

Radiation Protection of Poly(vinyl Chloride) by N,N-Dialkyl Dithiocarbamate Substitution

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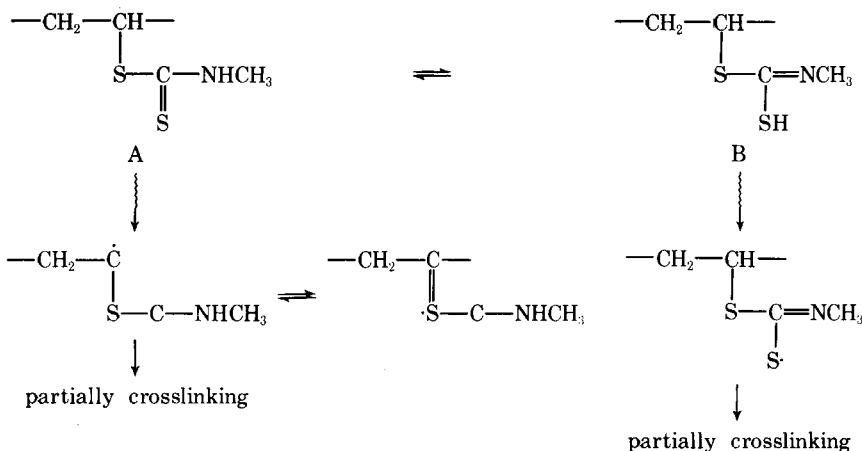
Synopsis

The effect of N,N-dialkyl dithiocarbamate substitution on the radiation stability of poly(vinyl chloride) (PVC) film was studied. PVC containing 6.5–15.7 mole-% N,N-dimethyl dithiocarbamate (PDM) and PVC containing 8.3–17.5 mole-% N,N-diethyl dithiocarbamate (PDE) was irradiated with γ -rays from a Co-60 source at room temperature under vacuum. The evolved gaseous products were measured and analyzed with a mass spectrometer. The apparent G values for gas evolution of PDM and PDE decreased remarkably. For example, a G value of 0.10 was obtained for a PDE which contains 17.5 mole-% diethyl dithiocarbamate group. The mass spectrum of the evolved gas from the same PDE sample with 10-Mrad irradiation showed no hydrogen chloride to be present. The external protection was studied using polymer-blended films of PVC and PDE or PDM. The stabilization coefficients for internal protection and external protection in polymer blends were calculated. Although the ESR spectrum of the irradiated PDM, PDE, and PVDE which is synthesized by polymerization of S-vinyl-N,N-diethyl dithiocarbamate (VDE) showed the same sulfur radicals, they were different from those of the irradiated cysteamine hydrochloride and PVC containing N-methyl dithiocarbamate (PMD). From these results, the protection of a polymer by a covalently bound dithiocarbamate was discussed.

INTRODUCTION

In the previous papers, one of the authors reported that modified poly(vinyl chloride) containing N-methyl dithiocarbamate group (hereafter to be called PMD) has properties of photosensitivity and chelate formation with metals,¹ and, moreover PMD film has an excellent antiradiation property against γ -irradiation in the viewpoint of a negligible small gaseous products, especially hydrogen chloride which was generated by radiolysis.²

The sulfur radicals have also been previously demonstrated to exist in the irradiated PMD film as stable species by ESR spectroscopy,² which seemed to be strongly related to the protection against the radiolysis of poly(vinyl chloride). However, the precise mechanism of protection of N-methyl dithiocarbamate group, in other words, the formation of the sulfur radical, was uncertain, because the sulfur radical was considered to arise from the following two schemes:



It is clear that the sulfur radical arising from scheme A is formed through the electron-sharing $3d$ orbital resonance, whereas the radical from scheme B is formed by eliminating a hydrogen radical from the hydrosulfuryl group. Each sulfur radical was expected to show a different ESR spectrum, therefore, the sulfur radical formed in the irradiated PMD must be determined. Recently, Mönig et al. have studied the radiolysis of poly(vinyl mercaptan-vinyl pyrolydone) and elucidated the mechanism of protection of mercaptan against the radiolysis of vinyl pyrolydone component.³ That is, the carbon radical formed in the main chain by irradiation extracts the hydrogen atom from the neighboring sulfhydryl group, and thus the main chain was repaired. David et al.⁴ also reported the protection action of ethyl mercaptan added to poly(methyl methacrylate) against radiolysis. However, the protective action of the sulfhydryl group in the Mönig result or scheme A cannot be considered in the case of *N,N*-dialkyl dithiocarbamate group if the PVC containing this group will show the antiradiation property.

The objects of the present research are to investigate the radiolysis of PVC containing *N,N*-dialkyl dithiocarbamate group and to help elucidate the role of the dithiocarbamate group in the protective action.

EXPERIMENTAL

Synthesis of PVC Containing *N,N*-dialkyl Dithiocarbamate Group

PVC (Sumikathene SX-800) manufactured by Sumitomo Chemical Co., Ltd., was purified by repeated precipitation with methanol from a dioxane solution and dried under vacuum. PVC containing *N,N*-diethyl dithiocarbamate group and *N,N*-dimethyl dithiocarbamate group (hereafter called PDE and PDM, respectively) were prepared from purified PVC and the corresponding sodium *N,N*-dialkyl dithiocarbamate [$\text{NaSCSN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$, $\text{NaSCSN}(\text{CH}_3)_2 \cdot \text{H}_2\text{O}$] in dimethyl formamide at 50°C by the method described by Okawara et al.⁷ The degree of substitution of dithiocarbamate group was calculated from the nitrogen content.

The membranes of PDM and PDE were cast at room temperature from a tetrahydrofuran solution on glass plates and were removed from the plates

when they were quite dry. The membranes were then immersed in methanol for several days and dried under vacuum. The resulting membrane thickness was about 30–50 μ .

Synthesis of Poly(S-vinyl-N,N-diethyl Dithiocarbamate)

The monomer S-vinyl-N,N-diethyl dithiocarbamate (hereafter called VDE) was prepared from ethylene bis(N,N-diethyl dithiocarbamate) which was prepared from the reaction of 1,2-dichloroethane with sodium N,N-diethyl dithiocarbamate by the thermal decomposition under reduced pressure by the method described by Nakai et al.⁸ The resulting VDE formed a pale-yellow liquid, $n_D^{25.5} = 1.5890$ (lit. $n_D^{25} = 1.5942$, $n_D^{27} = 1.5862$); nitrogen content: 8.0% (calcd 8.0%), bp 73–76°C (3 mm Hg), lit. 93–94°C (1 mm Hg) 92–93°C (2 mm Hg).

Polymerization of VDE was carried out as follows. In a Pyrex glass tube was placed 17.5 g (0.1 mole) VDE and 0.082 g (0.0005 mole) AIBN as initiator and sealed under vacuum. After the polymerization reaction was allowed to remain for about 25 hr at 80°C, a viscous pale-yellow liquid was obtained. The precipitate was formed by dropping the liquid into methanol and filtered and dried. This was a polymer of VDE (hereafter to be simply called PVDE), and the molecular weight was determined by vapor pressure osmometer. The total yield was 6.0 g, 34.3% of the theoretical value.

ANAL. Calcd for $(C_7H_{13}NS_2)_n$: C, 47.8%; H, 7.5%; N, 8.0%. Found: C, 48.0%; H, 7.4%; N, 8.0%.

Synthesis of S-Ethyl-N,N-diethyl Dithiocarbamate

To a solution of 25 g (0.15 mole) sodium N,N-diethyl dithiocarbamate in 50 ml dimethylformamide was added 17 g (0.15 mole) ethyl bromide very slowly. The mixture was allowed to stand for 2 hr at room temperature. After filtering the white precipitate, the filtrate was extracted with ether and dried under reduced pressure, yielding 17 g (65%) of a pale yellow liquid, bp 76.5–77.5°C (0.18 mm Hg).

Preparation of Membranes of PDM–PVC Blend, PDE–PVC Blend, and PVDE–PVC Blend

PDM and PDE whose degree of substitution was 15.7 mole-% and 17.5 mole-%, respectively, were used for the blend. PVC and PDE or PDM were dissolved in tetrahydrofuran separately, and then both solutions were mixed and stirred at room temperature. The membranes of blend polymers were prepared with the technique described for PDM and PDE membranes. The membrane thickness was about 50 μ . PVDE–PVC blend membrane was also prepared by the identical technique with the procedure for the PDE–PVC blend membrane.

Measurement of Evolved Gaseous Products Consequent to Irradiation

The measurement of evolved gaseous products consequent to γ -irradiation was made by the identical technique as that described in detail elsewhere.²

ESR Spectra

Samples of PDM and PDE membranes were put in quartz tubes separately and irradiated with 10 Mrad under vacuum at 23–25°C at a dose rate of 1.0 Mrad/hr. PVDE and cysteamine hydrochloride were irradiated in a powder state. The irradiated tubes were stored in liquid nitrogen immediately, and ESR spectra were obtained at -196°C with a Varian E-9 ESR spectrometer.

RESULTS AND DISCUSSION

Preparation of PDM and PDE

Figure 1 shows the infrared spectra of the PDE-24 whose degree of substitution is 17.5 and the corresponding model compound, S-ethyl-N,N-diethyl dithiocarbamate (SEDE). The characteristic strong absorption bands at 1480 cm^{-1} , 1200 cm^{-1} , and 920 cm^{-1} attributable to $\nu_{\text{C}=\text{N}}$, $\nu_{\text{C}=\text{S}}$, and $\nu_{\text{C}-\text{S}}$, respectively, seen in SEDE were also seen in PDE. The degree of substitution of dithiocarbamate group was calculated with the content of nitrogen. These depend on the temperature, reaction time, and the concentration of PVC and sodium dithiocarbamate. In this study, several PDE and PDM were obtained by using different reaction time. They are summarized in Table I.

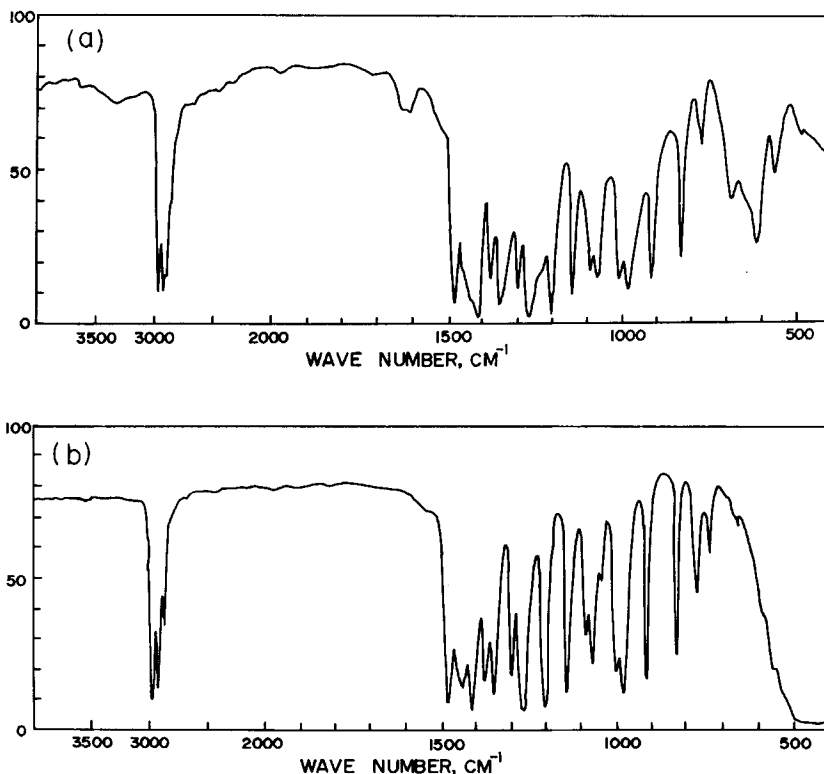
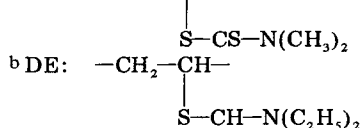
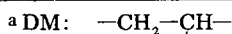


Fig. 1. (a) Infrared spectrum of PVC film containing 17.5 mole-% of N,N-diethyl dithiocarbamate; (b) infrared spectrum of S-ethyl-N,N-diethyl dithiocarbamate.

TABLE I
PVC Containing N,N-Dimethyl Dithiocarbamate (PDM) and
N,N-Diethyl Dithiocarbamate (PDE)

Polymer	Nitrogen, wt-%	DM ^a or DE ^b in polymer	
		mole-%	weight-%
PDM-11	1.33	6.45	14.1
PDM-12	2.04	10.4	21.5
PDM-13	2.45	12.8	25.7
PDM-14	2.69	13.2	26.4
PDM-15	2.90	15.7	30.5
PDE-21	1.74	8.33	20.2
PDE-22	2.42	13.4	30.3
PDE-23	2.64	15.0	33.1
PDE-24	2.99	17.5	37.3
PVDE	8.00	100	100



Preparation of Poly(S-vinyl-N,N-dimethyl Dithiocarbamate)

The limiting viscosity number $[\eta]$ of the polymer obtained from the polymerization of SDE determined at 30°C in benzene solution was 0.084, and the molecular weight determined by the vapor pressure osmometer was 8300 ($\bar{P} = 48$). PVDE was soluble in benzene, toluene, tetrahydrofuran, N,N-dimethylformamide, and methyl ethyl ketone, and insoluble in methyl alcohol, acetone, ethyl acetate, carbon tetrachloride, petroleum ether, and dimethylsulfoxide. Figure 2 shows the infrared spectra of the PVDE and monomer VDE. There is an excellent coincidence between them, except for the absorption band at 1600 cm^{-1} ($\nu_{\text{C}=\text{C}}$) which is seen only in the monomer. The bands at 1485 cm^{-1} and 1200 cm^{-1} , 920 cm^{-1} were assigned to be S=C—N—C and C—S, respectively.

Antiradiation Properties of PDE, PDM, and PVDE

Internal Protection

The amounts of gaseous products evolved from PDE and PDM with varying amounts of $-\text{CH}_2-\text{CH}-\text{SCSNR}_2$ are plotted versus total dose in Figure 3, and the relation between the degree of substitution and G values of the evolved gaseous products is also shown in Figure 4. For the comparison with monoalkyl dithiocarbamate group, the values of PMD were shown from the results of our previous work.²

The trace of hydrogen chloride was detected by mass spectrometer in the gaseous products evolved from PDE-21 at a dose of 10 Mrad. However, in the case of PDE-24, no hydrogen chloride was detected. Therefore, traces of gaseous products arising from the radiolysis of PDE-24 are believed to be the result of the decomposition of the $-\text{CH}_2-\text{CH}-\text{SCSN}(\text{C}_2\text{H}_5)_2$ (hereafter

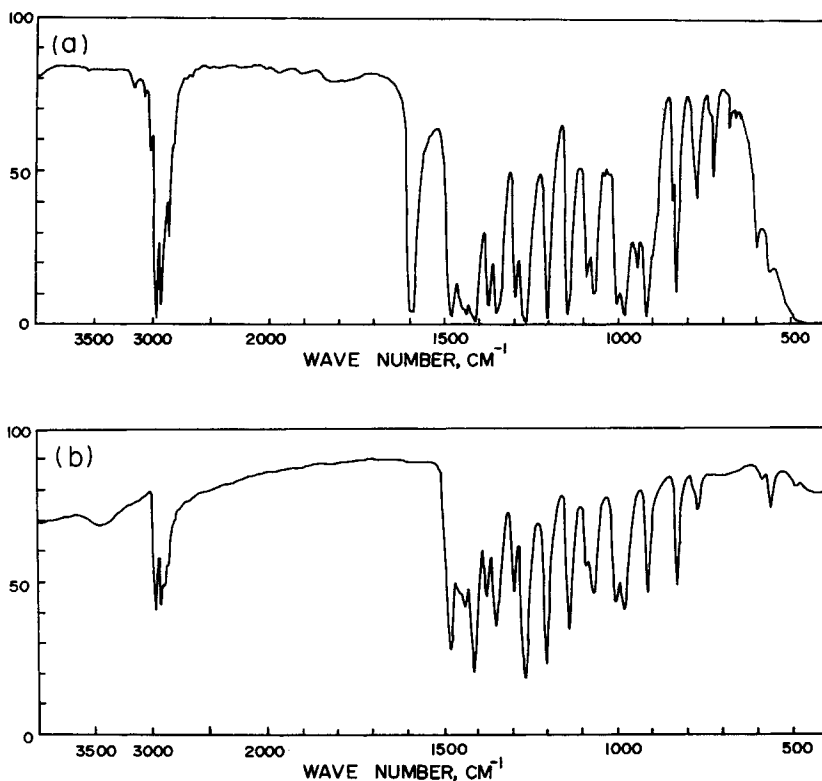


Fig. 2. (a) Infrared spectrum of S-vinyl-N,N-diethyl dithiocarbamate; (b) infrared spectrum of poly(S-vinyl-N,N-diethyl dithiocarbamate).

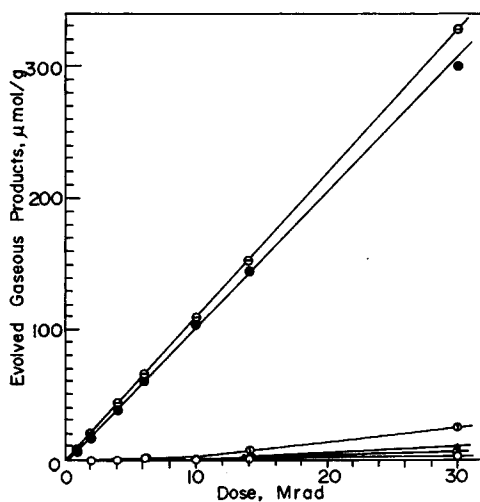


Fig. 3. Stability of PVC and copolymer of vinyl chloride-vinyl acetate (vinyl acetate: 32 mole-%) and PVC containing N,N-dialkyl dithiocarbamate (PDM, PDE): (⊕) PVC film; (●) copolymer; (⊙) PDM-11 film; (Δ) PDE-21 film; (⊙) PDM-15 film; (○) PDE-24 film.

called DE) component. This means that about 17.5 mole-% of DE component gives the perfect protection to the radiolysis of the neighboring PVC component. In the previous paper,² the stabilization coefficient of the internal protection was defined as follows:

$$\text{stabilization coefficient} = \frac{G(\text{gas})_{\text{pvc}}}{G(\text{gas})_{\text{vc}}}$$

$G(\text{gas})_{\text{vc}}$ can be calculated from the total volume of gaseous products generated from the irradiated PDE and the estimated volume of gaseous product generated from the DE component. $G(\text{gas})_{\text{pvc}}$ is the G value of the gaseous products from the irradiated PVC:

$$G(\text{gas})_{\text{vc}} = \left(q - \frac{W_{\text{DE}}}{100} \times V_{\text{DE}} \right) \times 9.6 \times 10^6 \times \frac{1}{W_{\text{vc}}}$$

where q is the total volume of the evolved gas from PDE and V_{DE} is the gas volume from DE component, which should be calculated from the total gaseous product from the irradiated PDE-24. W_{DE} and W_{vc} are the weight per cent of DE component and vinyl chloride component, respectively. In order to confirm V_{DE} , PVDE was irradiated under the same experimental condition as the irradiation of PDE, and 2.50 $\mu\text{mole/g}$ of gaseous products was measured at 10 Mrad. 0.92 $\mu\text{mole/g}$ of gaseous products arising from the irradiated PDE-24 as shown in Table II correlates well with the calculated value, 2.44 $\mu\text{mole/g}$, using the weight per cent of DE component and the volume of gaseous products evolved from the irradiated PVDE.

In Tables II and II are given the volume of the gaseous products, $G(\text{gas})$, and the stabilization coefficient in PDE and PDM. No hydrogen chloride was also detected in the case of the irradiated PDM-15 as shown in Figure 5. V_{DM} which is the volume of the gaseous product arising from DM component, $-\text{CH}_2-\underset{|}{\text{CH}}-\text{SCSN}(\text{CH}_3)_2$, was calculated using the same method as used for the calculation of V_{DE} . As shown in Table II, the stability of PDE-24 against γ -irradiation is quite similar to that of polystyrene which is the most stable antiradiation polymer.⁹

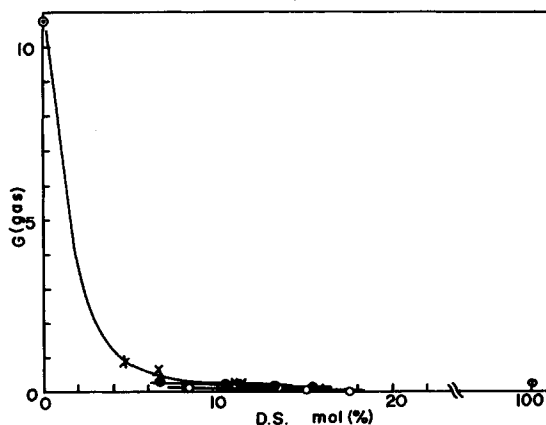


Fig. 4. G values for gas evolved from PVC, PMD, PDM, PDE, and PVDE. Dosage, 10 Mrad.

TABLE II
Stabilization Coefficient of DM in PDM Irradiated with 10 Mrad

Polymer	DM, wt-%	q , $\mu\text{mole/g}$	$G(\text{gas})$	$G(\text{gas})_{vc}$	Stabilization coefficient
PDM-11	14.1	3.4	0.33	0.31	35
PDM-12	21.5	3.1	0.30	0.26	42
PDM-13	25.7	2.5	0.24	0.17	64
PDM-14	26.4	2.0	0.19	0.10	104
PDM-15	30.5	1.8	0.17	0.00	∞
PVC	0	111.8	10.8	10.8	1

TABLE III
Stabilization Coefficient of DE in PDE Irradiated with 10 Mrad

Polymer	DE, wt-%	q , $\mu\text{mole/g}$	$G(\text{gas})$	$G(\text{gas})_{vc}$	Stabilization coefficient
PDE-21	20.2	1.40	0.14	0.108	100
PDE-22	30.3	1.27	0.12	0.070	154
PDE-23	33.1	1.10	0.11	0.039	277
PDE-24	37.3	0.92	0.09	0.00	∞
PVDE	100	2.50	0.24	0.24	—
PVC	0	111.8	10.8	10.8	1

External Protection

The external protections of PDE-24, PDM-15, and PVDE to PVC were also investigated by the same method as that reported for PMD-PVC.² PDE-24 and PDM-15 were chosen for the blend polymers as the protective additive, because no hydrogen chloride was detected in the gaseous products generated from both polymers at a dose of 10 Mrad. In Table IV are given

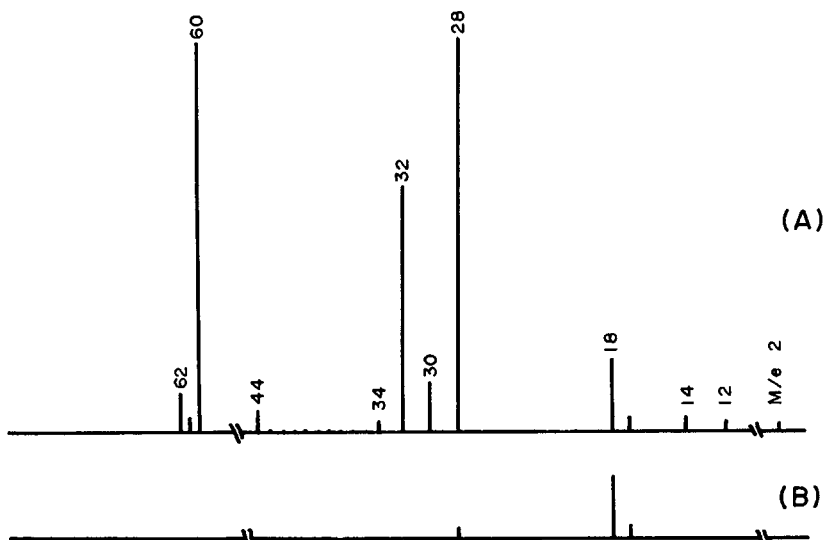


Fig. 5. Mass spectra of gaseous products evolved from irradiated PDM-15. Dosage, 30 Mrad; (A) PDM-15; (B) blank.

TABLE IV
Stabilization Coefficient of PDE-24, PDM-15 and PVDE in Blend Polymers
Irradiated with 10 Mrad

Polymer	PDE-24, PDM-15, or PVDE, wt-%	DE or DM, wt-%	q, $\mu\text{mole/g}$	$G(\text{gas})_{\text{PVC}}$ in B.P	Stabilization coefficient
PDE-PVC-1	22.4	8.3	14.2	1.73	6.2
PDE-PVC-2	40.3	15.0	12.8	2.01	5.4
PDE-PVC-3	59.6	22.2	7.2	1.06	6.8
PDM-PVC-1	22.1	6.7	22.6	2.75	3.9
PDM-PVC-2	38.3	11.7	16.0	2.39	4.5
PDM-PVC-3	59.7	18.2	9.2	1.94	5.6
PDM-PVC-4	76.8	23.4	7.3	2.35	4.4
PVDE-PVC-1	8.4	8.4	42.3	4.08	2.4
PVDE-PVC-2	14.6	14.6	27.8	2.68	3.5
PVDE-PVC-3	21.4	21.4	19.2	1.85	4.7
PVDE-PVC-4	31.3	31.3	10.5	1.02	7.9
PVC	0	0	111.8	10.8	1

the total volume of the gaseous products q and the G values of the gaseous products arising from PVC in the blended polymer, $G(\text{gas})_{\text{PVC}}$ in B.P., and the stabilization coefficient of the external protection in PDE-PVC, PDM-PVC, and PVDE-PVC blend polymers. These results indicate that both N,N-diethyl dithiocarbamate group play roles as protective groups against γ -irradiation to the neighboring PVC component, at the same time to the neighboring PVC present in the blended polymers.

Comparing the stabilization coefficients of DE and DM groups with MD group in the external protection, these are quite similar, although the order was $\text{DE} > \text{DM} > \text{MD}$. This minor differences might come from differences between the compatibility of PDE, PDM, and with PVC.

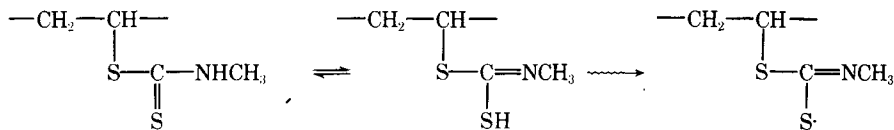
ESR

ESR spectra of the irradiated PDE, PVDE, PMD, and cysteamine hydrochloride are shown in Figure 6. All the samples were irradiated at room temperature and kept at -196°C immediately after the irradiation, and measurements were made at -196°C . As can be seen, the ESR signals of PDE and PVDE were virtually identical and showed strong anisotropic and high g values between 2.010 and 2.055. Comparing the ESR spectra of the irradiated PDE and PVDE with that of the irradiated PMD, the most pronounced difference observed was the absorption of the g value of 2.043 or 2.046 seen in the irradiated PDE and PVDE. The spectrum of the irradiated PMD corresponds to that of the irradiated cysteamine hydrochloride. Moreover, recently Mönig and Ringsdorf investigated the formation and the behavior of the radiation-induced radicals in poly(vinyl mercaptan) and the copolymers of vinyl mercaptan and N-vinyl pyrrolidone.³ The ESR spectra of the RS-radical which were found in their polymers were virtually identical with that of the irradiated PMD.

The radiation-induced radicals in PMD were formed preferably by the di-

rect cleavage of the mercapto group; and in the case of PDE and PVDE, the $RS\cdot$ radicals were considered to form as follows. First, the carbon radical was formed by losing the hydrogen radical, and then the sulfur radical was formed by the electron-sharing resonance which is relating the d -orbital of sulfur. In addition, PMD was easily crosslinked by the irradiation, whereas PDM, PDE, and PVDE were not crosslinked.

These were summarized as follows. In the case of PMD, the sulfur radical forms according to the following scheme:



and in the case of PDM, PDE, and PVDE, the sulfur radical forms according to the following scheme:

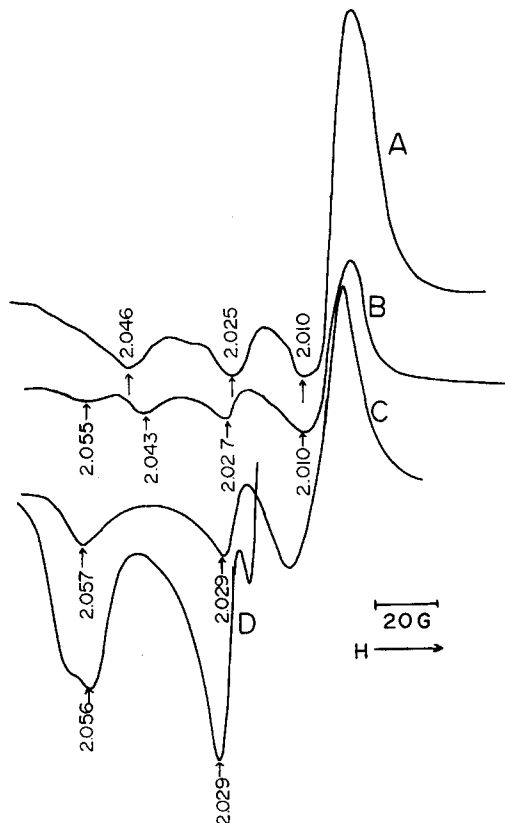
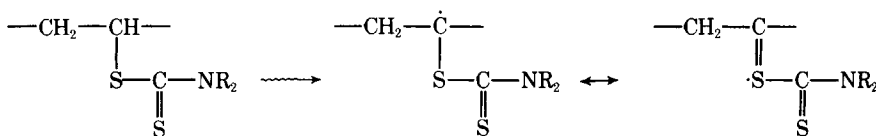


Fig. 6. ESR spectra of γ -irradiated PVDE, PDE-24, PMD, and cysteamine hydrochloride. Dosage, 10 Mrad, (A) PVDE; (B) PDE-24; (C) PMD; (D) cysteamine hydrochloride.

References

1. T. Nakagawa, Y. Taniguchi, and M. Okawara, *Kogyo Kagaku Zasshi*, **70**, 2382 (1967).
2. T. Nakagawa, H. B. Hopfenberg, and V. Stannett, *J. Appl. Polym. Sci.*, **15**, 747 (1971).
3. H. Mönig and H. Ringsdorf, *Makromol. Chem.*, **127**, 204 (1969).
4. C. David, D. Fuld, and G. Geuskens, *Makromol. Chem.*, **139**, 269 (1970).
5. G. Geuskens, D. Fuld, and C. David, *Makromol. Chem.*, **160**, 135 (1972).
6. G. Geuskens, D. Fuld, and C. David, *Makromol. Chem.*, **160**, 347 (1972).
7. M. Okawara, G. Morishita, and E. Imoto, *Kogyo Kagaku Zasshi*, **69**, 761 (1966).
8. T. Nakai, K. Shioya, and M. Okawara, *Makromol. Chem.*, **108**, 95 (1967).
9. W. Burlant and J. Neerman, *J. Polym. Sci.*, **58**, 491 (1962).

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