

Ultraviolet-induced graft reaction of quinoid compounds onto polypropylene films

Effect of synthesis conditions on vitamin K₁-g-polypropylene

Heung-Jae Chun, Richard B. Beard*

Biomedical Engineering and Science Institute, Drexel University, Philadelphia, PA 19104, USA

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Summary

Ultraviolet irradiation in the presence of benzophenone (BP) as a photosensitizer was used to graft vitamin K₁ (VK₁) onto a film of medical grade isotactic polypropylene. The effects of various reaction conditions on the graft yield of the samples and the changes in physicochemical properties of the sample surfaces were determined by FTIR and surface tension measurements. Increases in the ultraviolet irradiation time for the first 60 minutes markedly increased the graft yield linearly before leveling off above the 0.3 vol.% vitamin K₁ concentration. A 2 wt.% concentration of BP produced the maximum graft of VK₁. The surface tension of the samples increased to a value of 38 dyne/cm with increasing graft yield.

Introduction

Electron spin resonance spectroscopy studies have shown that naphthoquinones are the free radical generating compounds [1-3]. Free radicals at the intermediate stage are formed by the conversion of isoprenoid quinones (vitamin E, K, and their derivatives) into their quinols [1,2]. This conversion is affected by a variety of enzymatic systems: NADPH-, NADH-, cytochrome c reductase, vitamin K₁ reductase; etc. [4]. Grafting of these quinoid compounds not only provides the functionality to have primary and/or secondary bonding with integrins but also produces strong interaction between enzymatically formed free radicals and the free radicals on the surface of abnormal cells.

In this study, vitamin K₁ was selected as a free radical generating chemical for grafting onto the surface of medical grade isotactic polypropylene. In this paper the photo-graft reaction procedures of vitamin K₁-g-polypropylene with the aid of benzophenone, photosensitizer for pre-irradiation of substrate is reported along with the evaluation methods of structural surface changes of the samples.

Experimental

Materials

Vitamin K₁ (Sigma Chemical Co., St. Louis, MO) was used without further purification. Benzophenone (Junsei Chemical Co., Japan), recrystallized from methanol and vacuum dried, was used as the photosensitizer. Medical grade isotactic polypropylene film, 25 mm of thickness and 0.905 g/cm³ of density, was provided by the Polymer Materials Lab. in KIST (Korea Institute of Science and Technology). The film was immersed in acetone and soxhlet-extracted with methanol and acetone, consecutively for 48 hrs. each to remove additives, and vacuum dried.

Preparation

The reaction medium for pre-irradiation was prepared by dissolving a given concentration of benzophenone into the spectrophotometric grade cyclohexane (Aldrich Co., Milwaukee, WI). 10x10 cm² of PP film was immersed into the reaction medium. The reaction chamber, which contains the reaction medium, was deoxygenated by purging with nitrogen gas. A 450-W Hanovia

* Corresponding author

medium pressure mercury lamp in a temperature-controlled bath was used to irradiate the film, as shown in previous report [5]. After 2 hours of pre-irradiation, a given concentration of vitamin K₁-cyclohexane solution was added to the reaction medium, and UV light was irradiated up to 2 hrs. The distance between the UV lamp and the reaction chamber was controlled by a screw gear in order to provide the optimum amount of photo intensity ($\cong 0.7 \text{ KJ/m}^2$) to the reaction system [6].

A series of grafting reactions was performed by changing the VK₁ concentration from 0.1 to 0.6 vol. % and reaction time from 20 to 120 minutes. Grafted films were taken out from the reaction solution and washed with acetone to remove the absorbed unreacted chemicals. After the washing procedure a soxhlet extraction was done with methanol for 48 hours followed by an acetone soxhlet extraction for 48 hours. The films were then dried in a vacuum until a constant weight was reached.

Infrared Spectroscopy

FTIR (Fourier transform infrared spectroscopy) studies were performed to confirm the structural changes of chemicals used and the changed chemical composition of the polypropylene film, by using a Nicolet DX system spectrometer.

Determination of graft yield

The graft yields of the samples were determined by weight measurement methods using an Electronic Analytical Balance (Mettler AT 281 Delta Trac.)

Contact angle measurement

Contact angles of liquid-solid interfaces (water, methylene iodide-PP, VK₁ introduced PP) were measured with the use of an Erma contact angle meter G-1. Surface tensions of all samples were calculated by Owens Equation [5,7].

Effects of reaction conditions

In order to get the optimal reaction conditions, such as the effect of benzophenone concentration, VK₁ concentration, and irradiation time on the graft yield, a series of exploratory graft reactions were performed.

Results and discussion

Benzophenone, which is activated to a triplet state via a singlet state by UV radiation, abstracts hydrogen atoms from the PP film, producing polymer radicals. Benzophenone can also abstract hydrogen atoms from the VK₁ hydrocarbon chain to produce free radicals [8]. Therefore, it is expected that the radicals in the backbones of PP and VK₁ combine with each other, as a basis for a graft reaction (i.e., free radical recombination reaction), as shown in Figure 1-(A).

The presence of the graft was confirmed by using infrared spectroscopy. The FTIR spectra of PP and samples of different graft ratios are shown in Figure 2. In the IR spectrum of polypropylene (Figure 2-A), the absorption in the region between 2850 and 2930 cm^{-1} is due to $-\text{CH}_2$ stretching, and the absorption bands in 1455 and 1375 cm^{-1} might be related to $-\text{CH}_3$ bending of polypropylene [9].

In the spectra of the grafted samples, shown in Figure 2-B and -C, the characteristic VK₁ bands around 1600 cm^{-1} appear. The absorption in the region 1690 cm^{-1} is ascribed to the aromatic C=O stretching of VK-1. The absorption band around 1660 cm^{-1} is related to the C=C bond, and the band in the region of 1580 cm^{-1} is due to the aromatic C=C bond [10, 11].

Referring to Figure 2-B and -C, the intensity of the C=O and the aromatic C=C bands of VK₁ increase. This increase can be attributed to an improved reaction condition. This shows that VK₁ is incorporated as a graft onto the PP film. C-H stretching bands between 2930 cm^{-1} and

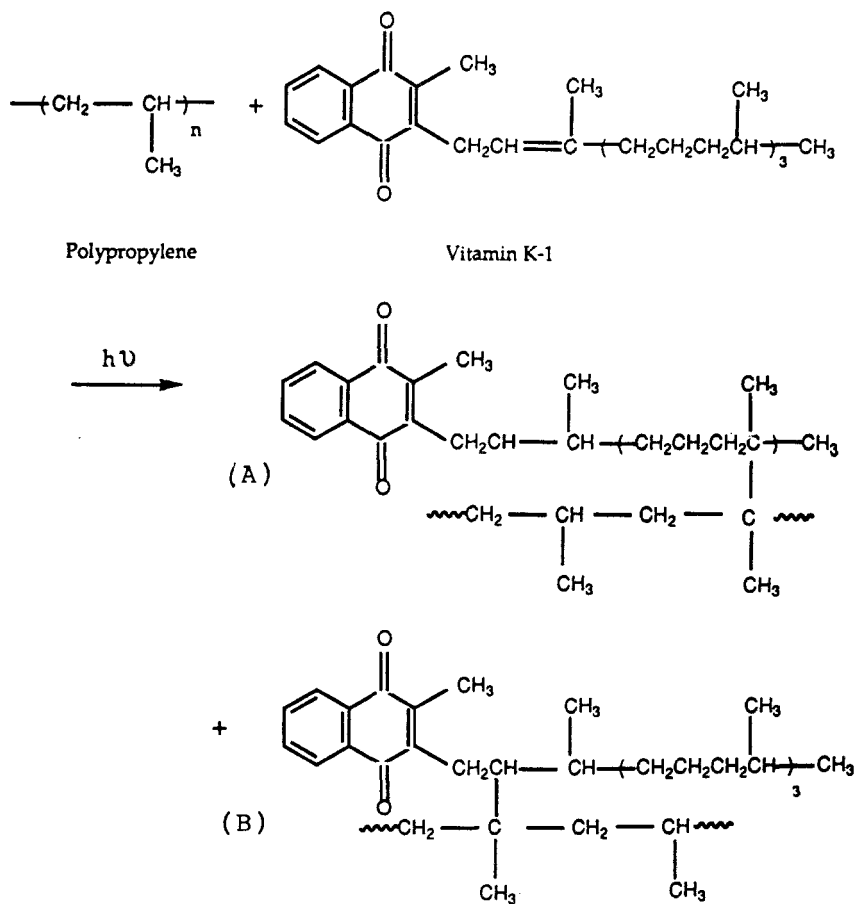


Figure 1 Proposed reaction mechanism of VK₁-g-PP.

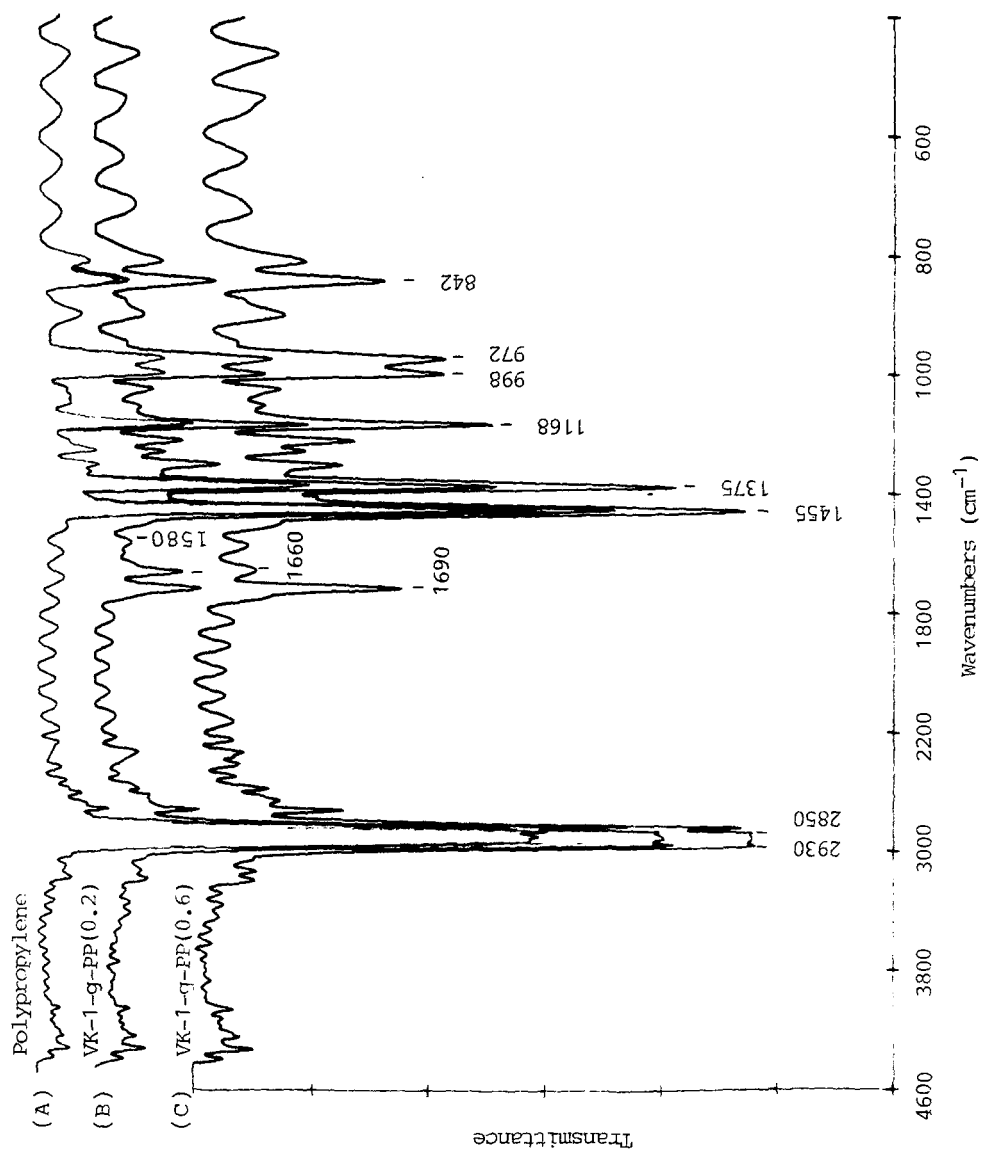


Figure 2 FTIR spectrum of polypropylene (control) and VK1-g-PP samples.

2850 cm^{-1} increases slightly with increase in VK₁ grafting yield. Furthermore, the intensity of bands 1168 , 998 , 972 , and 842 cm^{-1} of infrared absorption spectrum for both PP and VK₁ are increased with an increase in grafting yield. However, the absorption band of aliphatic C=C at 1660 cm^{-1} is decreased with an increase in graft yield. Beside the radical-radical recombination reaction between tertiary carbons of polypropylene and vitamin K₁, the addition reaction of tertiary carbons of the polypropylene chain to unsaturated carbons in vitamin K₁, as shown in Figure 1-(B), can also be expected.

Effect of VK₁ concentration on graft reaction

The graft reaction was performed for 30 minutes with 4 wt.% of Benzophenone at a reaction temperature of $40\text{ }^{\circ}\text{C}$ in order to examine the graft yield with respect to changes in the concentration of VK₁.

In Figure 3, the graft yield increases with increases in VK₁ concentration up to 0.6 ml of VK₁ (0.3 vol.%), and then reaches an equilibrium. The initial increasing slope is mainly due to the increase in the quantity of VK₁, which facilitates the diffusion of VK₁ onto the substrate surface through the early grafted layer. Further increases of VK₁ concentration causes the accumulation of grafted VK₁ on the substrate surface which shields the activated sites of the polypropylene, making it more difficult for the unreacted VK₁ to bind with polypropylene [12-14].

Effect of the photosensitizer concentration on graft reaction

Figure 4 shows the effects of BP concentration on the graft yield with a 40°C reaction temperature and 0.3 vol.% of VK₁. The graft yield increases with an increase of benzophenone concentration 2 wt.% of BP concentration. Above a 2wt.% BP concentration the graft yield decreases at the same rate from a maximum value of 6% to 3% at 3 wt.% of BP. Above 3 wt.% of BP the graft yield is relatively constant at 3%. It is postulated that when the concentration of BP introduced into the reaction system is less than 2 wt.%, the activation of the PP chain and the VK₁ chain increases with an increase of BP concentration, which provides greater probability for them to combine with each other. When an additional amount of BP is applied, above 2 wt.% of BP the reaction system can obtain an increase in the numbers of activated VK₁ molecules; increasing the probability of the bimolecular recombination reaction between the activated VK₁ molecules. This bimolecular recombination of VK₁ molecules results in a decrease of graft yield. The leveling of the graft yield curve of figure 4 above a concentration of 3 wt.% BP indicates that the concentration of the activated VK₁ molecules and the activated sites of PP substrate remain relatively constant.

Effect of reaction time

Figure 5 shows the effect of irradiation time on the graft yield of VK₁-g-PP films at various VK₁ quantities. The concentration of BP is fixed to 2 wt.%, and the amount of VK₁ is varied from 0.1 to 0.3 vol.%. Graft yield increases with increase of reaction time up to 100 min., and after which it reaches an equilibrium.

Surface tension

Figure 6 represents the change of surface tension with respect to the graft yield. VK₁ may show slightly more hydrophilic properties than does PP, since it has two polar groups, C=O, in its head. Thus, the wettability of VK₁-g-PP is expected to increase with an increase of the graft ratio, as shown by, the increase in surface tensions of the samples with an increase of graft yield.

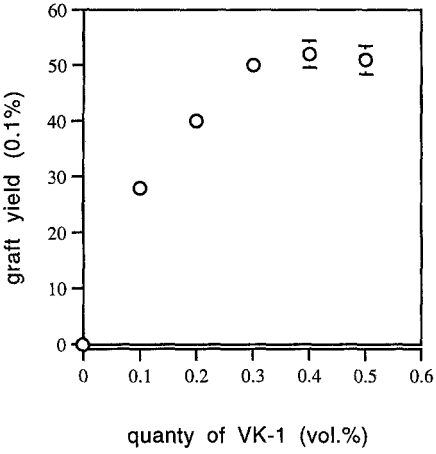


Figure 3 Effect of VK₁ Concentration on the graft yield of VK₁-g-PP (BP Conc.: 4 wt%, Irradiation Time: 60 min., Temp.: 40 Deg.C, UV intensity: 0.7 KJ/m²).

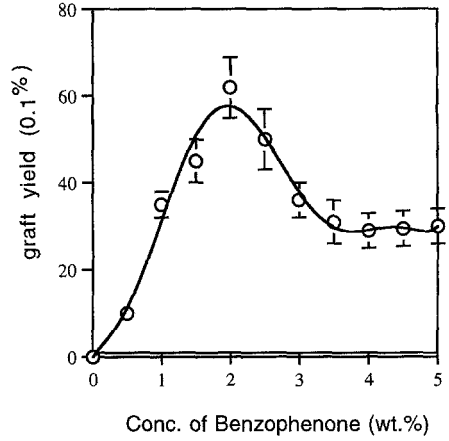


Figure 4 Effect of benzophenone concentration on graft yield of VK₁-g-PP (VK₁ Conc.: 0.3 %, Irradiation Time: 60 min, Temp.: 40 Deg.C, UV intensity: 0.7 KJ/m²).

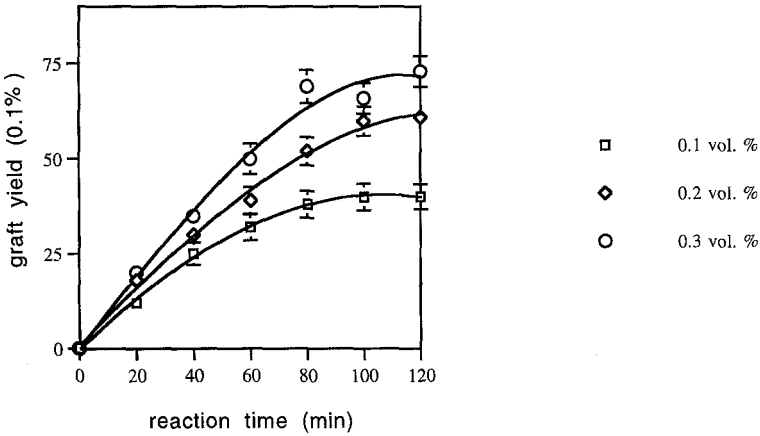


Figure 5 Effect of irradiation time on graft yield of VK-1-g-PP (BP Conc.: 2 wt%, Temp.: 40 Deg. C, UV intensity: 0.7 KJ/m²).

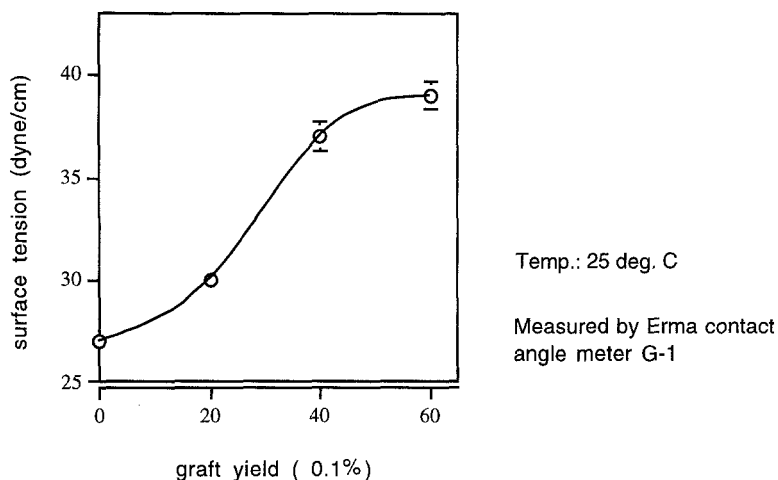


Figure 6 Changes in surface tension with respect to graft yield of samples.

Conclusion

1. Vitamin K₁ grafted isotactic polypropylene films can be fabricated under liquid-phase ultraviolet irradiation reactor.
2. The appearance of IR peaks of aromatic ketone, as well as of aromatic double bonds possessed by vitamin K₁ confirmed the presence of the graft.
3. The proposed reaction mechanisms are i) the addition reaction between tertiary carbon in polypropylene and tertiary carbon in hydrocarbon chain of vitamin K₁ and ii) the addition reaction of tertiary carbon on polypropylene backbone to the unsaturated double bonds in vitamin K₁.
4. At a concentration of 0.3 vol.% of VK₁ and a reaction time of 100 minutes, the optimal reaction condition of VK₁-g-PP takes place in a reaction medium of 2 wt.% BP with respect to the weight of PP film.
5. It is concluded that the surface tension of VK₁-g-PP increases with an increase in graft yield.

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