Photocrosslinking of Chlorinated Polydimethylsiloxanes

HIROSHI INOUE and SHIGEMI KOHAMA, *Osaka Municipal Technical Research Institute, 6-50, 1-Chome, Morinomiya, Joto-ku, Osaka 536, Japan*

Synopsis

Photocrosslinking behavior of chlorinated polydimethylsiloxanes (C-PDMS) has been studied. It was found that the viscous C-PDMS were readily crosslinked to form the rubberlike materials on irradiation from a high pressure mercury lamp. The crosslinking mechanism was proposed on the basis of infrared spectroscopy. It was suggested that the photolysis of the carbon—chlorine bond induced by the ultraviolet irradiation is a primary step for crosslinking, and is followed by mutual combination of $SiCH_2\cdot$ radicals, eventually, to form the crosslinked C-PDMS. The effect of halogens and atmosphere on the crosslinking was also discussed.

INTRODUCTION

Polysiloxanes are widely employed as protective coatings for outdoor uses because of remarkable resistance to ultraviolet (UV) exposure. However, several studies have been made which indicate that the UV irradiation promotes crosslinking in the polysiloxane chains, but is less efficient for production of crosslinked polysiloxanes.[1-3]

Organic halides containing chlorine, bromine, or iodine are well known to dissociate at carbon—halogen bonds by photoabsorption, followed by complex reactions of resulting radicals.[4] Similarly, in the polymer field, coloring and deterioration of poly(vinyl chloride) and poly(vinylidene chloride) upon outdoor exposure are typical examples of this phenomena. In addition, some other chlorine-containing polymers were reported to crosslink with not only deep UV light, but also electron beam and X-ray exposure, suggesting as promising candidates for high sensitive negative resists.[5-8] Therefore, the introduction of chloromethyl groups into the side chain of polydimethylsiloxane (abbreviated as PDMS, hereafter) is expected to improve the crosslinking sensitivity.

In this work, chlorine-containing polysiloxanes, i.e., chlorinated polydimethylsiloxanes (C-PDMS), were examined for photocrosslinking to improve sensitivity. The crosslinking mechanism was also discussed on the basis of infrared (IR) spectroscopic analysis.

EXPERIMENTAL

Materials

Polydimethylsiloxane used here was a commercial product, KE-76 of Shin-Etsu Chemical Industry (1,000,000 cs of viscosity) without any further purification. Chloromethylheptamethylcyclotetrasiloxane (CHCS) was pre-

Journal of Applied Polymer Science, Vol. 32, 3853–3862 (1986)
CCC 0021-8995/86/033853-10$04.00

pared according to the procedure of Krible and Elliot.[9] The other reagents and solvents were used after recrystallization or distillation.

Preparation of C-PDMS

Photochlorination of PDMS. In a 500 mL photochemical reaction flask, a given amount of PDMS was dissolved in CCl_4 in ca. 10% concentration by stirring magnetically. The light source (100 W high pressure mercury lamp, Eikosha PIH-100) was vertically inserted into the flask attached with a gas inlet and a condenser. Dry nitrogen gas was introduced through the gas inlet for 10 or more minutes to substitute the atmosphere in the flask with nitrogen. The UV light was then irradiated with introduction of dry chlorine gas at room temperature. The solution turned yellow during the reaction. After ca. 1 h, nitrogen gas was again introduced to sweep the residual chlorine and hydrogen chloride. The solvent was removed by means of vacuum evaporator. The concentrated C-PDMS was washed by methanol several times. Finally, the C-PDMS was dried *in vacuo* at 45°C for 6 h.

Peroxide-Catalyzed Chlorination of PDMS. Ca. 10% CCl_4 solution of PDMS was admitted into a 1-L four-necked flask attached with a stirrer, a gas inlet, a dropping funnel, and a condenser. The atmosphere in the flask was substituted with nitrogen gas by bubbling through a gas inlet. Then chlorine gas was slowly admitted into the flask adjusted at 90°C with stirring at 500 rpm. The benzoyl peroxide solution (2 mol % based on the dimethylsiloxy group) was dropwise added over 5 h. After additional sirring for 1 h, the flask was swept with nitrogen, and the solution was concentrated by means of a vacuum evaporator. The resulting C-PDMS was washed with methanol several times and dried *in vacuo* at 45°C for 6 h.

Ring-Opening Polymerization of CHCS. Homo- and copolymerization of CHCS was described elsewhere.[10]

Synthesis of Bromine-Containing C-PDMS (Br–C-PDMS). Br–C-PDMS was prepared by photobromination of PDMS catalyzed by chlorine gas using the same apparatus as that of C-PDMS. On irradiation of UV light, 3.0 g (0.019 mol) of bromine in 50 mL of CCl_4 was gradually dripped into 350 mL of CCl_4 solution containing 25.00 g of PDMS with introduction of chlorine gas over 1 h. After 75 min, the red-brown solution turned to yellow, and the irradiation was completed. The solution was repeatedly washed with dilute ammonia and water until neutral. Then the solution was vacuum-evaporated to concentrate it. The resulting Br–C-PDMS was separated by addition of a large amount of methanol and finally dried *in vacuo* at 45°C: yield 26.85 g; viscosity $[\eta] = 0.21$ dL/g; $BrCH_2$ content 4.1 mol %; $ClCH_2$ content 3.3 mol % (^1H-NMR).

Synthesis of Iodine-Containing C-PDMS (I–C-PDMS). I–C-PDMS was prepared by iodide substitution of C-PDMS. In a 200 mL three-necked round flask, 1.00 g of C-PDMS ($ClCH_2$ 5.3 mol %, $[\eta] = 0.59$ dL/g) was dissolved in 30 mL of THF. Then 0.34 g (2.1×10^{-3} mol) of KI and 0.44 g (1.4×10^{-3} mol) of tetra-*n*-butylammonium bromide in 20 mL of DMF was added to the C-PDMS solution. The substitution reaction was carried out at 60°C with stirring magnetically for 10 hr. The solution was evaporated to dryness. Then the residue was washed with methanol–water mixture several times, and finally with methanol. The polymer was dried *in vacuo* at 50°C. Yield 1.40 g; viscosity $[\eta] = 0.55$ dL/g; ICH_2 content 1.6 mol %, $ClCH_2$ content 3.8 mol % (^{1}H-NMR).

Photocrosslinking of C-PDMS

On a slide glass (JIS 1st grade, 76 × 26 × 1 mm), approximately, 0.2 g of the C-PDMS was coated as prepared or as solution (ca. 7.5 cm^2 of area and ca. 0.2 mm of thickness). The slide glass was placed horizontally in the 500 mL photochemical reaction flask described above. A 100 W high pressure mercury lamp was vertically mounted in the flask in the locus of 3 cm distance from the slide glass. The slide glass was then irradiated at 25°C in a stream of nitrogen or in air.

The slide glass was also irradiated in the locus of 10 cm distance from the same lamp in air.

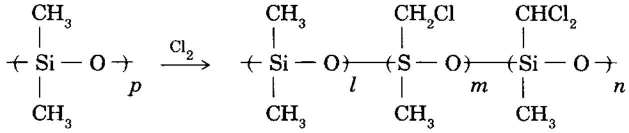
Analysis

The contents of $ClCH_2$, Cl_2CH, $BrCH_2$, and ICH_2 groups were determined by ^{1}H-NMR spectra using a Hitachi high resolution NMR spectrometer R-24 and a JEOL JNM FX90 FT NMR spectrometer in CCl_4 or $DCCl_3$ solution at room temperature. Infrared spectra of C-PDMS coated on NaCl or KBr plate were measured with a Shimadzu infrared spectrometer IR-435. Degree of crosslinking i.e., gel % in C-PDMS, was estimated by the extraction method using toluene. Intrinsic viscosity of polymers was measured at 25°C with a Ubbelohde viscometer using toluene as a solvent.

RESULTS AND DISCUSSION

Photocrosslinking of C-PDMS

Reyx and Guillaume reported that chlorination of PDMS using molecular chlorine formed not only chloromethyl groups, but also dichloromethyl groups even in relatively low chlorine (Cl) content.[11] In our study, also, both the photochlorination and peroxide-catalyzed chlorination were found to afford both of the chloromethyl and dichloromethyl groups not less than a certain Cl content, ca . 5 wt %, as shown in Figure 1. Relatively high reactivity of the chloromethyl group toward consecutive chlorination can be explained in terms of the α-chlorine effect[12]:



$$\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_p \xrightarrow{Cl_2} \left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_l\left(\underset{CH_3}{\overset{CH_2Cl}{S}}-O\right)_m\left(\underset{CH_3}{\overset{CHCl_2}{Si}}-O\right)_n$$

The C-PDMS samples obtained by photochlorination [C-PDMS(PC)] were examined for photocrosslinking. Figure 2 shows photocrosslinking behavior of C-PDMS(PC).

The viscous C-PDMS liquids changed to rubberlike materials on photoirradiation. The figure suggests that the crosslinking proceeds moderately,

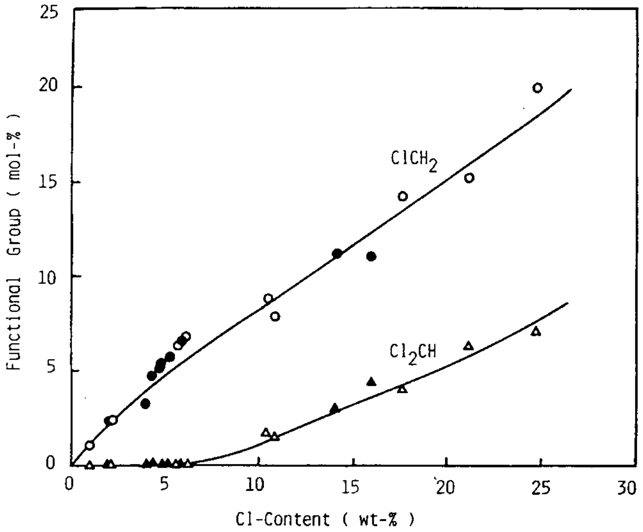


Fig. 1. ClCH$_2$ and Cl$_2$CH group contents vs. Cl contents in C-PDMS:

C-PDMS	ClCH$_2$	Cl$_2$CH
Photochlorination	(●)	(▲)
Peroxide-catalyzed chlorination	(○)	(△)

probably because of less sensitivity of C-PDMS in the UV region, and, in addition, of low electric power of the UV lamp.

It is probably that the dichloromethyl group enhances the crosslinking rate in preference to the chloromethyl group. The other experiments indicate that the crosslinking of C-PDMS is attributed not only to the dichloromethyl group, but also to the chloromethyl group. Figure 3 shows

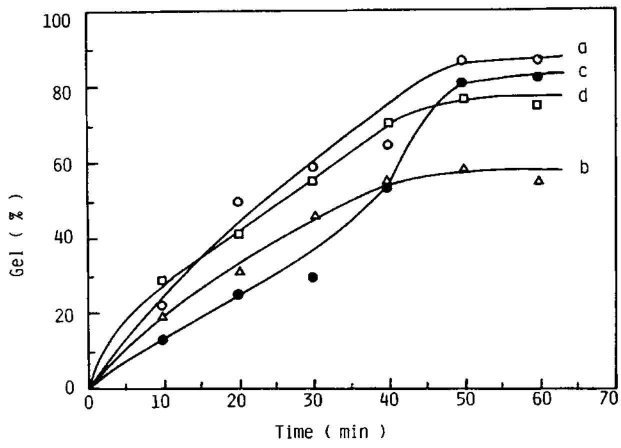


Fig. 2. Photocrosslinking of C-PDMS (PC) in air, light distance (10 cm): (a) (○) Cl 3.0 wt %, $[\eta] = 0.74$ dL/g; (b) (△) Cl 4.8 wt %, $[\eta] = 0.65$ dL/g; (c)(●) Cl 5.8 wt %, $[\eta] = 0.47$ dL/g; (d) (□) Cl 16.0 wt %, $[\eta] = 0.83$ dL/g.

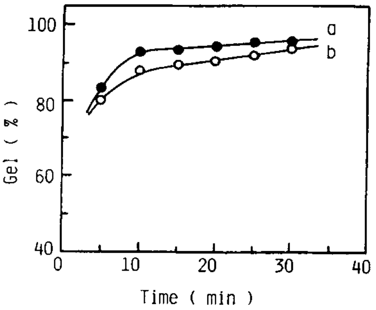


Fig. 3. Photocrosslinking of C-PDMS (ROP): $ClCH_2$ 6.6 mol %, $[\eta] = 0.39$ dL/g, light distance 3 cm; (○) in air; (●) in nitrogen.

photocrosslinking behavior of C-PDMS not having the dichloromethyl group, which was obtained by ring-opening polymerization (ROP).

As can be seen from Figure 3, the chloromethyl group on C-PDMS undoubtedly crosslinked both in nitrogen and air atmospheres, although the light distance was shortened to 3 cm to accelerate the photorection. Also, it was found that the crosslinking in air was slightly slower than in nitrogen atmosphere, probably because of oxidation before crosslinking which will be described later.

Figure 4 also shows photocrosslinking of C-PDMS (ROP) with some viscosity in nitrogen atmosphere. This behavior suggests that there was no significant difference in gel % within these ranges of chloromethyl content, independent of change in crosslink density.

Photocrosslinking behavior of C-PDMS containing bromine and iodine is shown in Figure 5. These kinds of C-PDMS were prepared by chlorine-catalyzed bromination of PDMS, and by iodide substitution of C-PDMS. Therefore, they contain mixed halogens, that is, copolymers. Br–C-PDMS was found to be more reactive toward photocrosslinking than the I–C-PDMS. This phenomena can be explained in terms of a combination of photodecomposition of carbon—halogen bonds and subsequent hydrogen abstraction with halogen atoms.

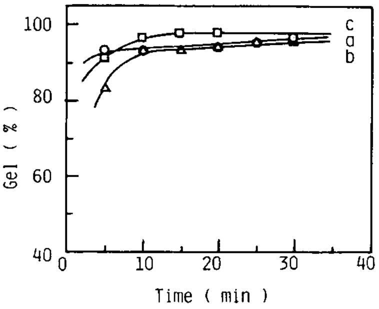


Fig. 4. Photocrosslinking of C-PDMS (ROP) in nitrogen, light distance 3 cm; (a) (○) $ClCH_2$ 3.3 mol %, $[\eta] = 1.12$ dL/g; (b) (△) $ClCH_2$ 6.6 mol %, $[\eta] = 0.39$ dL/g; (c) (□) $ClCH_2$ 12.5 mol %, $[\eta] = 0.82$ dL/g.

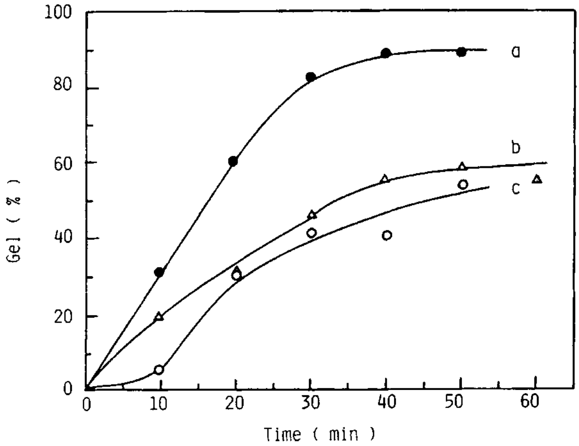


Fig. 5. Photocrosslinking of C-PDMS containing bromine and iodine in air, light distance 10 cm: (a) (●) Br–C-PDMS, $BrCH_2$ 4.1 mol %, $ClCH_2$ 3.3 mol %; (b) (△) C-PDMS, $ClCH_2$ 5.2 mol %; (c) (○) I–C-PDMS, ICH_2 1.6 mol %, $ClCH_2$ 3.8 mol %.

The UV absorption maximum based on $n-\sigma^*$ transition was observed at 266 nm for I–C-PDMS. On the contrary, the UV absorption maxima of C-PDMS and Br–C-PDMS was estimated to be 170 and 200 nm, respectively, based on poly(vinyl chloride) and poly(vinyl bromide).[13] Accordingly, the dissociation energy of carbon—halogen bonds, as suggested from UV excitation energy, decreases in the following order : C—Cl $>$ C—Br $>$ C—I. Contrary to this, ability for hydrogen abstraction with halogen atoms decreases in the following order : Cl $>$ Br $>$ I.[14] Consequently, the crosslinking fo C-PDMS is readily expected to proceed in the order, Br $>$ Cl $>$ I, as this reaction is a radical reaction process via photodissociation of the carbon—halogen bond, and hydrogen abstraction with halogen atoms, followed by coupling of polymer radicals.

Some additives were examined to improve photosensitivity of C-PDMS in crosslinking. However, photosensitizers, such as fluorescein, benzoin, benzophenone, Michler's ketone, benzoin ethyl ether, and anthracene in 10 mol % based on chloromethyl group were found to be less effective for crosslinking, probably because of less miscibility between C-PDMS and these types of sensitizers. Moreover, multifunctional vinyl compounds, such as divinylbenzene, polymethylvinylsiloxane, and ethylene–glycol diacrylate were employed as crosslinkers. Among these vinyl compounds, divinylbenzene was found to be somewhat effective compared with the others. In addition, *p*-hydroquinone exhibited a retarding effect on crosslinking.

Infrared (IR) Spectroscopic Study of Crosslinking

IR spectroscopy is useful to analyze the chemical structural change of C-PDMS during the photoreaction. Figures 6(a) and 6(b) show IR spectra of C-PDMS (ROP) and its photocrosslinked one made in nitrogen and air atmosphere, respectively. It is noted that both the IR spectra of crosslinked C-PDMS exhibit decreased C—Cl stretching absorption at 645 cm^{-1} (P_H type) and a trace of Si—CH_2CH_2—Si absorption at 1130 cm^{-1} with irradiation, indicating a decrease of the C—Cl bond and formation of the Si—CH_2CH_2—Si bond.[2,15-18]

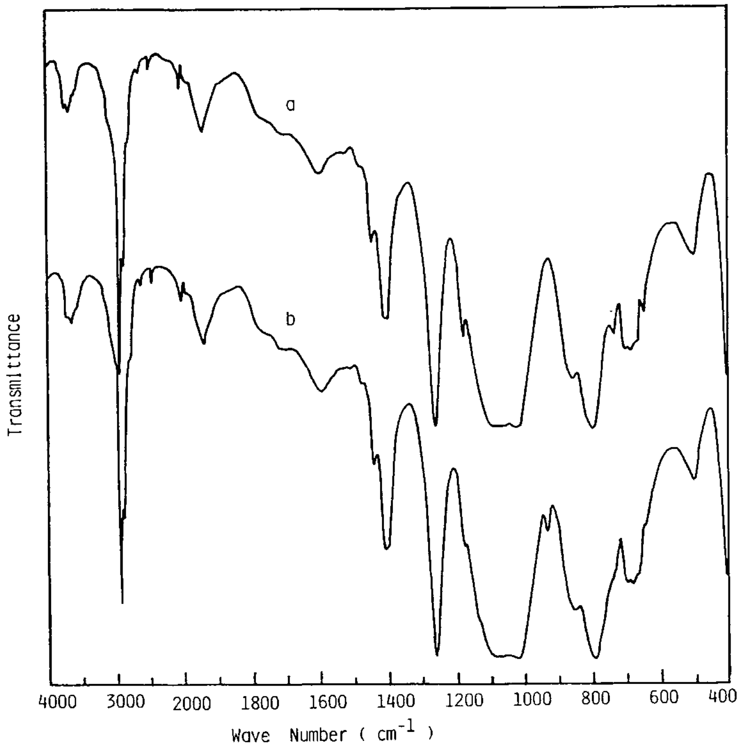


Fig. 6(a). IR spectra of C-PDMS (ROP) and its photocrosslinked one in nitrogen. C-PDMS (ROP): $ClCH_2$ 6.6 mol %, $[\eta]$ = 0.39 dL/g, on KBr plate; (a) before irradiation; (b) after irradiation for 30 min.

In these spectral measurements, the photocrosslinked C-PDMS samples were prepared under the conditions similar to those in Figure 3. Absorbance ratios in respective characteristic bands were plotted against irradiation time in Figures 7(a) and 7(b). In the IR spectra of photocrosslinked C-PDMS made in both atmospheres, an increase of another C—Cl absorption at 733 cm^{-1} (P_c type) was observed with a slight shift to higher wave number, with a decrease of C—Cl absorption at 645 cm^{-1}. These phenomena were not definitely described in terms of photodissociation of C—Cl bond, followed by disappearance of chlorine atom and coupling of silylmethyl radicals. Howevever, it is also noted that an absorption at 934 cm^{-1} (unidentified) and decrease in absorption at 1180 cm^{-1} ($ClCH_2$ group absorption) were observed simultaneously.[18]

In the air atmosphere, some other absorption bands caused by oxidation of radicals were perceived at 3550, 3400, 1743, 1722, and 1203 cm^{-1}, in addition to the absorption bands as same as those in the nitrogen atmosphere. The weak absorption at 3550 cm^{-1} is attributed to isolated hydroperoxide. On the other hand, the broad absorption band at 3400 cm^{-1} is assigned to that of hydrogen-bonded hydroperoxide and carboxylic acid.[19] The absorption band at 1722 cm^{-1}, therefore, corresponds to that of carboxylic acid. The formation of carbonyl group shows no apparent lag with regard to 3400 cm^{-1} absorption, suggesting concomittant formation of carboxylic acid derived from the hydroperoxide. The consumption of polymer

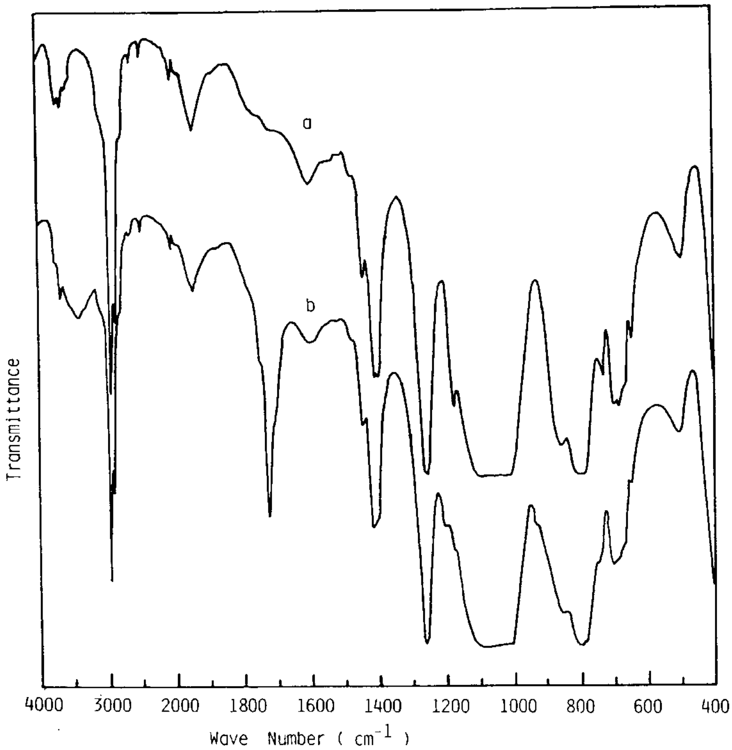


Fig. 6(b). IR spectra of C-PDMS (ROP) and its photocrosslinked one in air. C-PDMS (ROP); $ClCH_2$ 6.6 mol %, $[\eta]$ = 0.39 dL/g, on KBr plate; (a) before irradiation; (b) after irradiation for 30 min.

radicals due to oxidation seems to lower the crosslinking rate slightly, as seen from Figure 3.

Based on the findings described above, the following scheme is assumed for the crosslinking of C-PDMS in the presence of nitrogen and air:

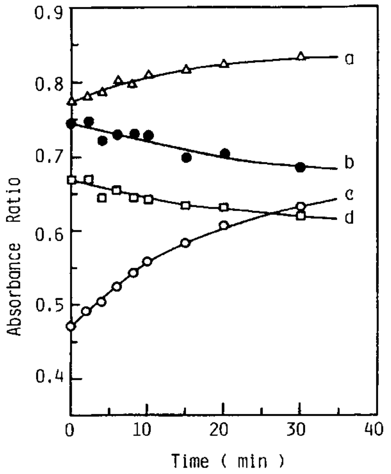


Fig. 7(a). Absorbance change during photocrosslinking of C-PDMS in nitrogen. C-PDMS (ROP): same sample as that of Figure 6(a); (a) (△) A_{733}/A_{2960}; (b) (●) A_{1180}/A_{2960}; (c) (○) A_{934}/A_{2960}; (d) (□) A_{645}/A_{2960}.

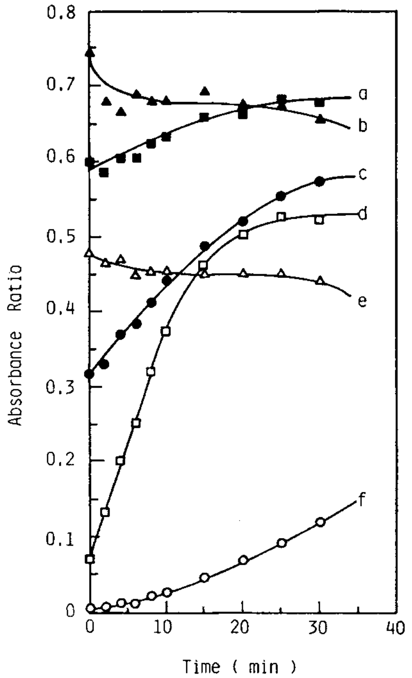
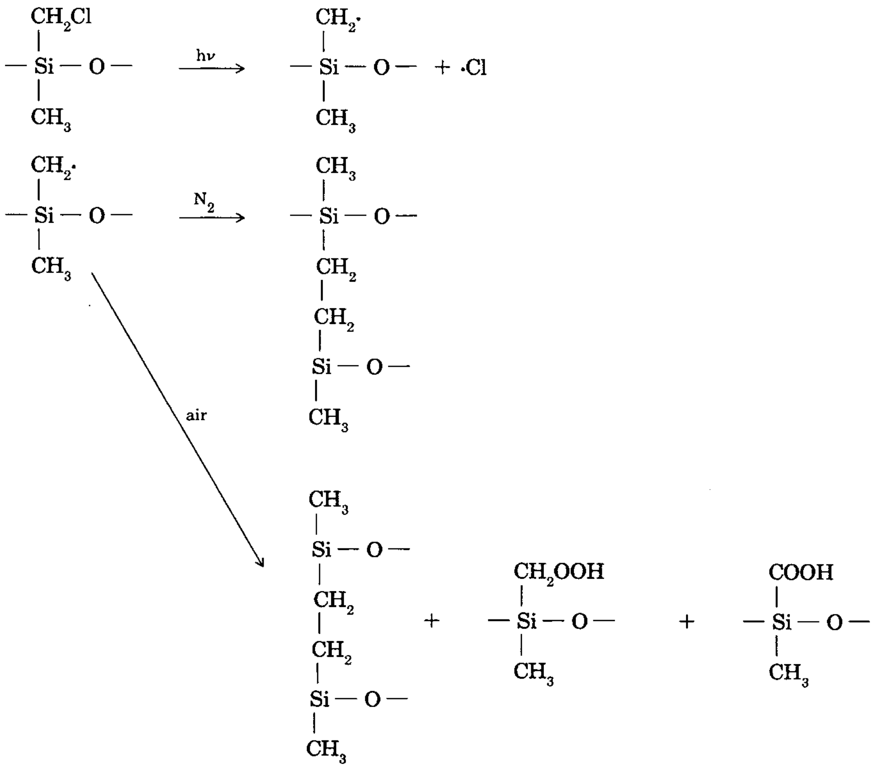


Fig. 7(b). Absorbance change during photocrosslinking of C-PDMS in air. C-PDMS (ROP): same sample as that of Figure 6(b); (a) (■) A_{733}/A_{2960}; (b) (▲) A_{1180}/A_{2960}; (c) (●) A_{934}/A_{2960}; (d) (□) A_{1722}/A_{2960}; (e) (△) A_{645}/A_{2960}; (f) (○) A_{3400}/A_{2960}.



(10)

The chlorine atom liberated in the photodissociation of C—Cl bond leads to the formation of acidic materials, such as hydrogen chloride and chlorine gas. It is already known that anhydrous hydrogen halides cause siloxane (Si—O—Si) bond cleavage readily with formation of silicon halide groups and silanol groups.[20] This process is followed by further reactions, a condensation of silanol groups to form siloxane bond with elimination of water, a reaction of silanol groups with hydrogen halide, a hydrolysis of silicon halide groups, and so on. However, the siloxane bond cleavage by anhydrous hydrogen chloride proceeds to a less extent than by the other hydrogen halides. In the present case, it is likely that a small amount of acidic gases liberated on UV irradiation of C-PDMS does not induce any significant siloxane bond cleavage, because of short time exposure under dry conditions.

The photocrosslinking behavior of C-PDMS shown above is expected to serve for a new type of photosensitive adhesive or coating, differing from those of well-known vinyl type photosensitive silicones.

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Received August 14, 1985
Accepted September 28, 1985