

Crosslinking of Poly(Vinyl Chloride) —I. Grafting of Vinyltri(alkoxy)silanes Using UV Irradiation

V. P. GUPTA,* G. R. BROWN

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec Canada H3A 2K6

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ABSTRACT: In a nitrogen atmosphere the UV irradiation of thin PVC films (ca. 0.1 mm thick) containing vinyltri(isopropoxy)silane results in a grafting reaction. By appropriate choice of conditions, dehydrochlorination can be kept to a minimum while up to 60% gel content is realized. Reaction of the pendent alkoxy groups, either with HCl byproduct or subsequent hydrolysis by exposure to water, results in the formation of Si–O–Si bonds that serve as chemical crosslinks. Although the addition of photosensitizers favors the grafting reactions at short exposure times, the ultimate level of crosslinking is greatly diminished by their presence. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1901–1906, 1998

Key words: poly(vinyl chloride); moisture crosslinking; vinyltri(alkoxy)silane; UV irradiation

INTRODUCTION

Crosslinking generally improves the physical properties of a polymer, particularly at elevated temperatures; for example, it results in improvements in dimensional stability, increased resistance to thermal deformation and stress cracking, and better resistance to solvents. The usual industrial method for crosslinking poly(vinyl chloride) is by exposure of the PVC construction containing crosslinking agents to high-energy radiation, such as an electron beam.^{1,2} Because such radiation is inherently nondiscriminatory, in addition to the crosslinking it tends to initiate degradation reactions in PVC that are exacerbated by any subsequent heat treatments, either in processing or in

application. Therefore, the utility of this method is limited to thin layers, because for thicker samples the surface regions are degraded before significant crosslinking occurs in the interior.

The conventional chemical method that is used for crosslinking polyethylene, which involves initiation with organic peroxides, has not been satisfactorily adapted for PVC because in this case degradation predominates over crosslinking.^{3–7}

Considerable success has been realized in crosslinking of polymers by modifying the macromolecules so as to incorporate active groups, such as organofunctional silanes, which, in the presence of water, produce a crosslinked product.⁸ After the end product has been fabricated the crosslinking is attained through hydrolysis that results in the formation of Si–O–Si bridges by the combination of two or more pendent silane groups, as shown in Scheme I below. To accelerate the crosslinking reaction a condensation catalyst is also employed.

There are several reports of attempts to produce PVC that can be crosslinked by the silane method. In 1969, the Dow Corning Co. patented a process of copolymerizing vinyl chloride with

Correspondence to: R. Brown, University of Northern British Columbia, Chemistry Programme, 3333 University Way, Prince George, B.C., Canada V2N 4Z9.

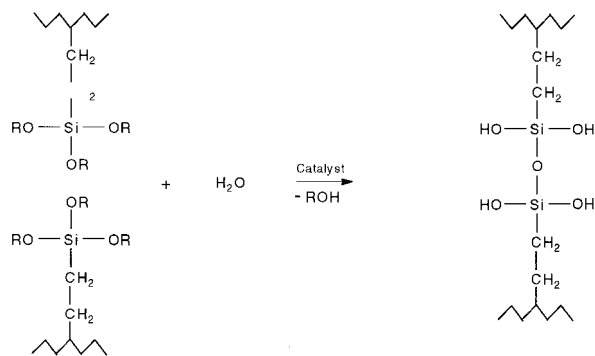
* Current address: Chemor, Inc., 236 St. Augustin, Montreal, Quebec, Canada H4C 2N6.

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Scheme 1.

vinyl silane.⁹ The same company obtained a second patent that describes a process in which the aminosilane is grafted to PVC by a reactive processing.¹⁰ Although there are several other references in the literature to the use of amino silane as a crosslinking agent, the process has not been exploited commercially to any extent.^{11–14} More recently, the use of mercaptosilanes as a grafting agent has also been reported.^{14–20} Kelnar and Schätz successfully crosslinked PVC with minimum degradation by using mercapto-alkoxy silanes.²¹

This article describes a procedure involving UV irradiation by which a vinyltri(alkoxy)silane is grafted to PVC under very mild conditions to keep the damage due to dehydrochlorination to a minimum. The effects of various changes in formulation, including photosensitizer addition, on gel formation are presented.

EXPERIMENTAL

Materials

A suspension grade PVC resin (Esso 366) of molecular weight $\overline{M}_n = 46,000$ and $\overline{M}_w = 83,000$ was used without further purification. In this study, vinyltri(isopropoxy)silane (VTIPS) (Petrarch Systems, United Chemical Technologies Inc.) was used as the grafting agent due to its low volatility (b.p.: 179–181°C).

Film Preparation

The PVC with VTIPS and an initiator were dissolved in reagent grade tetrahydrofuran (THF) and films (thickness ca. 0.110 to 0.120 mm) were obtained by solution casting onto a glass plate.

To remove the solvent the films were dried in a vacuum oven at room temperature for 5 days.

Crosslinking of the Silane-Grafted PVC

The films were irradiated for predetermined times with a UV lamp ($\lambda = 254$ nm) at room temperature under a nitrogen atmosphere. The source of the UV light was two fluorescent ultraviolet lamps (15 watts). During the UV exposure the temperature increased to 35°C.

To promote the crosslinking reaction of the alkoxysilane-grafted PVC, samples were heated in distilled water at 90°C for at least 72 h; separate studies demonstrated that this resulted in the maximum realizable gel formation. A small amount (0.5%) of dibutyltindilaurate was added to accelerate the condensation reaction.

Analysis of the Grafted/Crosslinked Sample

The degree of silane grafting onto PVC was evaluated indirectly by determining the degree of crosslinking after exposure to water. The percentage gel (residue) was determined gravimetrically after extraction with THF for at least 16 h.

The IR spectra were obtained with a Perkin–Elmer FTIR spectrometer (model 16PC) equipped with a Perkin–Elmer IR microscope. A Hewlett–Packard Diode Array spectrophotometer (model HP 8452) was used to collect the UV-visible spectra of the PVC films.

RESULTS AND DISCUSSION

Crosslinking with UV

Films of compounds, with various compositions, were subjected to UV irradiation in a nitrogen atmosphere for periods from 2 to 10 h. The percent gel formation (crosslinking) in these samples, shown in Figure 1, indicates that exposure to UV radiation initiates crosslinking, even in the absence of the VTIPS. However, addition of 10 parts per hundred parts of resin (phr) of VTIPS results in greater crosslinking, and it becomes significant at shorter times of irradiation; gel formation becomes measurable shortly after 2 h of irradiation. It is of note that even for the samples containing VTIPS crosslinking occurs without hydrolysis; in fact, hydrolysis has little, if any effect, on the ultimate percent gel. Addition of 1.0 phr of 2,2' azobis(isobutyronitrile)

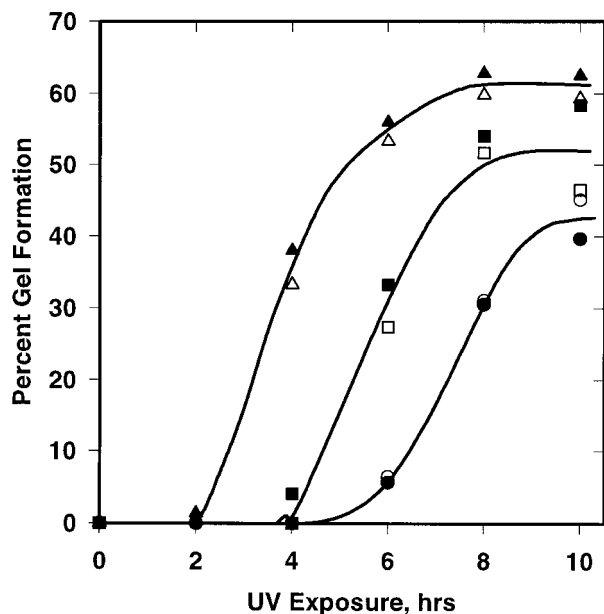


Figure 1 The effect of irradiation time on the extent of gel formation in PVC films: circles—pure PVC; triangles—PVC + 10 phr VTIPS; squares—PVC + 10 phr VTIPS + 1.0 phr AIBN (open symbols refer to as-irradiated samples and filled symbols correspond to hydrolyzed irradiated samples).

(AIBN), a common free radical initiator, actually inhibits UV initiated crosslinking.

Separate experiments were made in which films of similar composition to those described above were subjected to UV irradiation in an air environment. In these experiments, no gel formation was detected, indicating that under these conditions peroxy radical formation is predominant. This is consistent with previous studies that showed that UV initiated crosslinking of PVC in a nitrogen atmosphere is inhibited by the presence of oxygen.²²

Clearly, the UV initiated crosslinking of PVC samples in the absence of VTIPS involves the formation of C–C bonds. Because the extent of gel formation appears to be unaffected by hydrolysis, it could even be argued that no silane grafts are formed, even in the samples containing VTIPS. However, elemental analysis of the THF extracted gel residue (Galbraith Laboratories, Inc.) clearly showed the presence of silicon, hence, silane grafting. Furthermore, comparison of the FTIR spectra of VTIPS-containing PVC films before and after UV exposure shows the change in the shape of the peaks in the region 1000 to 1150 cm^{-1} (Fig. 2), indicating the presence of Si–O bonds. This is confirmed by comparison with the IR spectra

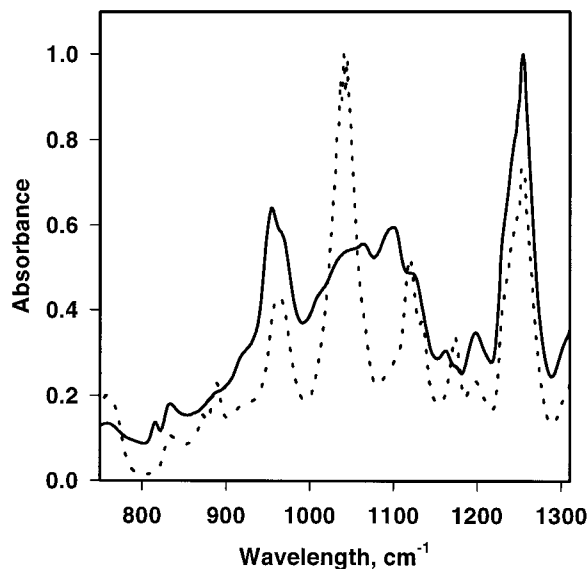


Figure 2 IR microscope spectra of VTIPS-containing PVC films before (dotted line) and after (solid line) UV exposure.

of polyethylene and vinyltri(methoxy)silane grafted polyethylene, given in Figure 3, which have peaks in the region of 1000 to 1250 cm^{-1} due to the silane as well as at 1094 cm^{-1} , which is assigned to Si–O–C and at around 1190 cm^{-1} due to the O–CH₃ group.^{23,24} In addition, Figure 4 shows the presence of the –OH group by the broad peak at 3300–3500 cm^{-1} . The peaks in this region

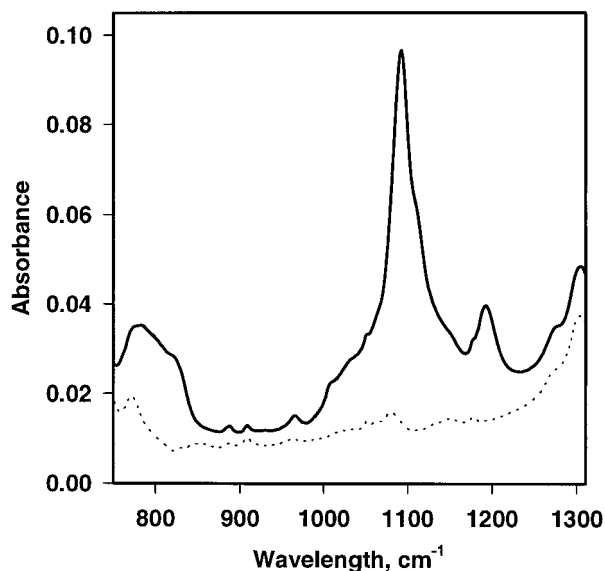


Figure 3 IR spectra of polyethylene (dotted line) and vinyltri(methoxy)silane-grafted polyethylene after hydrolysis (solid line).

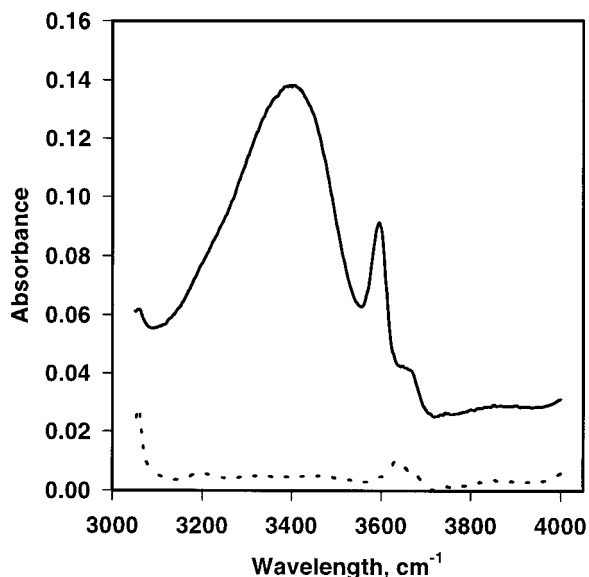


Figure 4 IR spectra of VTIPS-containing PVC films before (dotted line) and after UV exposure (solid line).

were not detected in pure PVC films following similar treatment. Therefore, it would appear that they result from the conversion of the isopropoxy group of VTIPS to Si-OH in the presence of HCl generated by UV degradation of PVC, according to the following scheme:

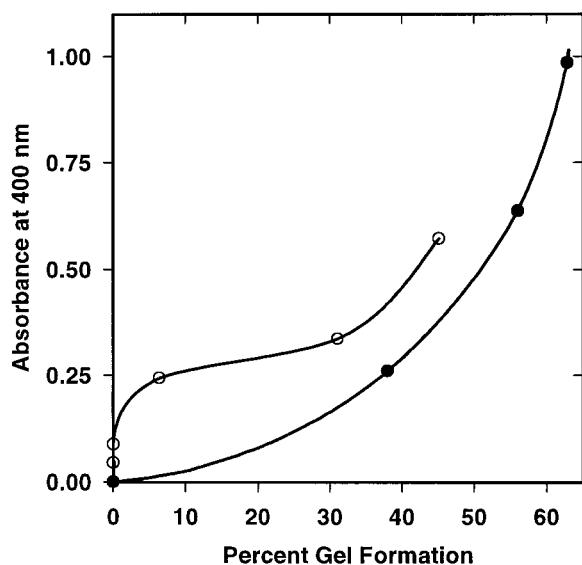
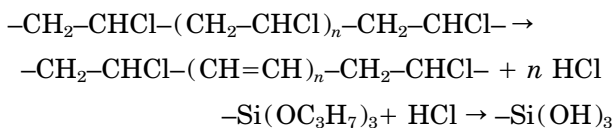


Figure 5 Absorbance at 400 nm of UV-irradiated PVC films: ○, no silane; ● 10 phr VTIPS.

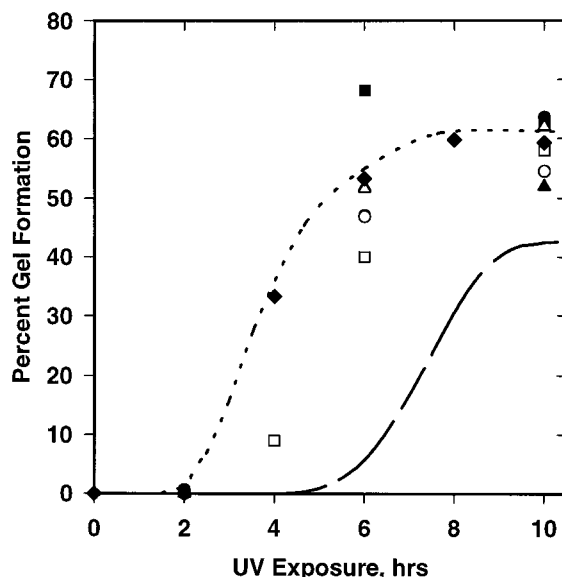


Figure 6 Studies of the effect of VTIPS concentration on the UV-initiated crosslinking of PVC: broken line—pure PVC; VTIPS-containing films: ●, 0.5; ○, 1.0; ■, 1.5; □, 2.0; ▲, 5.0; △, 7.5; ◆, 0 phr (fitted with the dotted line).

To consider this further, a VTIPS-containing PVC sample was treated with dry HCl without any UV exposure. The IR spectrum of this sample was similar to the spectrum of UV exposed sample shown in Figure 4, indicating the formation of the Si-OH group. These observations confirm that UV exposure causes both grafting of VTIPS to PVC as well as the formation of Si-OH bonds, which develop crosslinks by Si-O-Si bond formation.

The absorbance at 400 nm, obtained from the UV spectra of the films, is plotted as a function of percent crosslinking in Figure 5. It gives a measure of the degree of discoloration (yellow) that results from the formation of polyene sequences, particularly those with five or more conjugated double bonds. Clearly, in the absence of VTIPS UV irradiation initiates crosslinking in PVC only after a substantial amount of $-(\text{CH}=\text{CH})_5-$ is formed. By comparison, for the VTIPS-containing films crosslinks are formed as soon as active centers are created due to UV irradiation. Consequently, this yields a less colored product.

Effect of VTIPS Concentration

Film samples of PVC prepared with VTIPS concentrations ranging from 0 to 10 phr were exposed to UV, hydrolyzed, and the percentage gel was

Table I Film Compositions, Expressed in Parts by Weight

	PVSAP	PVSBP	PVSHC
PVC	100.0	100.0	100.0
VTIPS	10.0	10.0	10.0
Acetophenone	2.5	—	—
Benzophenone	—	2.9	—
Hexachloroacetone	—	—	4.1
Total	112.5	112.9	114.1

determined in the manner described above. As established above, samples with VTIPS develop a higher percentage of crosslinking than pure PVC (Fig. 6). Nonetheless, the increase with VTIPS concentration is not striking, and gel contents in the vicinity of 50% are attained in samples with only 1.0 phr VTIPS.

Effect of Photosensitizers

The substantial induction times for crosslink formation, seen in Figures 1 and 6, are not too surprising because defect-free PVC should not contain chromophores that absorb UV radiation. To address this matter, attempts were made to accelerate the crosslinking process by the addition of

photosensitizers. Films having the compositions given in Table I were prepared, hydrolyzed, and analyzed for percent gel formation. As indicated by the data plotted in Figure 7, addition of photosensitizer was effective in reducing the induction period but concomitantly decreased the ultimate extent of gel formation to an amount that depends on the photosensitizer. Indeed, for some unknown reason after 4 h of irradiation no further increase crosslinking was obtained.

CONCLUSIONS

The results presented above clearly show that UV irradiation of vinyltri(isopropoxy)silane-containing PVC films induces silane grafting. During irradiation, Si–O–Si crosslinks are formed due to the presence of HCl generated in the initial stages of the dehydrochlorination of the PVC. By suitable choice of formulation and irradiation conditions, the UV-initiated crosslinking of PVC in the presence of silane (the Si–O–Si crosslink) yields a suitable product with minimal discoloration. Although this method is probably not commercially practical, it does indicate the possibility of grafting (and crosslinking) of vinyltri(alkoxy)silanes to PVC with minimal discoloration (and degradation).

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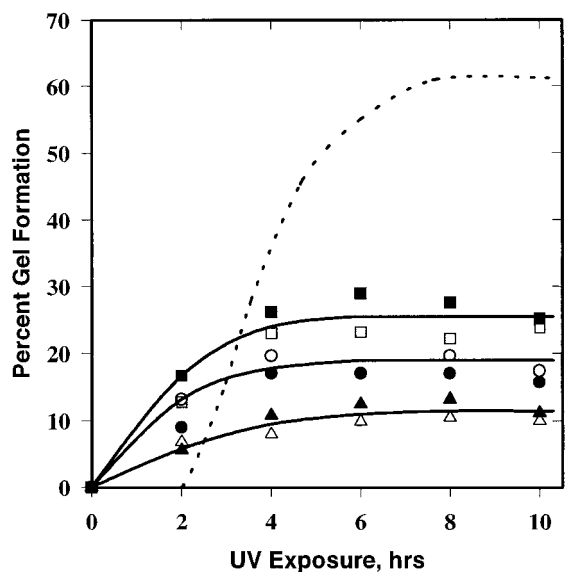


Figure 7 The effect of irradiation time on the extent of gel formation in PVC films containing photosensitizers: dotted line—PVC + 10.0 phr VTIPS; triangles—benzophenone; circles—hexachloroacetone; squares—acetophenone (open symbols refer to as-irradiated samples and filled symbols correspond to hydrolyzed samples).

REFERENCES

1. W. A. Salmon, *J. Appl. Polym. Sci.*, **16**, 671 (1972).
2. L. L. Valdiserri and G. V. Reed, *Rubber World*, **170**, 40 (1974).
3. A. A. Miller, *Ind. Eng. Chem.*, **51**, 1271 (1959).

4. K. Mori and Y. Nakamura, *J. Polym. Sci., A-1*, **9**, 639 (1971).
5. K. Mori and Y. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1981 (1978).
6. K. Mora and Y. Nakamura, *J. Appl. Polym. Sci.*, **22**, 2685 (1978).
7. T. Hjertberg, T. Dahl, and E. Sörvik, *J. Appl. Polym. Sci.*, **37**, 1239 (1989).
8. S. Cartasegna, *Rubber Chem. Technol.*, **59**, 724 (1985).
9. J. T. Lewis, D. Collins, and C. Malani, *Br. Pat.* 139,248 (1969).
10. J. C. Saam and B. Thomas, *Br. Pat.* 1,485,263 (1973).
11. Y. Shindo and T. Hirai, *Makromol. Chem.*, **155**, 1 (1972).
12. I. Kelnar, PhD Thesis, Institute of Chemical Technology, Prague (1988).
13. M. S. Hearn, J. D. Baird, L. P. Nethsinghe, and M. Gilbert, *Polym. Commun.*, **31**, 194 (1990).
14. I. Kelnar and M. Schätz, *Sb. Vysk. Sk. Chem.-Technol. Praze, Polym., Chem., Vlastnosti Zprac.*, **S17**, 31 (1988).
15. Fujikura Cable Works Ltd., *Jpn. Kokai* 565,854 (1981); *Chem. Abstr.*, **94**, 209757 (1981).
16. Fujikura Cable Works Ltd., *Jpn. Kokai* 5,796,048 (1982); *Chem. Abstr.*, **97**, 183070 (1982).
17. Fujikura Cable Works Ltd., *Jpn. Kokai* 5,796,049 (1982); *Chem. Abstr.*, **97**, 183071 (1982).
18. Fujikura Cable Works Ltd., *Jpn. Kokai* 5,787,438 (1982); *Chem. Abstr.*, **97**, 199068 (1982).
19. T. Yamamoto, M. Ogawara, and Y. Hirokawa, *Jpn. Kokai* 63010605 (1988); *Chem. Abstr.*, **109**, 38487w.
20. M. Schätz, I. Kelnar, and J. Vysoky, Ger. Offen. 3719151 (1987); *Chem. Abstr.*, **108**, 205319f.
21. I. Kelnar and M. Schätz, *J. Appl. Polym. Sci.*, **48**, 657, 669 (1993).
22. V. P. Gupta and L. E. St. Pierre, *J. Polym. Sci.*, **17**, 797 (1979).
23. H. G. Fritz and S. Ultsch, Abstract, Polymer Processing Society, 6th Annual Meeting, Nice, France, 1990, paper #12-04.
24. T. Yamamoto, H. Inada, S. Isozaki, and M. Okawara, *React. Polym.*, **22**, 129 (1994).