from PVC-1 and PMD with varying amounts of $\begin{array}{c} \text{—CH}_2\text{—CSCS—NHCH}_3 \\ | \\ \text{H} \end{array}$ (MD) is plotted versus total

H

dose in Figure 1. The G values for gas evolution from the irradiated PVC, $G(\text{gas})_{\text{PVC}}$, have been reported to depend on the irradiation temperature.⁶ In this work the $G(\text{gas})_{\text{PVC}}$ of 6–13 was obtained from PVC by irradiating with γ -irradiation at 25°C.¹³ From the data in Figure 1, $G(\text{gas})_{\text{PVC}}$ was found to be 0.8, and the gas evolution from irradiated PVC was linearly proportional to radiation dose. The gas evolution from the irradiated PMD occurred after a threshold value of the total dose. The gas evolution decreased monotonically with increasing N-methyl dithiocarbamate content. This is clearly demonstrated in Figure 2, in which the G values for the gas evolution from PMD, $G(\text{gas})_{\text{PMD}}$, were plotted against the MD content, and the broken line shows what one would expect if each component were contributing in proportion to the concentrations of MD and $\begin{array}{c} \text{—CH}_2\text{—CH—} \\ | \\ \text{Cl} \end{array}$

Cl

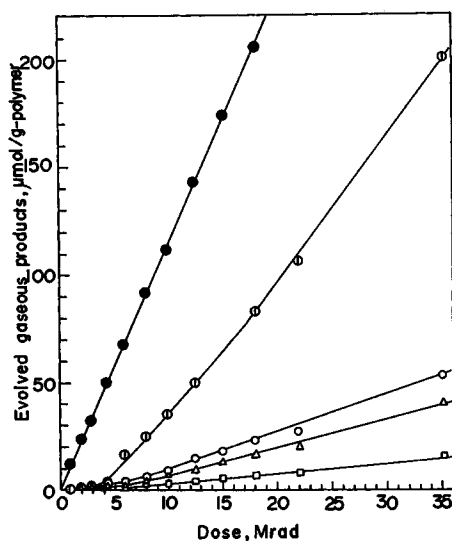


Fig. 1. Stability of PVC-1 and modified PVC containing N-methyl dithiocarbamate (PMD): (●) PVC-1 film, (0% MD by weight); (⊕) PMD-31 film (2.3% MD by weight); (○) PMD-32 film (4.6% MD by weight); (Δ) PMD-33 film (6.5% MD by weight); (□) PMD-34 film (11.2% MD by weight).

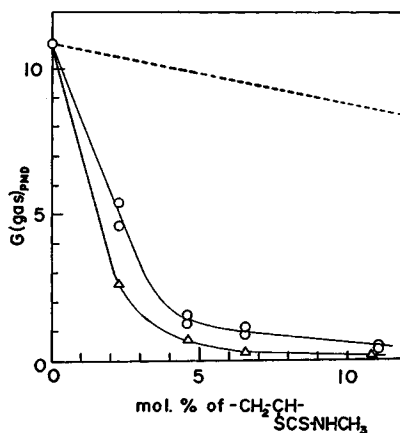


Fig. 2. G values for gas evolved from PVC-1 and PMD. Dosage: (○) 15-35 Mrad; (Δ) 6 Mrad.

(VC) components, that is, the case where MD merely dilutes the VC content in PMD.

As can be seen in Figure 3, the mass spectra of the evolved gas from the irradiated PVC with 6 Mrad showed strong peaks of ^{35}Cl , H^{35}Cl , ^{37}Cl , H^{37}Cl and weak peaks of ethylene and hydrogen. In contrast to this, the mass spectrum of the evolved gas from PMD-44 irradiated with 10 Mrad showed no HCl peaks and showed weak peaks of hydrogen, ^{32}S , and unknown prod-

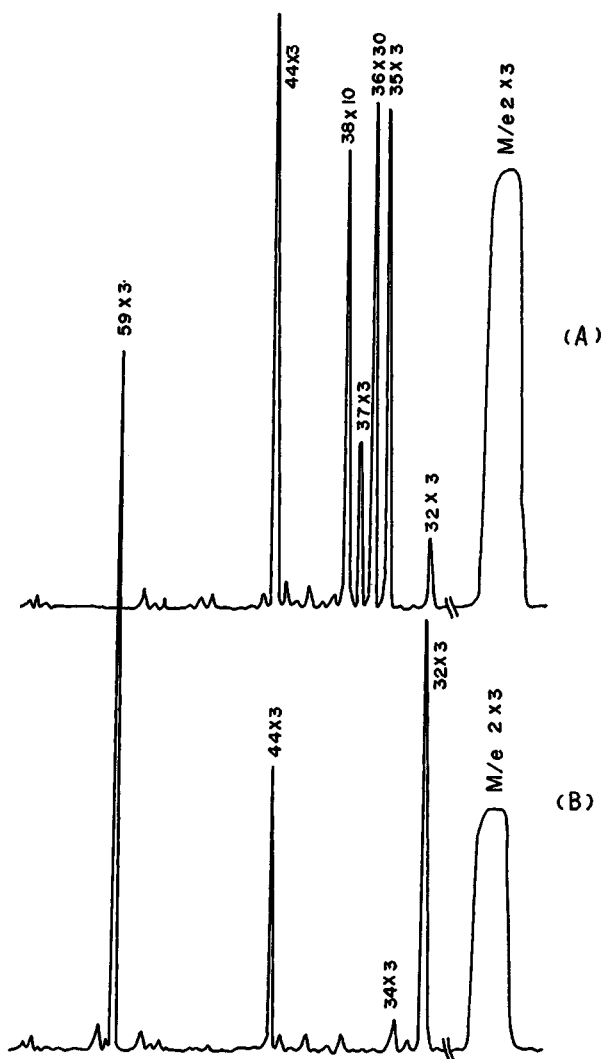


Fig. 3. Mass spectra of gaseous products evolved from PVC-1 and PMD-44 with irradiation: (A) PVC-1, dosage 6 Mrad ($\sim 45 \mu \text{ Hg}$); (B) PMD-44, dosage 10 Mrad ($\sim 20 \mu \text{ Hg}$).

ucts of mass number 59. The reason for this behavior will be discussed later. Based on the mechanism for the radiation degradation of PVC, the degradation appeared to start with scissions between Cl and/or H and C in the polymer chain, and, as a result, the chlorine radical formed hydrogen chloride and the hydrogen radical formed a hydrogen molecule. In any case, if PVC is protected by MD, the generation of both hydrogen chloride and hydrogen may be reduced. The fact that the irradiated PMD-44 evolved no hydrogen chloride and evolved a small amount of hydrogen

suggests another mechanism for the radiation degradation of PVC containing N-methyl dithiocarbamate. At present, we considered the hydrogen evolved from the MD component only. This hypothesis is supported by the ESR spectra. As a result, a G value of 1.35 was calculated for the gas evolution from the MD component itself at 10 Mrad total dose.

A stabilization coefficient may be defined as follows:

$$\text{stabilization coefficient} = \frac{G(\text{gas})_{\text{PVC}}}{G(\text{gas})_{\text{VC}}}$$

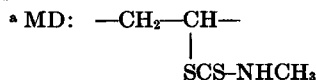
where $G(\text{gas})_{\text{PVC}}$ is the G value for the gas evolution from PVC which is used for the preparation of PMD, and $G(\text{gas})_{\text{VC}}$ is the G value for the gas evolution from the VC component in PMD. The latter is calculated by using the following equation:

$$G(\text{gas})_{\text{VC}} = \left(q_1 - \frac{W_{\text{MD}} \times 3.0 \times 10^{-6}}{21} \right) \times \frac{9.6 \times 10^6}{W_{\text{VC}}}$$

where q_1 is the moles of the evolved gas from PMD at 10 mrads, W_{MD} is a weight-per cent of MD in PMD, and W_{VC} is the weight-per cent of VC in PMD. The stabilization coefficients at 10 Mrad are summarized in Table III. From the viewpoint of the evolution of hydrogen chloride, the radiation protection of PVC by N-methyl dithiocarbamate in the solid state was found to be significant, and MD of 11 mole-% provided almost perfect

TABLE III
Stabilization Coefficient of MD^a in PMD Irradiated with 10 Mrad

Polymer	MD, wt-%	$G(\text{gas})_{\text{PMD}}$	$G(\text{gas})_{\text{VC}}$	Stabilization coefficient
PMD-31	4.8	3.37	3.41	3.2
PMD-32	9.4	0.93	0.87	12.4
PMD-33	12.9	0.71	0.60	18.0
PMD-34	21.2	0.30		
PMD-44	20.6	0.28		
PVC-1	0	10.8	10.8	1.0



protection. If the 11 mole-% of MD were distributed uniformly in PMD-44, approximately 10 moles of VC exists between each MC, which means MD protects 5 vinyl chloride units on each side, i.e., a total protection range of about 10 atoms of carbon. Charlesby and Groves¹ irradiated linear dodecanes containing a naphthyl group at various positions along the alkyl chain. Their results indicated an approximate range of protection of a naphthyl group against crosslinking was also about 4 to 5 carbons.

External Protection of PVC by PMD

Since no hydrogen chloride was detected in the gas evolved from PMD-44 with 10 Mrad, PMD-44 was used as an external additive to study the external protection afforded by PMD addition to PVC. Figure 4 is a plot of the G value for the gas evolution $G(\text{gas})_{\text{B.P.}}$ versus the PMD-44 content in the blend polymers. The broken line shows hypothetical results assuming that the PMD-44 and PVC-2 were contributing to gas evolution in

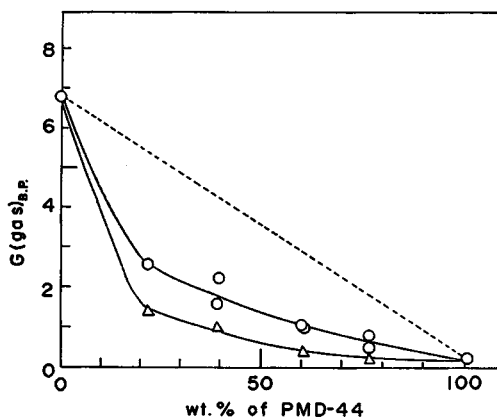


Fig. 4. G values for gas evolved from PVC-2 and blend polymers of PVC-2 and PMD-44. Dosage: (O) 15-35 Mrad; (Δ) 6 Mrad.

proportion to their concentration in the blend polymer. Since the data fall below this line, energy is presumably being transferred from the PVC to the MD component where it is harmlessly dissipated as heat. A stabilization coefficient for external protection can also be defined as follows:

$$\text{stabilization coefficient} = \frac{G(\text{gas})_{\text{PVC}}}{G(\text{gas})_{\text{PVC in B.P.}}}$$

where $G(\text{gas})_{\text{PVC}}$ is the G value for the gas evolution from PVC and $G(\text{gas})_{\text{PVC in B.P.}}$ is the G value for the gas evolution from PVC in the polymer blend. The latter is calculated with the following equation for the case of 10 Mrad irradiation:

$$G(\text{gas})_{\text{PVC in B.P.}} = \left(\frac{q_2 - (3.0 \times 10^{-8} \times W_{\text{PMD}})}{W_{\text{PVC}}} \right) \times 9.6 \times 10^6$$

where q_2 is moles of evolved gas from the blend polymer with 10 Mrad, W_{PMD} is the weight-per cent of PMD-44 in the blend polymer, and W_{PVC} is the weight-per cent of PVC-2 in the blend polymer. The results are summarized in Table IV. Comparing these results with those presented in Table III, it is apparent that the N-methyl dithiocarbamate group combined with a polymer chain was more effective in reducing radiation damage than that mixed physically with PVC. In the film state, the protective

TABLE IV
Stabilization Coefficient of PMD-44 in PMD-PVC
Blend Polymer Irradiated with 10 Mrad

Blend polymer	PVC, wt-%	MD, wt-%	$G(\text{gas})_{\text{PVC}}$	$G(\text{gas})_{\text{PVC}}$ in B.P.	Stabilization coefficient
PMD-PVC-1	22.7	15.9	0.38	0.82	8.2
PMD-PVC-2	39.5	12.5	0.72	1.46	4.6
PMD-PVC-3	60.5	8.1	1.24	1.93	3.5
PMD-PVC-4	78.2	4.5	2.22	2.72	2.5
PVC-2	100	0	6.75	6.75	1.0

group may contact the VC component within the same polymer chain as well as in different neighboring polymer chains. For this case, the stability of PMD against γ -irradiation degradation may be the result of internal and external protection.

ESR Spectra

ESR spectra of the irradiated PVC-1 and PMD-44 are shown in Figure 5. Both samples were kept at -196°C immediately after irradiating at room

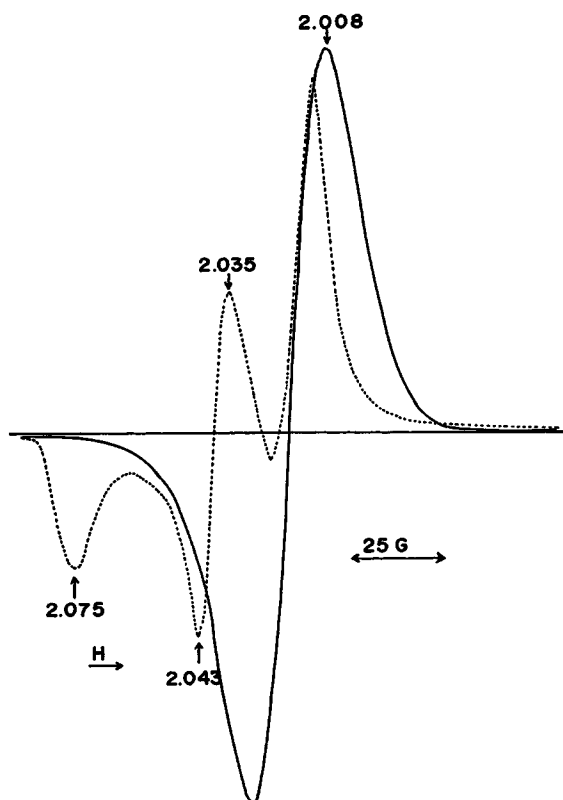
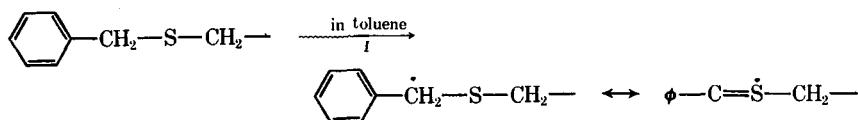


Fig. 5. ESR spectra of γ -irradiated PVC-1 and PMD-44. Dosage: 917 Mrad; (—) PVC-1; (.....) PMD-44.

temperature under vacuum, and measurements were made at -196°C . The irradiated PVC showed a single spectrum with a line width at the maximum slope (ΔH_{ms}) of 25 gauss. These results are consistent with those published on irradiated PVC under vacuum at -196°C and then warmed to room temperature,^{7,11} which were attributable to the polyenyl radical, $-\text{CH}_2-\text{CH}-(\text{CH}=\text{CH})-\text{CH}_2-$. As can be seen, the ESR signal of the irradiated PMD-44 is quite different; the strong anisotropy and the high g value might indicate a radical with the single electron largely localized on the sulfur atom.¹⁴ Ando and co-workers¹⁵ have studied the energy transfer from solvent to sulfides such as dibenzyl sulfides and postulated the formation of a sulfur radical by the stabilization through the following electron-sharing 3- d orbital resonance with a sulfur atom when the sulfides were irradiated:



The radical concentrations in the irradiated PVC and PMD-44 were calculated from the double integral of the curves in Figure 4, using the radical concentration of the strong pitch as a standard. Values of $6.2 \times 10^{16}/\text{g}$ (1.03×10^{-7} mole/g) and $7.2 \times 10^{16}/\text{g}$ (1.19×10^{-7} mole/g) were obtained in the irradiated PVC and the irradiated PMD-44, respectively. The lower radical concentration observed in the irradiated PMD-44, compared with the amount of the evolved gas, 30×10^{-7} mole/g, with 10 Mrad suggests the formation of crosslinks by coupling of the polymer radicals.

Gel Formation in the Irradiated PMD

The degree of insolubilization in THF is shown as a function of radiation doses in Figure 6 for PMD-44 and PVC-1. Lawton and co-workers¹⁶ listed PVC as one of the degrading polymers, whereas Charlesby¹⁷ observed cross-

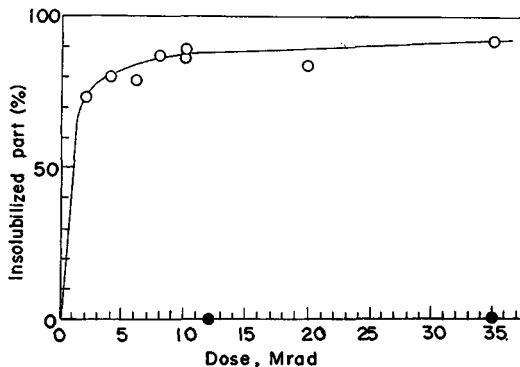
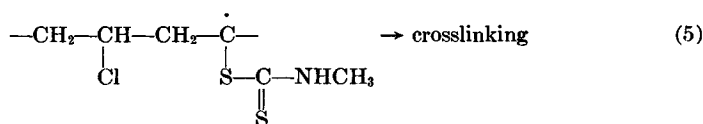
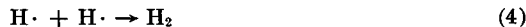
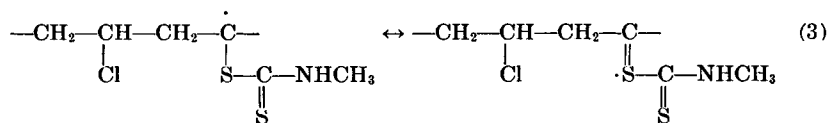
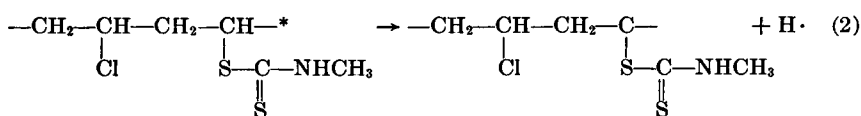
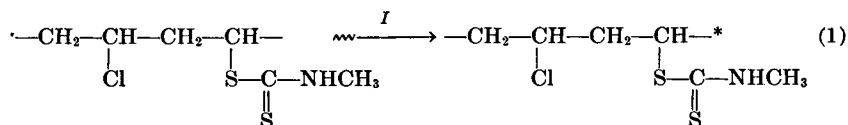


Fig. 6. Effect of irradiation dose on insolubilization of PVC-1 and PMD-44: (○) PMD-44; (●) PVC-1.

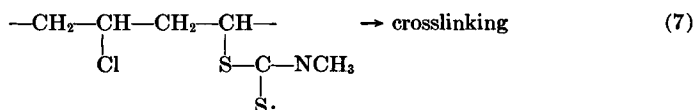
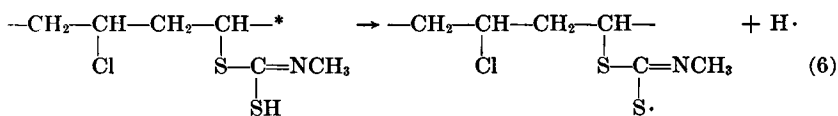
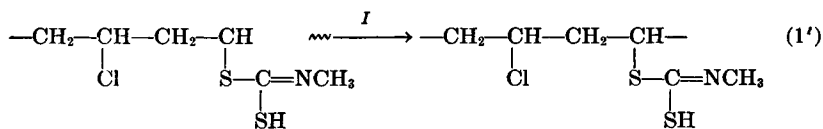
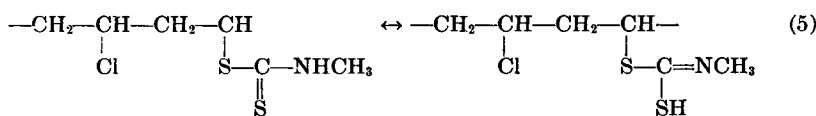
link formation. In our case, the irradiated PVC dissolved completely in THF at room temperature even after a total dose of 35 Mrad. The irradiated PMD-44, however, formed an insolubilized product with rather small doses.

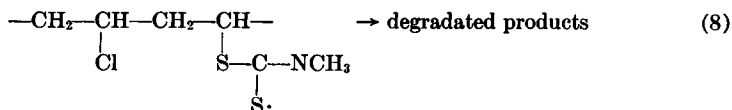
Mechanism of the Radiation Protection of PVC by N-methyl Dithiocarbamate

The following conclusions regarding the mechanism of the radiation protection of PVC by N-methyl dithiocarbamate are suggested by the results and discussion mentioned above:



and/or





It is possible that the formation of a hydrogen radical from a sulfur-bearing carbon atom is favored as shown in reaction (2) by stabilization of the residue radical through resonance as shown in reaction (3). Reactions of PMD of a thiol-type isomer are also considered.

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