

## Transport of Fixed Gases in Radiation-Stabilized Poly(Vinyl Chloride)

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### Synopsis

Poly(vinyl chloride) was reacted with sodium N-methyl dithiocarbamate to produce a modified PVC containing N-methyl dithiocarbamate of varying degrees of substitution. The resulting adducts were markedly more stable when subjected to  $\gamma$ -radiation than the unmodified PVC. The transport parameters (permeability, solubility, and diffusivity) of fixed gases were determined in modified and unmodified films. Although the radiation stability was dramatically improved by this novel substitution, the barrier properties of the PVC were only slightly changed by the controlled substitution of N-methyl dithiocarbamate.

### INTRODUCTION

In order to characterize certain structural aspects of polymer films, and to determine their efficiencies as separation barriers and food packaging materials, numerous investigations have been carried out to measure the gas permeability of these films.<sup>1</sup> Gas permeability of poly(vinyl chloride) (PVC) film has been studied by Coleman and Kammermeyer<sup>2</sup> and Yamaguchi,<sup>3</sup> who reported the effect of plasticizer content in PVC film on the gas permeability. Recently, in this laboratory, the gas transport behavior in the vicinity of the glass transition temperature of PVC film has been studied, and it was found that for calendered PVC film, distinct break points near the glass transition point of PVC were shown in the Arrhenius plots of the permeability and diffusion constants for krypton and argon.<sup>4</sup> One of the authors<sup>5</sup> studied the effect of conjugated double bonds formed by  $\gamma$ -irradiation of PVC film on the gas permeability; the gas permeability was reduced and the activation energy of permeation  $E_p$  was increased in the irradiated PVC film.

Recently, work has been performed to stabilize PVC against  $\gamma$ -ray irradiation, and it has been found that the generation of gaseous products was reduced markedly by introducing dithiocarbamate groups into PVC film, as shown in Figure 1. Data are given here for the transport of permanent gases in radiation-stabilized PVC film to determine whether the

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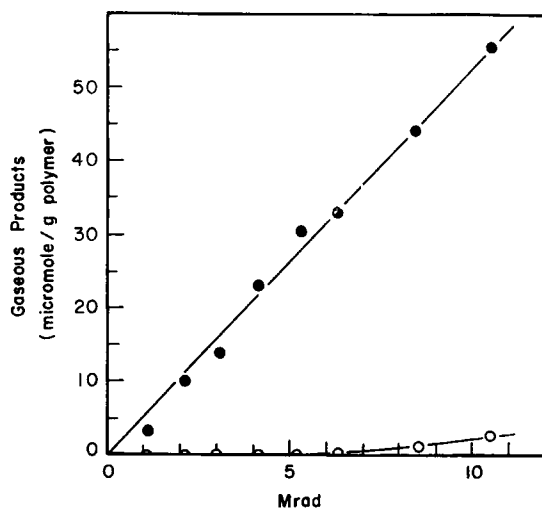


Fig. 1. Stability of PVC and modified PVC containing N-methyl dithiocarbamate (PMD): (●) PVC film; (○) PMD film.

structural changes which provide radiation stabilization significantly affect the transport of small-molecule penetrants in these modified films.

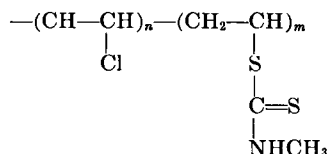
In order to study the permeation phenomena of modified poly(vinyl chloride) in a controlled experiment, it was necessary to cast all PVC film samples by identical techniques, because small differences in morphology resulting from the film-forming technique can lead to significant differences in permeation behavior. Alter<sup>6</sup> reported that permeability values of polyethylene to nitrogen reported by several investigators varied significantly even though the density of polyethylene was essentially the same in all cases. These property changes may arise from different degrees of anisotropy introduced by the film-forming process.

## EXPERIMENTAL

### Materials

**PVC Containing N-Methyl Dithiocarbamate (PMD).** A detailed discussion of the synthesis of PMD has been published elsewhere.<sup>7</sup> Sodium N-methyl dithiocarbamate and PVC ( $\overline{DP} = 600$ ) manufactured by Sumitomo Chemical Co., Ltd., were dissolved in dimethylformamide separately, and then both solutions were mixed in an amber-colored flask equipped with mechanical stirrers. During the reaction, the flask was immersed in a constant-temperature bath. The reaction product was precipitated by a methanol-water mixture, and the precipitated polymer was washed with methanol and then dried in a vacuum oven. The polymer was reprecipitated once from a dioxane solution, washed, and dried prior to determining its degree of substitution. The degree of substitution was calculated from the nitrogen content. PMD whose degree of substitution was 10.9% was

used in this research. A transparent film of PMD was prepared by casting from tetrahydrofuran solution. The thickness of the film used was 30–40  $\mu$ . The structure of PMD has been confirmed as follows<sup>7</sup>:



where  $n = 89.1$  and  $m = 10.9$ .

**Irradiated PMD Film.** PMD film was irradiated at a dose rate of 1.05 Mrad/hr from a Co 60 source at 40°C under vacuum to a total dose of 10 Mrad.

**PVC Film.** PVC film, 25  $\mu$  thick, was prepared by casting from tetrahydrofuran solutions. The sample of PVC used was identical to that used to synthesize PMD. This film was annealed at 70°C for about two days before measurements were made.

The gel content was measured as follows. About 50 mg ( $W_1$ ) of the membrane thermally treated or irradiated was weighed carefully and then immersed in 100 ml of tetrahydrofuran for about two days. Insolubilized parts of the samples, separated and weighed ( $W_2$ ), were measured after complete desiccation. The gel content was calculated as  $(W_2/W_1) \times 100$ . The measurement of the density of the membranes was carried out by density matching with an inert liquid. The test specimens were immersed in the mixture of trichlorobenzene and methanol whose density was approximately 1.3. Methanol or trichlorobenzene was added carefully until the test specimens were suspended in the mixture solution. The density of the solution which suspended the test specimens was measured in an Ostwald pycnometer.

### Permeability Measurements

The general theory of gas transport in polymers and detailed discussions of the methods of measurement and calculation of the permeability, diffusion, and solubility constants have been published elsewhere.<sup>1,8</sup> The experimental method used in this study was an adaptation of the high-vacuum gas transmission technique described by Stannett and co-workers.<sup>4</sup> Two time-lag stations were used. One station was equipped with a mercury McLeod gauge to monitor the pressure increase downstream of the membrane; this station was used to monitor the transport of carbon dioxide, oxygen, argon, nitrogen, and krypton. The second time-lag station was equipped with an MKS Baratron Model 90 pressure transducer; this Baratron-equipped station was used to achieve accurate measurement of the diffusion constant for helium, since the time lags for such a small penetrant were a few seconds in some cases and manual pressure determination with a McLeod gauge could not provide meaningful data.

## RESULTS AND DISCUSSION

**PMD Film and PVC Film Prepared from Solution.** It has been found that PMD was insolubilized in good solvents by crosslinking when heated over 100°C and that double bonds were formed concurrently. Intermolecular thermal reaction in the solid polymer might be accelerated above

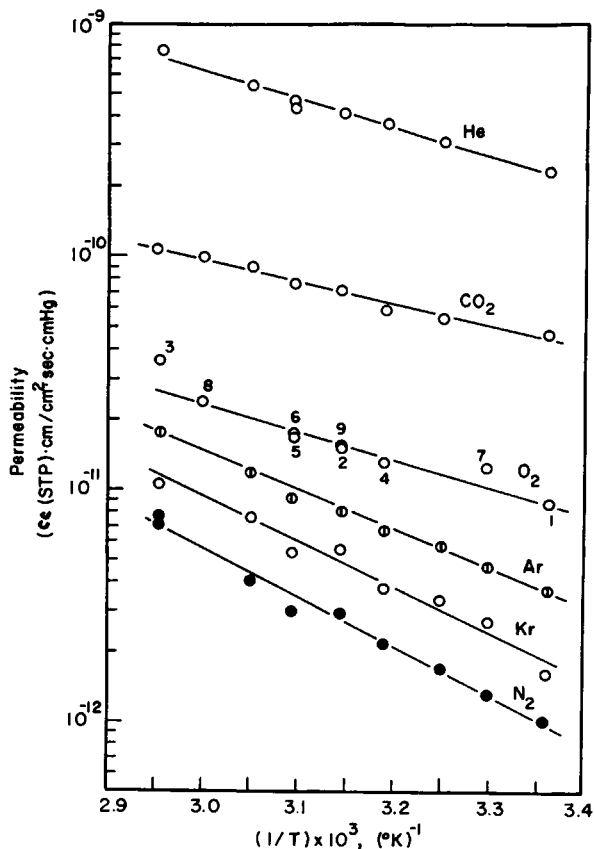


Fig. 2. Temperature dependence of permeability of PMD to helium, carbon dioxide, oxygen, argon, krypton, and nitrogen.

the glass transition temperature of the polymer. Accordingly, gas permeability experiments of PMD films were performed below 65°C and then above 75°C in order to examine the effect of crosslinking and/or C=C double bond formation on the transport process.

The results are shown in Figures 2 to 5. The activation energies of permeation,  $E_p$ , and diffusion,  $E_D$ , the enthalpy of solution,  $\Delta H$ , and

the preexponential factors  $P_0$ ,  $D_0$ , and  $S_0$  were calculated from the data of Figures 2 and 3 using the following equations:

$$P = P_0 \exp(-E_p/RT)$$

$$D = D_0 \exp(-E_D/RT)$$

$$S = S_0 \exp(-\Delta H/RT)$$

$$\Delta H = E_p - E_D$$

Experimentally determined values of  $P$ ,  $D$  and  $S$  at 25°C and  $E_p$ ,  $E_D$ ,  $\Delta H$ ,  $P_0$ ,  $D_0$ , and  $S_0$  for PMD film are summarized in Table I.

The results obtained between 70–85°C for PMD film are shown in Figures 8 to 11. Permeability constants and diffusion constants of PMD in the glassy state were greater than those of PVC. This difference might accrue from internal plasticization by the N-methyl dithiocarbamate group reducing the compactness or packing of the PVC structure and also de-

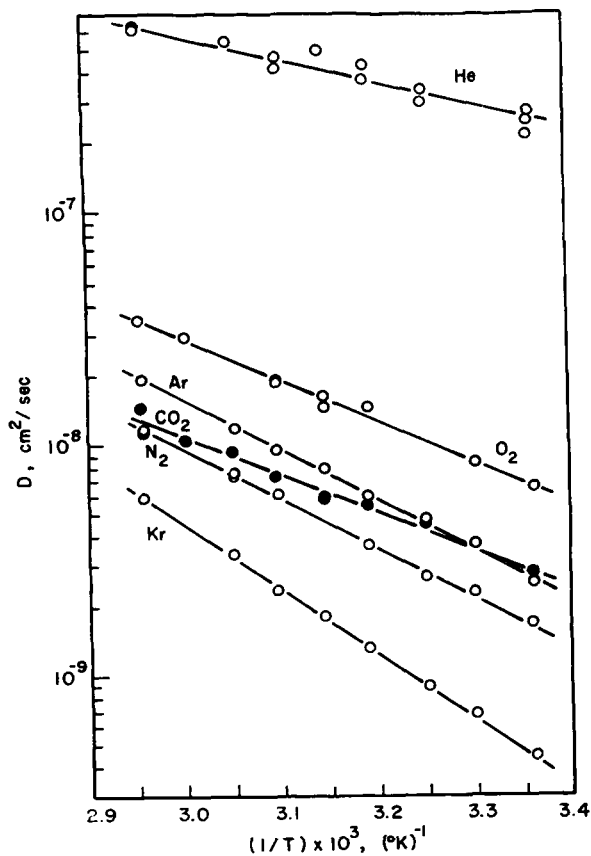


Fig. 3. Temperature dependence of diffusivity of helium, oxygen, argon, carbon dioxide, nitrogen, and krypton in PMD.

TABLE I  
Permeability, Diffusion, and Solubility Data of PMD Film, Irradiated PMD Film, and PVC Film (25°C)

Penetrant	$P \times 10^{12}$			$D \times 10^8$			$S \times 10^3$		
	PMD	Ir-PMD*	PVC	PMD	Ir-PMD*	PVC	PMD	Ir-PMD*	PVC
He	233	184	220	284	218	174	0.94	0.94	1.95
N <sub>2</sub>	1.02	0.50	1.15	1.68	1.09	1.01	6.07	0.46	0.99
Ar	3.68	1.66	2.00	2.45	2.56	1.45	1.50	0.65	1.38
O <sub>2</sub>	8.94	4.46	4.40	6.50	5.44	3.48	1.38	0.82	1.92
CO <sub>2</sub>	46.5	22.4	14.9	2.79	0.99	1.25	16.7	22.6	22.7
Kr	1.61			0.45			3.59		
		$E_p$ , kcal/mole		$E_D$ , kcal/mole			$\Delta H_s$ , kcal/mole		
He	5.49	4.32	7.03	4.36	4.44	6.33	1.13	-0.08	0.70
N <sub>2</sub>	9.67	6.93	16.7	9.77	6.95	17.4	-0.02	-0.02	-0.78
Ar	7.67	8.20	17.7	9.84	8.24	11.9	-2.17	-0.04	5.75
O <sub>2</sub>	5.52	7.18	16.6	8.12	8.12	11.8	-2.60	-0.92	4.79
CO <sub>2</sub>	4.06	6.35	15.1	7.58	7.91	16.1	-3.52	-1.56	1.00
Kr	8.83			12.8			-3.97		



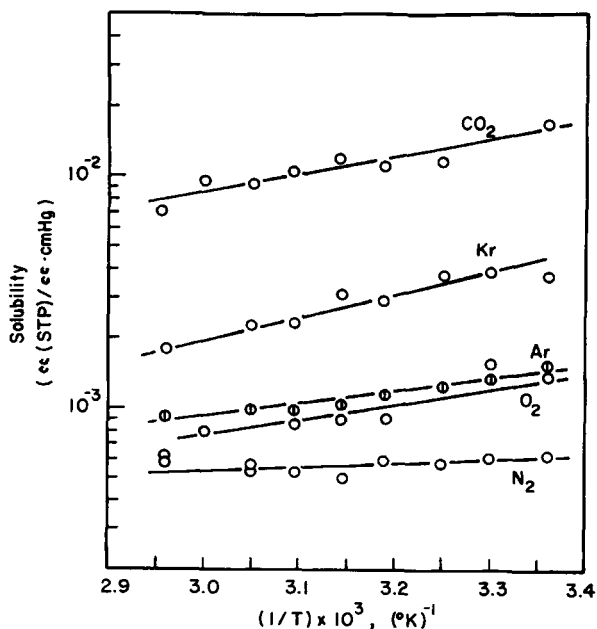


Fig. 4. Temperature dependence of solubility of carbon dioxide, nitrogen, krypton, argon, and oxygen in PMD.

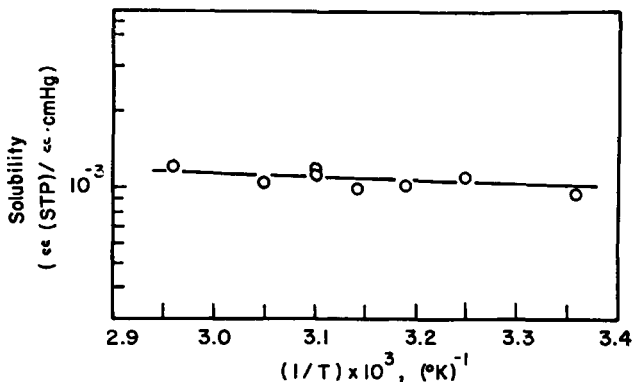


Fig. 5. Temperature dependence of solubility of helium in PMD.

creasing the activation energy of diffusion. The densities of PMD film and PVC were 1.344 and 1.390, respectively.

Because chemical postreactions involving the dithiocarbamate group seemed to be proceeding above the glass transition temperature,  $P$ ,  $D$ , and  $S$  above  $75^{\circ}\text{C}$  should depend upon the time of the experiment in this elevated temperature range. In this study (Figs. 6 and 7), the membrane was kept at  $70^{\circ}\text{C}$  in the diffusion cell for about 6 hr before the measurements were started. The intervals between each run were at least 2 hr, except runs no. 3 and no. 4 (17 hr), no. 9 and no. 10 (10 hr), no. 11 and no. 12, (10 hr), and no. 14 and no. 15 (4 hr). It is seen from the results that, for



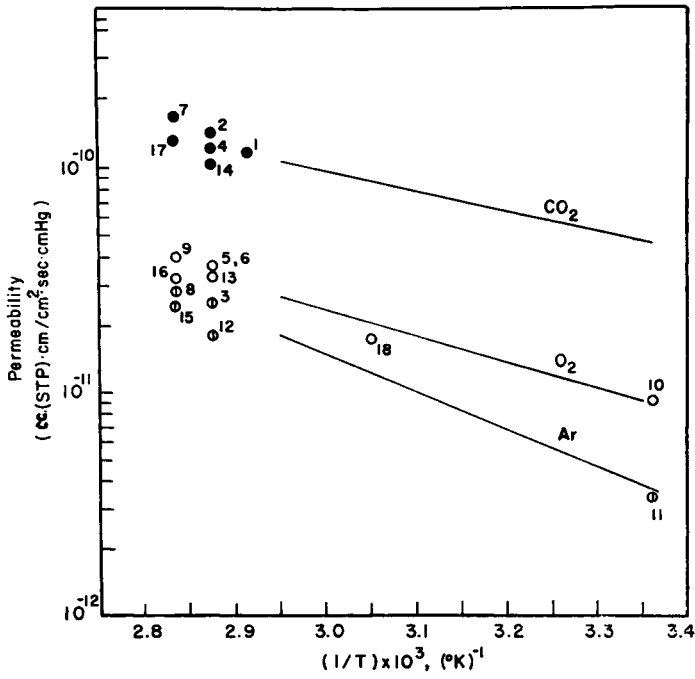


Fig. 6. Temperature dependence of permeability of PMD to carbon dioxide, oxygen, and argon: (●) carbon dioxide; (○) oxygen; (⊙) argon. Solid lines are taken from the previous experiments (Fig. 2).

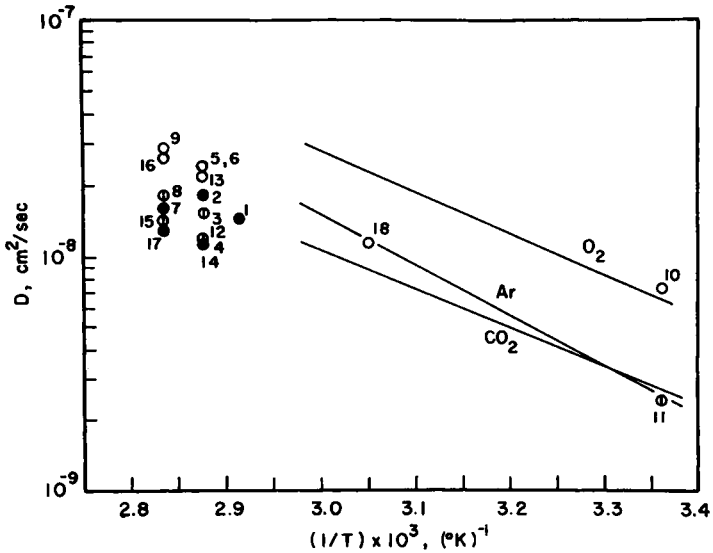


Fig. 7. Temperature dependence of the diffusivity of carbon dioxide, oxygen, and argon; (●) carbon dioxide; (○) oxygen; (⊙) argon. Solid lines are taken from the previous experiments (Fig. 3).

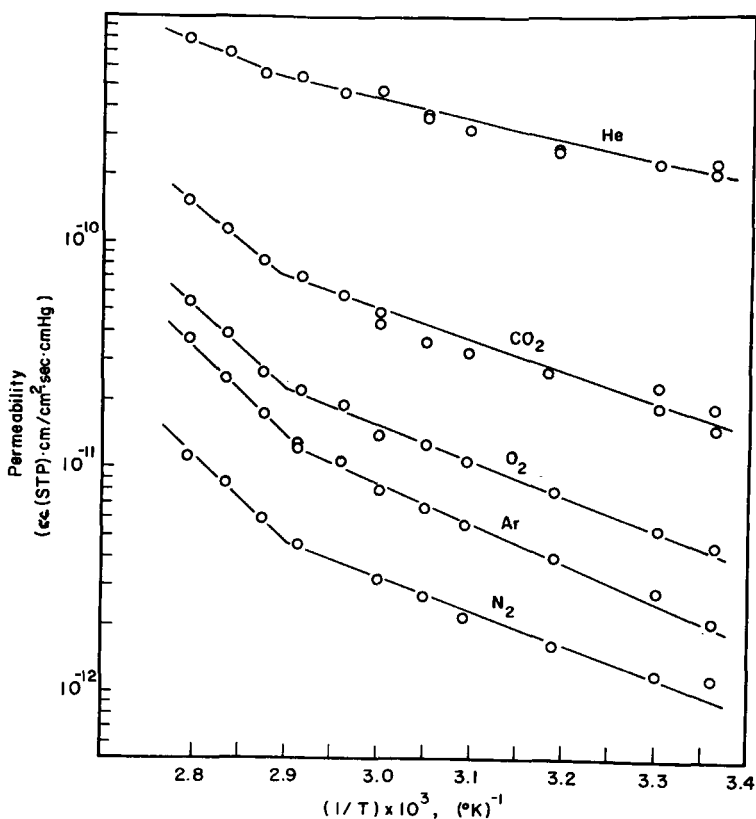
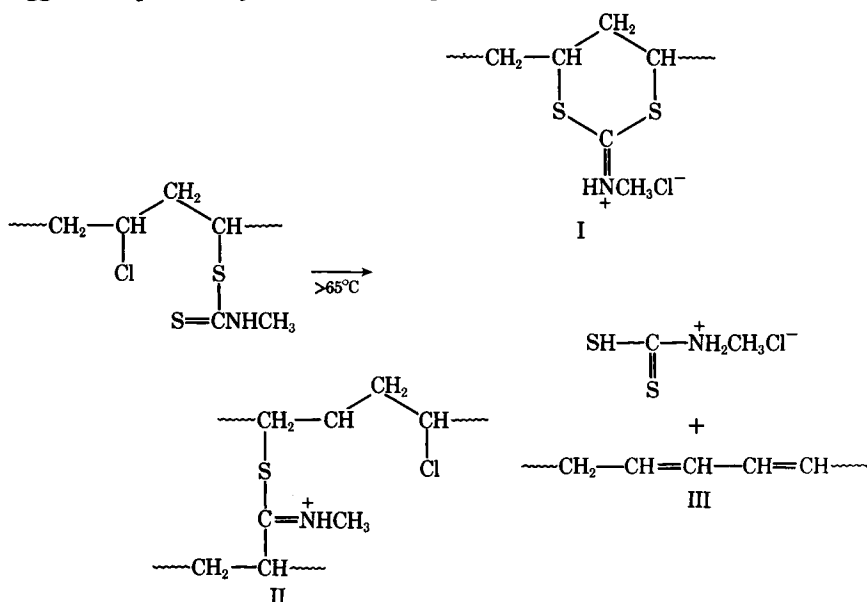


Fig. 8. Temperature dependence of permeability of PVC to helium, carbon dioxide, argon, and nitrogen.

PVC, permeability and diffusivity increased markedly above the glass transition temperature, i.e., clear break points in the Arrhenius plots were observed. Conversely, for PMD, the diffusion constants above 75°C were quite different from PVC, i.e., clearly smaller, although the reduction of permeability constants was not considerable. These results suggest crosslinking may have occurred in the PMD. To study this possibility, three samples of PMD film were examined by infrared spectroscopy and by measuring the gel content; the first sample had been used in the diffusion experiment and the temperature never exceeded 65°C; the second sample was heated to 75–80°C for 20 hr; and the third was the membrane which was removed from the diffusion cell just after the measurements were finished at 85°C, as shown in Figures 6 and 7. The gel contents were 65%, 80%, and 89%, respectively. The infrared spectra are shown for each of the first and third samples on Figure 12. These spectra showed a reduction in C—N stretching at 1500  $\text{cm}^{-1}$ , a shift of N—H stretching at 3200  $\text{cm}^{-1}$  toward lower wave number, and the appearances of strong and broad absorptions at 1560  $\text{cm}^{-1}$  and around 2500  $\text{cm}^{-1}$ , which were assigned as C=N and C=NH stretching, respectively. In addition to these

spectral changes, the film turned pale yellow to pale brown. The changes suggest the possibility of the following reactions:



It was impossible to distinguish between structures I and II on the basis of the infrared spectra, but from the gel content the formation of II seemed to be more likely.

Bixler and co-workers<sup>9</sup> reported that irradiated polyethylene film in which the number of crosslinks was 3.7 per 1000 carbon atoms reduced the diffusion constant by 30%–40%. Theoretically, the maximum number of crosslinks (via structure II in the thermally treated PMD film) is the same number as the degree of substitution of the dithiocarbamate group, namely, 10.9 per 100 monomer units if structures I and III were not formed. At this stage, the relation between the gel contents and the number of the crosslinks in PMD film has not been obtained. However, considering the residual dithiocarbamate content and the formation of intramolecular crosslinks and double bonds, and the number of crosslinks

TABLE II  
Permeability, Diffusion, and Solubility Constants at 80°C  
of the Thermally Treated PMD Film and PVC and PVC Film

	Run no. in		Penetrant	$P \times 10^{12}$	$D \times 10^9$	$S \times 10^3$
	Figs.					
	6 and 7					
PMD film	15	Ar	25.0	14.6	1.71	
	16	O <sub>2</sub>	31.6	16.2	1.95	
	17	CO <sub>2</sub>	103	13.3	7.74	
PVC film		Ar	25.0	15.8	1.58	
		O <sub>2</sub>	39.8	34.7	1.15	
		CO <sub>2</sub>	111	15.8	7.03	

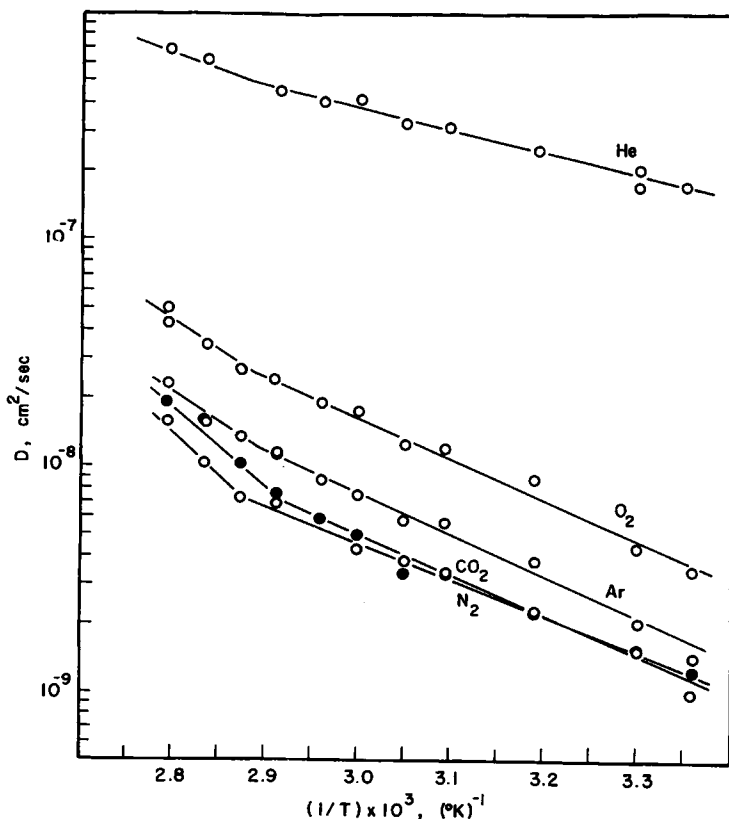


Fig. 9. Temperature dependence of the diffusivity of helium, oxygen, argon, carbon dioxide, and nitrogen in PVC.

formed at 65% gel content in the range of 25–65°C, the  $P$ ,  $D$ , and  $S$  values of PMD film were not influenced by the 65% gel content. Conversely, above 75°C, diffusion constants were influenced markedly by 80–89% gel content. The  $P$ ,  $D$ , and  $S$  values at 80°C are summarized in Table II. If the amorphous polymer chain segments were restricted above the glass transition temperature via crosslinking, the diffusion constant reduces by the reduction of  $\Delta S^*$  as follows:

$$D = e\lambda^2(\bar{k}T/h)e^{\Delta S^*/R}e^{-\Delta E/RT}$$

where  $\lambda$  is the length of a successful diffusion step,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $\Delta S^*$  is the entropy of activation.<sup>1</sup> The activation energy of diffusion above 75°C was not obtained, because the diffusion constants depended on time because of the concurrent chemical reaction. The effect of crosslinking was not observed in the range of 25–65°C, as shown in Figure 7; therefore the motion of the polymer segments above 75°C in the thermally treated crosslinked PMD film would be quite different from the motion below 65°C. In other words, above the glass transition temperature, a significant reduction may occur in the probability that gas

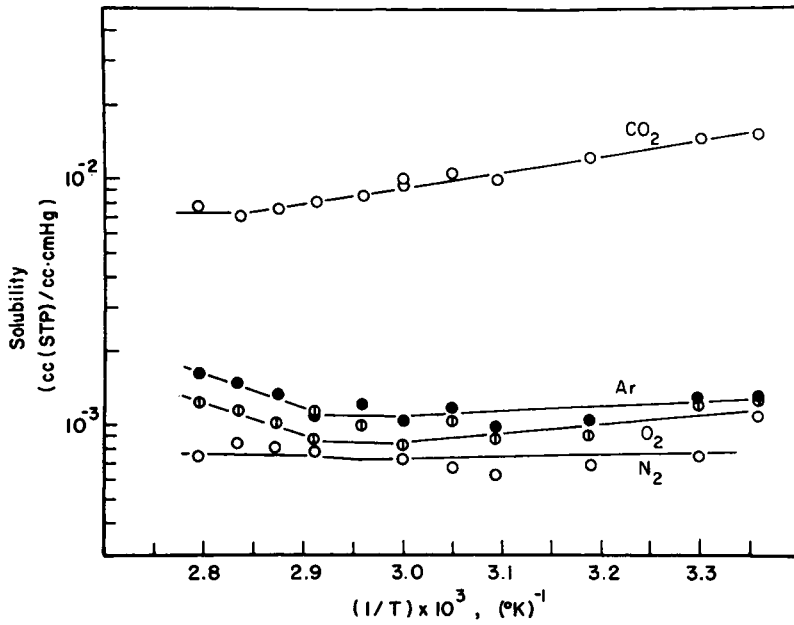


Fig. 10. Temperature dependence of solubility of carbon dioxide, argon, oxygen and nitrogen in PVC.

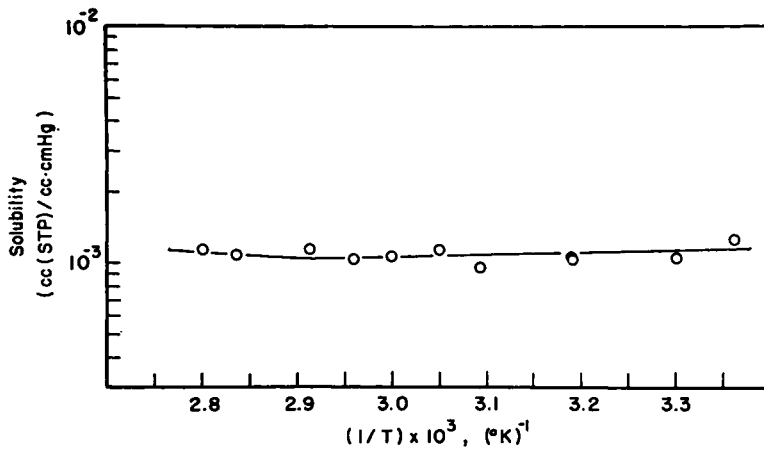


Fig. 11. Temperature dependence of solubility of helium in PVC.

molecules will find regions in the polymer where conditions favorable for a diffusion step exist. For thermally treated PMD film, the values of  $S$  at  $80^\circ C$  are higher for all gases examined. The increased gas solubilities may stem from the chemical changes in the polymer. Barrer<sup>10</sup> has suggested that a solution process may be considered to consist of two separate steps: (1) the formation of a hole or site and (2) the occupancy of this site by the solute molecule. The crosslinks interfere with step 1, but step 2 might be increased by the formation of the carbon-carbon double bonds

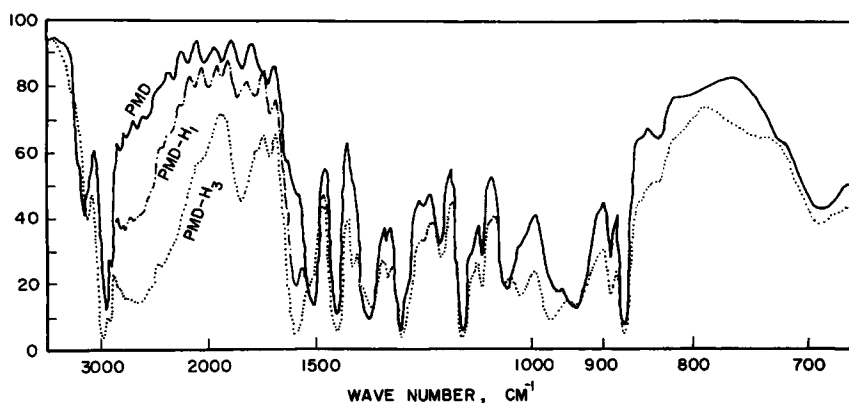
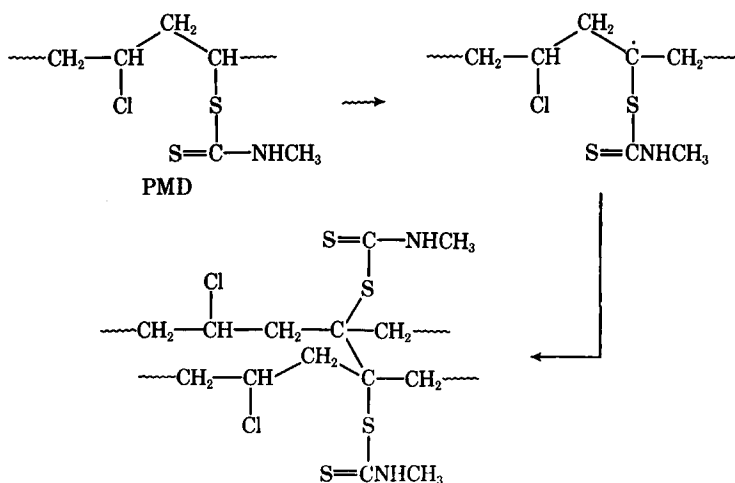


Fig. 12. Infrared spectra of modified PVC (PMD): (—) PMD film containing 10.9 mole-% of N-methyl dithiocarbamate; (---) PMD-H<sub>1</sub>, PMD treated below 65°C for 2 months; (···) PMD-H<sub>3</sub>, PMD heated at 80–85°C for 16 hr.

which would be at a higher concentration in the high temperature region than at low temperature.

**Irradiated PMD.** The infrared spectra of PMD film were unchanged before and after irradiation, even after a total dose of 35 Mrad. However, the gel content reached 89% after 10 Mrad irradiation under vacuum. The values of  $P$ ,  $D$ , and  $S$  at 25°C were summarized in Table I. The permeability constants of the irradiated PMD film were lower than those of the unirradiated PMD film. Solubility constants of the irradiated PMD were also smaller than those of the unirradiated PMD. The formation of carbon-carbon double bonds and C=N were not observed; therefore, the chemical reaction and thus-formed structure of crosslinking in the irradiated PMD is different from that formed in the thermally treated PMD. The crosslinked structure of the irradiated PMD might be considered as follows:



### Notation

$D$	diffusion coefficient, cm <sup>2</sup> /sec
$D_0$	preexponential factor in Arrhenius expression for diffusivity
$E_D$	activation energy for diffusion, kcal/g-mole
$E_p$	activation energy for permeation, kcal/g-mole
$h$	Planck's constant
$k$	Boltzman's constant
$P$	permeability, cc (STP) cm/(cm <sup>2</sup> sec cm Hg)
$P_0$	preexponential factor in Arrhenius expression for permeability
PMD	poly(vinyl methyl dithiocarbamate)
PVC	poly(vinyl chloride)
$R$	gas constant, kcal/(g-mole °K)
$S$	solubility, cc(STP)/(cc cm Hg)
$S_0$	preexponential factor in Vant Hoff expression for solubility
$T$	absolute temperature, °K
$W_1$	total weight of polymer, mg
$W_2$	weight of insolubilized polymer, mg

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