Modification of Polyolefin Films by Photochlorination

TSUTOMU NAKAGAWA and SUMIO YAMADA, *Industrial Products Research Institute, Shimomaruko Ota-ku, Tokyo, Japan*

Synopsis

Composite polyolefin membranes with graded chlorination gradient were obtained by photochlorination of polyethylene, polypropylene, and polystyrene films using ultraviolet and visible light. The maximum chlorine contents of these membranes were 12%, 8.5%, and 6.5%, respectively. As for polyethylene, the surface photochlorination reduced gas permeation of carbon dioxide and oxygen down to $1/_{30}$ and $1/_{21}$ of the original polyethylene; it also improved the wettability without changing substantially other favorable physical properties such as tensile strength, elongation, and water vapor permeation. The water contact angle of chlorinated polyethylene was comparable to that of poly(vinyl chloride). The infrared spectra suggest the presence of the chlorine of the —CHCl—CHCl— type rather than of the —CCl$_2$— type in the photochlorination of polyethylene. In an effort to obtain useful membranes with a photocrosslinking functional group as a side chain, surface-photochlorinated polyethylene was allowed to react with sodium N,N-dimethyldithiocarbamate or sodium N-methyl-N-carboxymethyldithiocarbamate in dimethylformamide at 50°C for 48 hr according to the procedure by which poly(vinyl chloride) was previously reacted. The polymer thus obtained has 4.1 mole-% —SCS—NMe$_2$ and 3.4 mole-% —SCS—N(CH$_3$)CH$_2$COONa groups.

INTRODUCTION

Polyolefin films (polyethylene, polypropylene, and polystyrene) have extensively been used in various fields such as packaging, agriculture, building, and electrical outlets. In spite of their excellent properties, and bonding capacity, printability, and permeability remain to be improved, except for the wettability of polystyrene. The substantial chlorination of polyethylene and polypropylene has been studied widely under a variety of conditions in the presence or absence of light for the main purpose of improving impact strength, flexibility, and flame resistance.[1-5]

The chlorination of polystyrene has also been the subject of a few investigations.[6,7] Chlorination can be considered to decrease gas permeability and increase wettability of the polyolefin films, because introduction of the polar atom, chlorine, may be expected to enhance intermolecular forces and also affinity of individual molecular chains. If chlorination is carried out on films by the use of light, the reaction should occur on the surface and consequently hardly affect the favorable bulk properties of polyolefins, Moreover, the surface-concentrated reaction will improve the wettability and gas barrier more efficiently.

During the course of this work, Luttinger and co-workers[8] studied substantial chlorination of polyethylene films in gaseous phase and in a liquid

medium saturated with chlorine by the use of various light sources. However, their work refers to only tensile strength, elongation, and fusion point of modified polyethylene by chlorination.

The present work deals with the effect of surface photochlorination on permeability, wettability, and mechanical properties of polyolefin films. In addition, the reaction of photochlorinated polyethylene with sodium dithiocarbamate was described in order to obtain a useful film with a specific functioning group on the surface.

EXPERIMENTAL

Films. Two low-density and a high-density polyethylene film were used in the experiment. The two resins of low-density polyethylene were Yukalone (PE-1) and Sumikathene (PE-2), supplied by Mitsubishi Petrochemical Co. and Sumitomo Chemical Co., respectively. The former film (PE-1), which had a density of 0.918, a melt index of 4, and a crystallinity of 50%, was specially prepared by the T-dye extrusion process without any additive. The latter (PE-2) had a density of 0.922, a melt index of 7, and a crystallinity of 63%. PE-1 film was used throughout the experiment unless otherwise noted in the text.

The high-density polyethylene (Hi-zex) was obtain from Mitsui Petrochemical Co. and had a density of 0.955, a melt index of 0.04, and a crystallinity of 81%.

The polypropylene film was bioxially oriented extruded Tolefan manufactured by Toyo Rayon Co.

The polystyrene film (Styrex) was supplied by Mitsubishi Plastics Co. Ltd. The film thickness was always approximately 30 microns, and the samples were used without any pretreatment.

Photochlorination. Photochlorination was carried out in two different cells, a diffusion cell and a irradiation cell, attached to a vacuum manifold, as illustrated in Figure 1. The diffusion cell was originally designed to carry out permeation experiments under light irradiation. Accordingly, the cell was a conventional stainless steel diffusion cell with a quartz glass win-
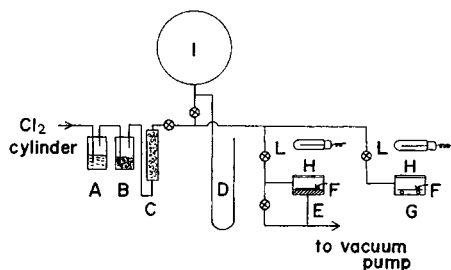

Fig. 1. Photochlorination apparatus: (A) sulfuric acid trap; (B) calcium chloride trap; (C) phosphorus pentachloride tube; (D) gas supply manometer; (E) diffusion cell; (F) sample film; (G) irradiation cell; (H) quartz glass window; (I) chlorine gas reservoir; (L) mercury or tungsten lamp; (⊗) glass stop cock.

dow on the top half. During the irradiation in the diffusion cell, the downstream side of the film was kept pumped out with a rotary vacuum pump. The irradiation cell was one which was commonly used for light irradiation experiments. Usually, the diffusion cell was employed throughout the experiment unless otherwise noted.

After a section of sample film was mounted on either of these cells, the apparatus was thoroughly degassed for an appropriate time, and then chlorine gas was introduced through the traps from a commercial gas cylinder. The gas pressure was monitored with a gas supply manometer. Once the gas reservoir was filled with the gas, the gas was supplied directly from the reservoir. Photochlorination was started with the light sources on, which were usually set 12 cm distant from the sample film unless otherwise noted. A Toshiba mercury lamp (SHL-100UV 75 W) was used for ultraviolet irradiation and a tungsten lamp (100 V 200 W) for visible light irradiation.

The intensity of the UV radiation source at the film surface in the cell was accurately determined to be 1.48×10^{15} quanta/cm² sec. by uranyl oxalate actinometry.[9]

The whole set of the apparatus was placed in a draft chamber which was so well aerated that it kept the light source cool during the irradiation. The ambient temperature remained 15–21°C although it was not controlled.

Permeation Measurements. An improved permeation apparatus was designed and built in our laboratory based on the high-vacuum technique originally introduced by Barrer.[10] The details have been described elsewhere.[11] Permeation measurements were carried out with helium, carbon dioxide, and oxygen gases at 20°C. The permeation and diffusion experiments of chlorine gas were made with the automatic recording equipment, which follows the increase in height of the mercury column in the mercury manometer with a photoelectric tube. The pressures of the gas on the high-pressure side and the low-pressure side of the apparatus were maintained at approximately 1 atm and less than 4 mm Hg, respectively. The gas permeability P was calculated from the expression

$$P = (\Delta p/\Delta t)\,(273\ V.l)/760\,(273 + t)p.A$$

where $\Delta p/\Delta t$ is the measured pressure rise per unit of time. V and t are the volume and temperature, respectively, of the measuring chamber, p is the pressure of the test gas over the film, A is the area of the film exposed to the test gas, and l is the thickness of the film.

The measurement of water vapor permeation was made according to the JIS Z0208 procedure of the Japanese Standards for Testing and Materials, which is the counterpart of the U.S. ASTM E96-63T.

Chlorine Content. The chlorine contents of the polymers were determined by Semimicro Carius[12] or by elemental analysis with the Shimazu Organic Microanalyser UM-3.

Contact Angle. A telescopic goniometer was used for the measurement of contact angle of a sessile drop of water with the polyolefin and photo-

chlorinated polyolefin surfaces. The measurements were made at a temperature of 20°C.

Electron Microscope. Film surfaces of polyethylene were examined electromicroscopically before and after photochlorination. A Hitachi electron microscope was used to photograph the polymer surfaces by the two-step replica method (methylcellulose and carbon) and Pt–Pd shadowing.

Infrared Spectra. Infrared spectra of the samples were obtained on a Hitachi EP1-G2 infrared spectrometer.

Mechanical Properties. Stress-strain properties of photochlorinated polyethylene were measured on an Instron tensile testing instrument (TM-M). Runs were made on 30- × 10-mm samples at a speed of 10 cm/min.

Reaction of Photochlorinated Polyethylene with Sodium Dithiocarbamate. The chlorinated polyethylene film (4.0 g) with 18.0% chlorine content (by the irradiation cell) was immersed in 50 ml dimethylformamide solution (0.02 mole-%) of sodium N,N-dimethyldithiocarbamate or sodium N-methyl-N-carboxymethyldithiocarbamate. The reaction was carried out for 48 hr in a constant-temperature bath of 50°C under an atmosphere of nitrogen. The films were washed with water and dried under vacuum prior to determining the degree of substitution. The degree of substitution was calculated from the nitrogen content.

RESULTS AND DISCUSSION

Effect of Photochlorination on Permeation. The effect of photochlorination on gas permeation of polyethylene (PE), polypropylene (PP), and poly-
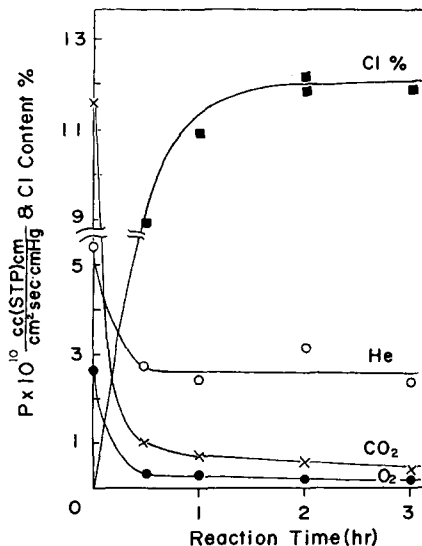

Fig. 2. Gas permeability and chlorine content of potochlorinated polyethylene as a function of reaction time: (■) chlorine content. Gas permeability constants at 20°C to: (O) helium; (×) carbon dioxide; (●) oxygen.
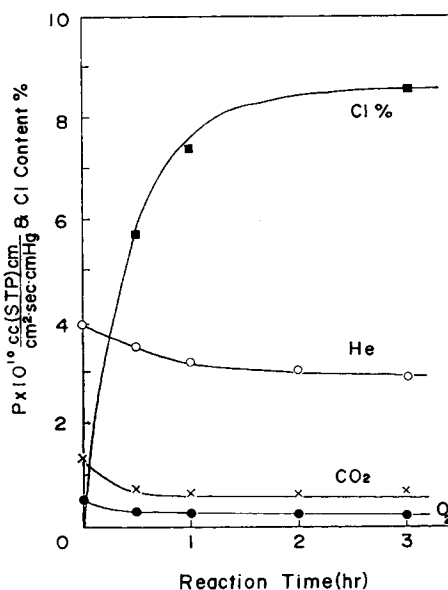
Fig. 3. Gas permeability and chlorine content of photochlorinated polypropylene as a function of reaction time: (■) chlorine content. Gas permeability constants at 20°C to: (O) helium; (X) carbon dioxide; (●) oxygen.

styrene (PSt) to helium, carbon dioxide, and oxygen is shown in Figures 2, 3, and 4. The chlorine content increases with increase in reaction time in all instances; each curve has the same tendency to rise markedly at first up to about 1 hr and then to level off. The plateau value of chlorine content increases in the order of PSt, PP, and PE (PSt 6.5%, PP 8.5%, PE 12.0%). This may suggest that steric effects of side chains in PSt and PP hinder the reaction; the diffusion of chlorine gas cannot be considered a limiting factor because the permeability constant inversely decreases in this order. On the other hand, gas permeation rapidly decreases in the short reaction time and reaches a plateau value within 0.5 hr in all these figures. Apparently, introduction of a polar atom, chlorine, into the carbon chain restricts the segmental chain mobility leading to the reduction of gas permeation. Photochlorination lowered oxygen permeation PE, PP, and PSt to $^1/_{21}$, $^1/_2$, and $^1/_2$ the original values, respectively. It is apparently clear in Table I that, provided that PS is substantially photochlorinated to the same extent as poly(vinyl chloride) (PVC), the oxygen gas permeation should be lowered to $^1/_{25}$ of the original value of PE.

From the practical standpoint, it can be said that photochlorination is a very useful and powerful tool for reducing gas permeation of PE. In PE film, a significant decrease in gas permeation was realized even with low substitution of chlorine.

The distinction between these polyolefin films in the reduction of permeability is too large to be explained only by the difference in chlorine content.

TABLE I
Gas Permeability Constant (P) of Polyolefin
and Poly(vinyl Chloride) Films

Film	$P \times 10^{10}$, cc(STP)cm/cm² sec cm Hg (20°C)		
	CO_2	O_2	N_2
Polyethylene	11.6	2.68	0.88
Polypropylene	1.31	0.45	0.25
Polystyrene	10.0	2.01	0.34
Poly(vinyl chloride)[a]	0.51	0.11	0.033

[a] Poly(vinyl chloride) film was made by casting at room temperature from a tetrahydrofuran solution of PVC ($DP \simeq 600$) on glass plates floating on mercury.
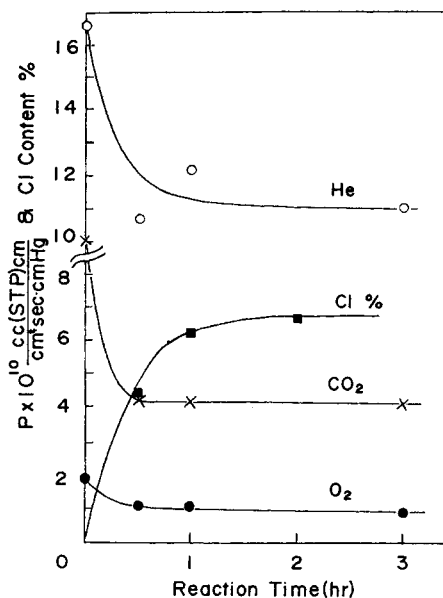

Fig. 4. Gas permeability and chlorine content of photochlorinated polystyrene as a function of reaction time: (■) chlorine content. Gas permeability constants at 20°C to: (O) helium; (×) carbon dioxide; (●) oxygen.

It can be interpreted that side chains such as methyl and phenyl groups in PP and PSt depress the polar effect of chlorine that restricts the segmental chain mobility.

Permeation measurements of PE and photochlorinated PE (PE–Cl) film were made also with chlorine gas at room temperature, as given in Table II. It was found that the permeability constant of chlorine was rather large with regard to the molecular size. The diffusion and solubility constants were determined by the time lag method.[13] The high permeation constant can be attributed to high solubility of chlorine gas into PE. Photochlorination reduced the permeation of chlorine remarkably, down to $1/100$, and presumably lowered the diffusion at the same ratio. This allowed us to

TABLE II
Permeation and Diffusion Constants of Polyethylene to Chlorine Gas at 20°C

| | Permeation constant $\times 10^{10}$, cc(STP)cm/cm^2/sec cm Hg | | Diffusion constant $\times 10^8$, cm^2/sec | Solubility constant $\times 10^2$, cc(STP)/sec |
	PE-1	PE-2	PE-1	PE-1
Original PE	54.0	27.9	3.73	1.45
Chlorinated PE		0.290[a]		
		0.153[b]		

[a] Photochlorinated in diffusion cell at a distance of 12 cm for 1 hr.
[b] Photochlorinated in diffusion cell at a distance of 7 cm for 2 hr.

TABLE III
Comparison of Gas Permeation of the PE Films Photochlorinated
in Diffusion and Irradiation Cells[a]

| Cell | Cl % | $P \times 10^{10}$, cc(STP)cm/cm^2 sec cm Hg (20°C) | | |
		He	CO$_2$	O$_2$
Diffusion cell	12.2	2.97	0.541	0.163
Irradidation cell	15.9	2.16	0.340	0.120

[a] Both films were photochlorinated for 2 hr in the respective cells.

presume that the diffusion of chlorine gas was a rate-determining step in the photochlorination. Consequently, it can be concluded that the photochlorination takes place only on the film surface.

Photochlorination of PE was carried out both in diffusion and irradiation cells. The PE film was in contact with chlorine gas at both sides of the film in the latter cell. In the former cell, the film was allowed to stand in contact with chlorine gas at one side and was kept degassed through the other side during the light irradiation, whereas incident light came from only one side. A similar curve to that shown in Figure 2 (diffusion cell) was obtained for the PE film photochlorinated in the irradiation cell. However, the chlorine content of the film done in the irradiation cell was higher than that in the diffusion cell. Consequently, gas permeation of the former was lower than that of the latter, as shown in Table III.

In an effort to elucidate the difference of these photochlorination mechanisms, rather thick polyethylene films (Sholex film, 160 μ in thickness) were photochlorinated in both cells and were kept for several hours under osmium tetraoxide vapor at room temperature.

As a result, it was found that the film photochlorinated in the irradiation cell remained almost intact (slight grey) and that the film photochlorinated in the diffusion cell was dyed fairly dark, whereas the control film was dyed deep black. This can be interpreted in the following way: the vapor of osmium tetraoxide permeates into the untreated PE and accumulates on it as osmium metal by reduction, but the chlorinated layer of polyethylene prevents the penetration of OsO$_4$ vapor into the film. Thus, the PE film

TABLE IV
Variation of Contact Angle of Water at 20°C with Photochlorination

Reaction time, hr	Contact angle of water drop at 20°C, degrees			
	PE	PP	PSt	PVC
0	94	93	94	68
0.5	73		86	
1	67		81	
1.5	68			
2	69			
3	68	77	79	

photochlorinated in the diffusion cell reacted only on the high-pressure side that faced the light source, and the other side was scarcely reacted. In the irradiation cell, both sides of the PE film reacted, although one side was not irradiated with light. In another experiment it was confirmed that the back film irradiated in layers was also photochlorinated, even though it was not exposed to light.

It can therefore be presumed that photochlorination is initated by a chlorine radical originally produced by light irradiation, just as in the photochlorination of paraffins[14] as given below:

$$Cl_2 \xrightleftharpoons{h\nu} 2\ Cl\cdot$$

$$Cl\cdot + PH \rightarrow P\cdot + HCl$$

$$(polymer)$$

$$P\cdot + Cl_2 \rightarrow PCl + Cl\cdot$$
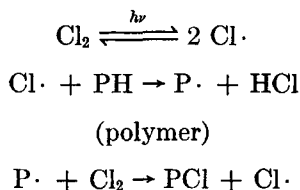
Wettability. The effect of modification of the polyolefin film surfaces by photochlorination is given by the wettabilities shown in Table IV. In all instances the contact angle of water decreased with increase in reaction time. It should be noted that the θ-values for PE chlorinated for more than 1 hr are comparable to that of PVC. Taken on their own, these results suggest that the surface of photochlorinated PE films (over 0.5 hr) was chlorinated to the same extent (the same chlorine content) as PVC, regardless of the arrangement of chlorine atoms in the polymer chain.

Electron Microscope Studies. Figure 5 shows that surface morphology of PE changed with photochlorination. Photochlorination appears to cause detectable roughness on the surface. It can easily be seen that the surface faced with chlorine gas of PE film chlorinated in the diffusion cell is remarkably rugged and that the back surface of the downstream side is little changed. On the other hand, there seems to be no difference between the pictures of the front surface and the back surface of PE films chlorinated in the irradiation cell, although both surfaces were roughened. These observations all coincide with the facts considered in the experiment with osmium tetraoxide vapor. The roughened surface appeared more wettable than the original. This is well illustrated by the black blots seen in picture B, which

are unremoved methylcellulose used as backing material for preparing carbon replicas.

Effect of Irradiation Distance. In Figure 6, the permeability constant of chlorinated polyethylene (reaction time 1 hr) is plotted against the distance
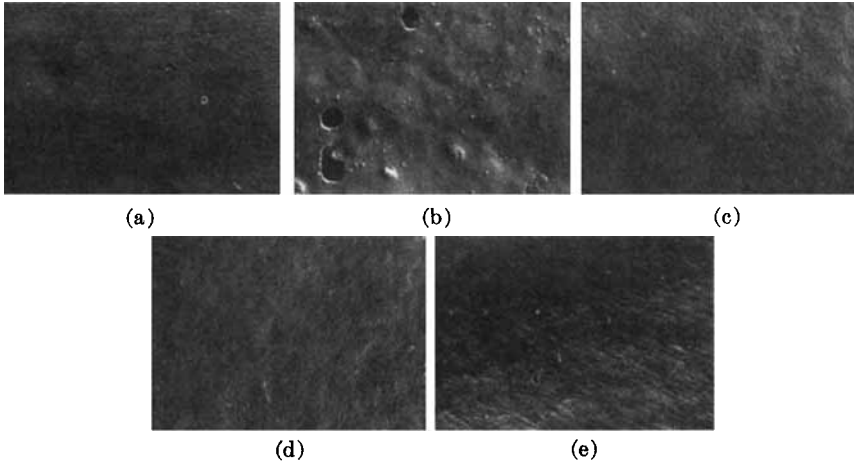

(a) (b) (c)

(d) (e)

Fig. 5. Electron-microscopic photograph of polyethylene and photochlorinated polyethylene surface (magnification ×3000 for A, B, and C; ×2000 for D and E): (A) untreated control PE; (B) front surface facing the light source; (C) back surface of polyethylene photochlorinated at a distance of 12 cm in diffusion cell for 5 hr; (D) front surface and (E) back surface of polyethylene photochlorinated at a distance of 7 cm in irradiation cell for 3 hr.
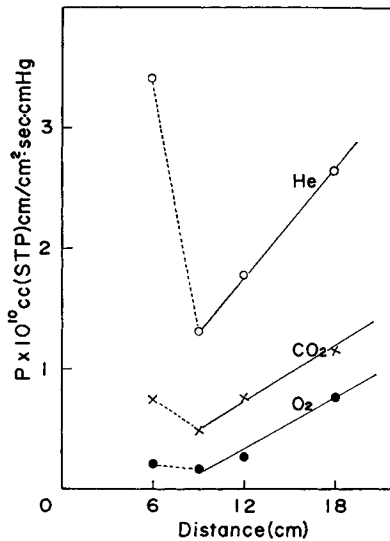

Fig. 6. Effect of distance between light source and sample film on permeability of photochlorinated polyethylene. Gas permeability constants at 20°C to: (O) helium; (×) carbon dioxide; (●) oxygen.
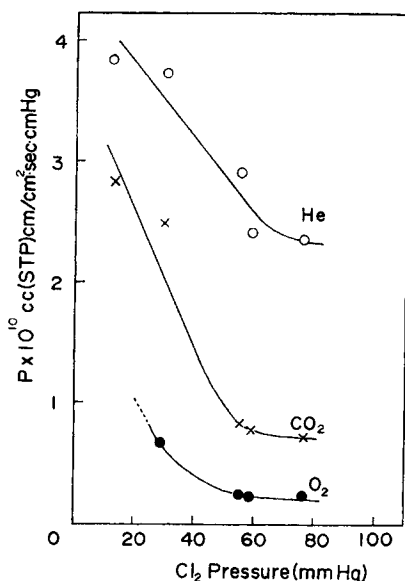
Figure 7. Effect of chlorine pressure on permeability of photochlorinated polyethylene. Gas permeability constants at 20°C to: (O) helium; (X) carbon dioxide; (●) oxygen.

between the surface of sample film and the center of the light source. It can be seen in the figure that permeability constants to all gases are proportional to the distance for distances longer than 8 cm. In distances of less than 8 cm, where the lamp tube almost came in contact with the window of the cell, chain scission or decrease in crystallinity might have been caused by the heat of the lamp, as suggested by Luttinger et al.[8] While not given here, similar results were obtained for 0.5-hr photochlorinated PE.

Effect of Chlorine Pressure. Gas permeation was measured under various chlorine pressures, with the results shown in Figure 7. It is clear that the permeation decreases proportionally to the chlorine pressure in the lower-pressure region and levels off in the high-pressure region around 1 atm, indicating that the chlorine content also comes to a plateau value. This is another proof for the fact that the diffusion of chlorine gas is a rate-determining step in the reaction.

Effect of Thickness of Chlorine Gas Phase. To elucidate the effect of thickness of the chlorine gas phase, a photochlorination experiment was made changing the position of the film sample to be irradiated in the cell. The oxygen permeability of PE photochlorinated in the irradiation cell at a distance of 7 cm for 1 hr was 0.151 cc(STP)cm/cm^2 sec cm Hg, in comparison with 0.0999 (in the same units) for PE photochlorinated in the irradiation cell at a distance of 12 cm for the same time of 1 hr. From this finding, it can be seen that the thicker chlorine gas phase is more advantageous for photochlorination.

The results also support the assumption that photochlorination of PE is initiated not by a polyethylene radical but by a chlorine radical, as

TABLE V
Comparison of Gas Permeation Between Polyethylene Films
Photochlorinated by Ultraviolet and Visible Light

Light source	$P \times 10^{10}$, cc(STP)cm/cm^2 sec cm Hg·(20°C)		
	He	CO_2	O_2
UV	2.74	0.752	0.249
Visible light	2.26	1.03	0.316

TABLE VI
Effect of Crystallinity on the Reduction of Permeation by Photochlorination[a]

	$P \times 10^{10}$, cc(STP)cm/cm^2 sec cm Hg								
	50%[b]			63%[b]			81%[b]		
Permeant	PE	PE–Cl[c]	Ratio[e]	PE	PE–Cl	Ratio[e]	PE	PE–Cl[d]	Ratio[e]
He	5.40	3.34	0.62	4.22	3.71	0.88	2.66		
CO_2	11.6	1.97	0.17	8.43	1.22	0.14	5.15	0.672	0.13
O_2	2.68	0.435	0.16	1.84	0.349	0.18	1.21	0.216	0.18

[a] All the polyethylene films here were photochlorinated for 1 hr in an atmosphere of chlorine gas without being dried in the drying tubes.

[b] Degree of crystallinity.

[c] Cl content 8.61%.

[d] Cl content 5.44%.

[e] Ratio of permeability constant of chlorinated polyethylene to that of control polyethylene.

described above. For, if the reaction were carried out by a polymer radical, the thin gas phase would be favorable for producing polymer radicals by light irradiation because thick chlorine gas of yellowish green weakens light intensity.

Effect of Light Source. If photochlorination is initiated by a chlorine radical as described above, the reaction should take place by light irradiation of less than 5000 Å because the dissociation energy of the Cl–Cl bond correspond to 4929 Å light.[14] In fact, through the use of a tungsten lamp, similar results were obtained, as shown in Table V. Obviously this shows that photochlorination starts with the formation of a chlorine radical by light irradiation, as indicated before.

Effect of Crystallinity on Reduction of Permeation by Photochlorination. As shown in Table VI, higher-crystallized polyethylenes are found to be more difficult to be chlorinated heterogeneously with light irradiation. Evidently, this is another proof for the fact that the diffusion of chlorine gas into PE film is a step-determining factor in the photochlorination reaction. However, the ratio of decrease in permeation by chlorination is almost the same in films with different crystallinity. It seems likely that the chain-packing effect of the chlorine atom is multiplied by the crystalline structure, apparently because in the crystalline PE chlorination occurs more densely in the smaller amorphous region and then suppresses the gas

TABLE VII
Effect of Moisture on Photochlorination of Polyethylene Film

Permeant	P of PE–Cl[a] $\times 10^{10}$, cc(STP)cm/cm^2 sec cm Hg (20°C)	
	With undried gas	With dried gas
He	3.34	2.74
CO$_2$	1.97	0.752
O$_2$	0.435	0.249

[a] Photochlorinated in diffusion cell for 1 hr.

TABLE VIII
Mechanical Properties of Photochlorinated Polyethylene

Sample	Tensile strength, kg/cm^2	Elongation, %
PE	107 ± 15	580 ± 50
PE–Cl[a]	110 ± 15	400 ± 50

[a] Photochlorinated in diffusion cell for 2 hr.   The Cl content was 12.2%.

TABLE IX
Effect of Photochlorination on Water Vapor Permeation

Sample	Water vapor permeation rate, g/m$^2\cdot$24 hr (0.1 mm)			
	PE	PP	PSt	PVC
PE	6.61	1.83	38.2	13.9
PE–Cl	7.50[a]	1.72[b]	35.3[c]	

[a] Photochlorinated for 2 hr.
[b] Photochlorinated for 3 hr.
[c] Photochlorinated for 5 hr.

diffusion more efficiently than in the amorphous polymer.   X-Ray diffraction indicated that no appreciable change occurs in the crystallinity of polyethylene.

Effect of Moisture on Photochlorination.   In order to clarify the effect of moisture in chlorine gas on the photochlorination of polyethylene, the photochlorination reaction was carried out in an atmosphere of usually dried chlorine and of undried chlorine gas with and without drying tubes. The results of the permeation are given in Table VII.   Clearly, moisture plays a large inhibitary role in the photochlorination reaction.

Physical Properties.   The results of tensile strength, elongation, and water vapor permeation are shown in Tables VIII and IX.   As would be expected, photochlorinated PE film with a 12.2% chlorine content exhibits no appreciable change in tensile strength and vapor permeation, suggesting that no bulk chlorination occurs in the film.   However, the chlorinated film shows a somewhat shorter elongation than that of the control film.   It is worth noting that transport of water vapor did not deteriorate, although it had
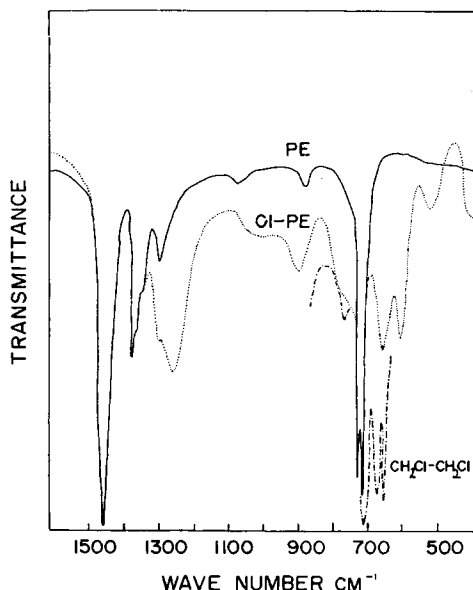
Fig. 8. Infrared spectra of polyethylene, photochlorinated polyethylene, and 1,2-dichloroethane: (———) polyethylene film; (- - -) photochlorinated polyethylene film (photochlorinated for 1 hr in diffusion cell); — · — ethylene dichloride (liquid film).

been predicted from the fact that PVC has a higher water vapor permeability than PE.

Infrared Spectra. Figure 8 shows the infrared spectra of the original PE, PE–Cl, and 1,2-dichloroethane. The changes caused by the chlorination are manifested by the appearance of two bands at 610 and 660 cm^{-1}, assigned to CCl- stretching mode, and a prominent increase in absorption at 1260 cm^{-1}, which is assigned to CH-deformation mode. So far, a few investigators have studied the molecular structure of chlorinated polyethylene by infrared spectroscopy[15,16] and by comparison of dipole moment.[17] They suggested that the chlorine atoms were substituted as —CH—CCl—, —CCl$_2$—, —CHCl—CHCl—, or —CHCl—CHCl$_2$— groups in substantially chlorinated polyethylene according to the extent of the chlorine content. In the present experiment, no band was observed at 750 cm^{-1}, which is found in the spectrum of poly(vinylidene chloride). The bands at 610 cm^{-1} correspond to the secondary CCl stretching mode of —CH$_2$—CHCl—CH$_2$—. The band which appears at 660 cm^{-1} is assigned to the mode of the deformed configuration of carbon chain or to —CHCl—CHCl— units in the trans position.[16] The characteristic bands of 1,2-dichloroethane appeared as a doublet in the same region of 660 and 670 cm^{-1}, and the —CCl absorption emerged at 770 cm^{-1}, as represented by a dashed line in Figure 8. The other characteristic absorptions of poly(vinyl chloride) can be seen at 920, 1060, and 1270 cm^{-1}. However, no absorption is detectable at 1196 cm^{-1}, presumably because this specific absorption of PVC is too weak. As
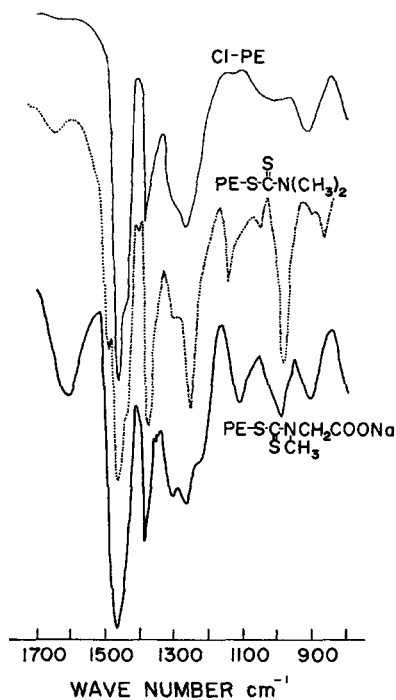
Fig. 9. Infrared spectra of polyethylene film treated with sodium dithiocarbamate.

a whole, the infrared spectra of the photochlorinated polyethylene are more closely analogous to those of poly(vinyl chloride) than poly(vinylidene chloride), except for the absorption at 530 cm^{-1}, which cannot be identified. Fredericks[18] confirmed that the β-, γ-, and δ-positions are more reactive than the α-position in chlorination of n-butyl chloride. These observations made us to conclude that polyethylene film is chlorinated in the form of —CH$_2$— CHCl— (vinyl chloride type) and —CHCl—CHCl— (1,2-dichloroethane type), and that hardly any —CH—CCl$_2$— units (vinylidene chloride type) are formed.

In the infrared spectra of polystyrene and the photochlorinated product, the bands at 2920, 2850, and 1370 cm^{-1} progressively decreased in intensity on substitution, as Haldon and Hay[7] have reported. They showed that the reduction in intensity at 1370 cm^{-1} was consistent with the substitution occurring on the α-position. Teyssie and Smets[19] have reported that chain substitution by chlorine on the α-position is favored by high temperature and low chlorine concentration. Since the specific band assigned to α-position substitution diminished without corresponding marked decrease in the methylene band at 1450 cm^{-1}, photochlorination of polystyrene film appeared to occur exclusively on the α-position.

The infrared spectrum of photochlorinated polypropylene was not distinguishable from that of polypropylene, except for a week absorption near 700 cm^{-1}.

Modified Polyethylene Film Obtained by Reaction with Sodium Dithio-carbamate. As shown in Figure 9, the infrared spectra of the photochlorinated polyethylene film reacted with sodium N,N-dimethyldithiocarbamate (PE–DMD) and sodium N-methyl-N-carboxymethyldithiocarbamate (PE–SDC) exhibit similar characteristic peaks as had been reported in the same reaction of poly(vinyl chloride).[20–22] The bands that appeared in the spectra can be assigned as follows:
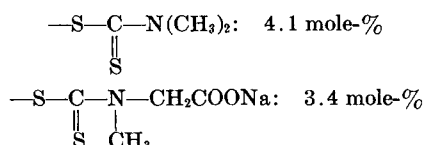
PE–DMD:

$$3200 \text{ cm}^{-1} \quad \nu_{N-H}$$
$$1500 \text{ cm}^{-1} \quad \nu_{C-N} \ (N-C(=S))$$
$$1330 \text{ cm}^{-1} \quad \nu_{C-N} \ (C-N(-C=S))$$
$$1170 \text{ cm}^{-1} \quad \nu_{C=S}$$
$$930 \text{ cm}^{-1} \quad \nu_{C-S}$$

PE–SDC:

$$1600 \text{ cm}^{-1} \quad \nu_{C=O}$$
$$1380 \text{ cm}^{-1} \quad \nu_{C-N} \quad (C-N(-C=S), \quad \nu_{COO^-}$$
$$1200 \text{ cm}^{-1} \quad \nu_{C=S}$$
$$990 \text{ cm}^{-1} \quad \nu_{C-S}$$

The band, which appeared at 1480 cm^{-1} ($\nu_{C-N}(N-C(=S))$) in the spectrum was not appreciable because of overlapping. bamate, of PVC reacted with sodium N-methyl-N-carboxymethyldithiocar-trum

The elemental analysis shows that the nitrogen content of PE–DMD and PE–SDC is 0.48% and 0.24%, respectively. The molar percentages of the functional groups were calculated from these values:

$$-S-\underset{\underset{S}{\|}}{C}-N(CH_3)_2: \quad 4.1 \text{ mole-}\%$$

$$-S-\underset{\underset{S}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-CH_2COONa: \quad 3.4 \text{ mole-}\%$$

On the bases of these data, it can be assumed that the reactions proceed by the following mechanism:

$$-CH_2-CH_2-CH_2-CH_2- \xrightarrow[\text{Cl}_2]{h\nu} -CHCl-CH_2-CHCl-CHCl-$$

$$(-CH_2-)_{91.4}(-CHCl-)_{8.6} + NaS-\underset{\underset{S}{\|}}{C}-N(CH_3)_2 \rightarrow$$

$$(-CH_2-)_{91.4}(-CHCl)_{8.0}(-CH-)_{0.6}$$
$$\underset{\underset{S}{\|}}{S-C}-N(CH_3)_2$$

$$(-CH_2-)_{91.4}(-CHCl-)_{8.6} + NaS-\underset{\underset{S}{\|}}{C}-\underset{\diagdown CH_3}{N}-CH_2COONa \rightarrow$$

$$(-CH_2-)_{91.4}(-CHCl-)_{8.3}(-CH-)_{0.3}$$
$$S-\underset{\underset{S}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-CH_2COONa$$
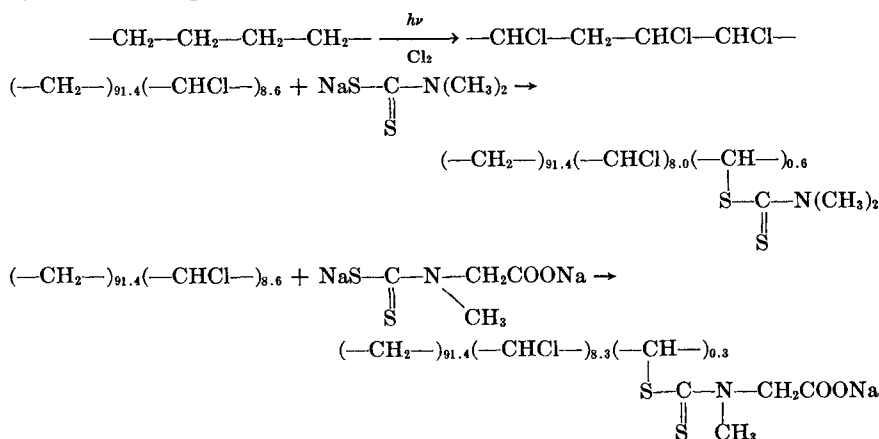
The functional side chains of PE–DMD and PE–SDC are already known to become insoluble by irradiation of light.[20–22]   These modified polyethylenes may be promising for use as specific package membranes.

In summary, surface chlorinated polyethylene, polypropylene, and polystyrene membranes were obtained by photochlorination of polyolefin films.   The photochlorination of these films remarkably modified their wettability and permeability.   The oxygen permeation of polyethylene, polypropylene, and polystyrene were reduced to $1/21$, $1/2$, and $1/2$ of those of the original films, respectively.   Moreover, the chlorinated polyethylene was allowed to react with sodium dithiocarbamate and turned out to be a membrane with a specific photocrosslinking group on the surface.   These unique properties promise to make the films useful membranes of great utility for packaging.

References

1. R. A. V. Raff and J. B. Allison, in *High Polymer*, Vol, XI, Interscience, New York, 1956, pp. 133 and 358.

2. A. Renfrew and P. Morgan, Eds., *Technology and Uses of Ethylene Polymers*, Interscience, New York, 1957, Chap. 14.

3. S. Kambara and T. Ohshika, *Kogyo Kagaku Zasshi*, **62**, 1781 (1959).

4. T. W. Campbell and J. Lyman, *J. Polym. Sci.*, **55**, 169 (1961).

5. C. N. Burnell and R. H. Parry, *Appl. Polym. Symposia*, **No. 11**, 95 (1969).

6. Ph. Tyssie, M. C. de Wilde, and G. Smets, *J. Polym. Sci.*, **16**, 429 (1955).

7. R. A. Haldon and J. Hay, *J. Polym. Sci. A-1*, **5**, 2297 (1967).

8. M. Luttinger, C. W. Cooper, and G. P. Hungerford, *J. Polym. Sci. C*, **24**, 257 (1968).

9. D. H. Grant and N. Grassie, *Trans. Faraday Soc.*, **55**, 1042 (1959).

10. R. M. Barrer, *Diffusion In and Through Solids*, Oxford University Press, Cambridge, 1951.

11. T. Nakagawa, *Kogyo Kagaku Zasshi*, **72**, 723 (1959); *idem.*, *Kogyo Gijitsu*, **6**, 20 (1965).

12. J. Arima, *Organic Analysis*, Iwanami, Tokyo, 1951, p. 165.

13. R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628, 644 (1939).

14. Y. Ogawa and Y. Izawa, *Photoorganic Reaction*, Asakura, Tokyo, 1967, Chap. 2.

15. H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 254 (1945).

16. K. Nambu, *J. Appl. Polym. Sci.* **4**, 69 (1960).

17. W. G. Oakes and R. B. Richards, *Trans. Faraday Soc.*, **42A**, 197 (1946).

18. P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

19. P. Teyssie and G. Smets, *Makromol. Chem.*, **46**, 187 (1954).

20. M. Okawara, K. Morishita, and E. Imoto, *Kogyo Kagaku Zasshi*, **69**, 761 (1966).

21. T. Nakagawa and M. Okawara, *Kogyo Kagaku Zasshi*, **71**, 2076 (1968).

22. T. Nakagawa, Y. Taniguchi, and M. Okawara, *Kogyo Kagaku Zasshi*, **70**, 2382 (1967).