

Ultraviolet-Induced Graft Reaction of Quinoid Compounds onto Polypropylene Films: Effect of Synthesis Conditions on Hydroquinone-*g*-Polypropylene

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SYNOPSIS

The liquid-phase graft reaction of hydroquinone (HQ) was carried out onto the surface of medical-grade polypropylene (PP) films with the photosensitizer, benzophenone (BP). The effects of various reaction conditions on the graft yield of the samples and the changes in physicochemical properties of the surface of the samples were determined by FTIR/FMIR and surface tension measurements. As BP concentration was increased, the graft yield increased up to a maximum at 2.5 wt % of BP and then decreased. Graft yield was increased with irradiation time and HQ concentration before leveling at 3.5 wt %, in 150 min. The surface tension of samples were increased with the increase of graft yield up to 37 dyn/cm.

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INTRODUCTION

In many experimental results and mechanisms for cell adhesion, it has been reported that the extent of cellular adhesion is considerably affected by physical and chemical properties of the substrate surface.¹⁻⁴ The wettability of the substrate due to changes in the physical property of the substrate affects cellular adhesion.³ The chemical properties of the interface can form primary or secondary bonds to enhance cellular adhesion.⁴ A substrate that has very reactive functional groups and can form covalent bonds with the glyco-proteins of the cell membrane, i.e., integrin, can produce permanent cellular adhesion. Substrates having polar groups such as hydroxyl, carboxyl, or other ionic groups can also interact with cellular proteins through hydrogen bonding. Malignant tumor cells which possess unusually high content of free radicals⁵ may further enhance their adhesion to an interface.

The aim of this study is to examine the influences of the surface properties of polymeric substrates on normal and abnormal cell adhesion. To do this, isotactic polypropylene film was selected as a substrate

because of its outstanding bioinertness. Quinoid compounds, which are free radical generating chemicals, were grafted on polypropylene films to provide an increased hydrophilic property, polar functionality, and the enhanced free radical generation at the interface. Enzymes redox reaction onto polypropylene surface generates the free radicals. The present investigation involves the changes in chemical and physical properties of hydroquinone-*g*-polypropylene with respect to the reaction condition.

EXPERIMENTAL

Materials and Reagents

Medical-grade isotactic polypropylene (PP) film, 25 μm thickness and 0.905 g/cm^3 of density, was provided by 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 h each to remove additives, and vacuum dried. Hydroquinone (HQ) (Sigma Chemical Co., St. Louis, MO) was used without further purification. Benzophenone (BP) (Junsei Chemical Co., Japan), recrystallized from methanol and vacuum dried, was used as the photosensitizer.

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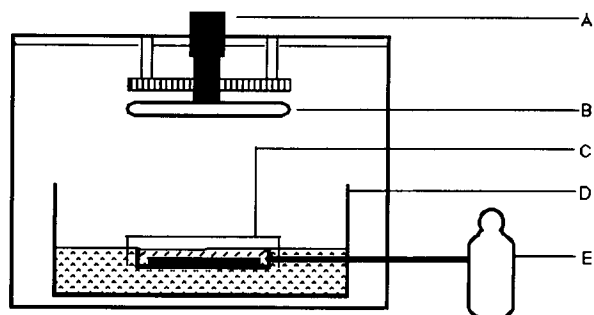


Figure 1 Schematic diagram of photoinduced graft reaction apparatus. (A) Control gear and lamp holder, (B) UV lamp, (C) reaction chamber containing PP film, reaction medium, and quartz window, (D) water bath, and (E) nitrogen gas supply.

Sample Preparation

The reaction medium was prepared by dissolving a given concentration of HQ from 0.5 to 5.5 wt % and BP from 1 to 4 wt % into the co-solvent system composed of 80 parts of the spectrophotometric grade cyclohexane (Aldrich Co., Milwaukee, WI) and 20 parts of the reagent grade of acetone (Aldrich Co., Milwaukee, WI); $10 \times 10 \text{ cm}^2$ of PP film was immersed into the reaction medium. The reaction chamber containing the reaction medium was deoxygenated by purging with nitrogen gas. A 450-W Hanovia medium-pressure mercury lamp in the temperature-controlled bath was used to irradiate the film, as shown in Figure 1.

The series of graft reactions were performed by changing the HQ concentration and reaction time up to 200 min. Grafted films were taken out from the reaction solution and washed with acetone to remove the absorbed unreacted chemicals, followed by Soxhlet-extraction with methanol for 48 h. The films were then dried in a vacuum until a constant weight was reached.

Infrared (IR) Spectroscopy Analysis

Fourier transform infrared interferometers (FTIR)/frustrated multiple-reflection IR (FMIR) studies were performed to confirm the structural changes of chemicals used and the changed chemical composition of the PP film by using a Nicolet DX system spectrometer.

Graft Yield Determination

The graft yields of the samples were calculated by Eq. (1). Electronic analytical balance (Mettler AT

Table I Surface Tension of Testing Solution⁶

Test Liquid	g_i^d dyne/cm	g_i^h dyne/cm	g_i dyne/cm
Water	21.8	51.0	72.8
Methylene iodide	49.5	1.3	50.8

281 Delta Trac.) was used to measure the weight of the samples.

$$\text{Graft yield (\%)} = \frac{W_g - W_i}{W_i} \times 100 \quad (1)$$

where W_i is the initial weight of the film, and W_g the weight of the grafted sample.

Contact Angle Measurement

Contact angles of liquid–solid interface (liquid : water, methylene iodide, solid : PP, PP-*g*-HQ) were measured by an Erma contact angle meter G-1. Surface tensions of all samples were calculated by Owens equation:⁶

$$1 + \cos \Theta = 2/g_i \times [(g_s^d \times g_i^d)^{1/2} + (g_s^h \times g_i^h)^{1/2}]$$

$$g_s = g_s^d + g_s^h$$

$$g_c = g_s - [(g_s^d)^{1/2} - (g_i^d)^{1/2}]^2 + [(g_s^h)^{1/2} - (g_i^h)^{1/2}]^2$$

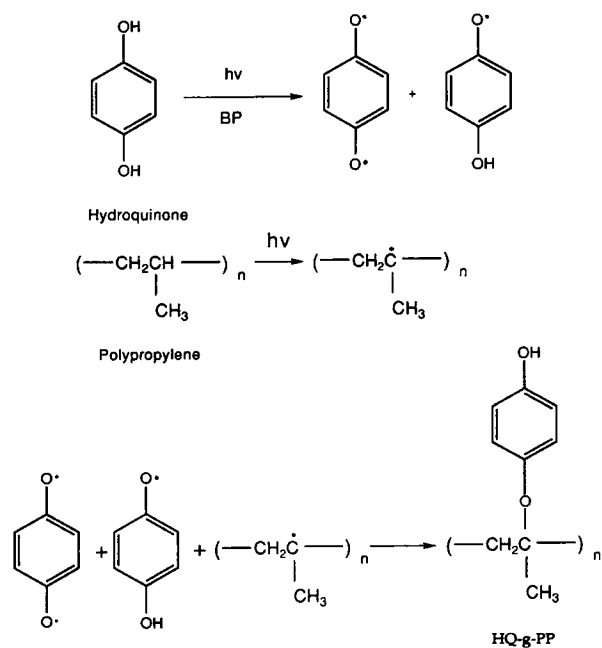


Figure 2 Reaction mechanism of HQ-*g*-PP.

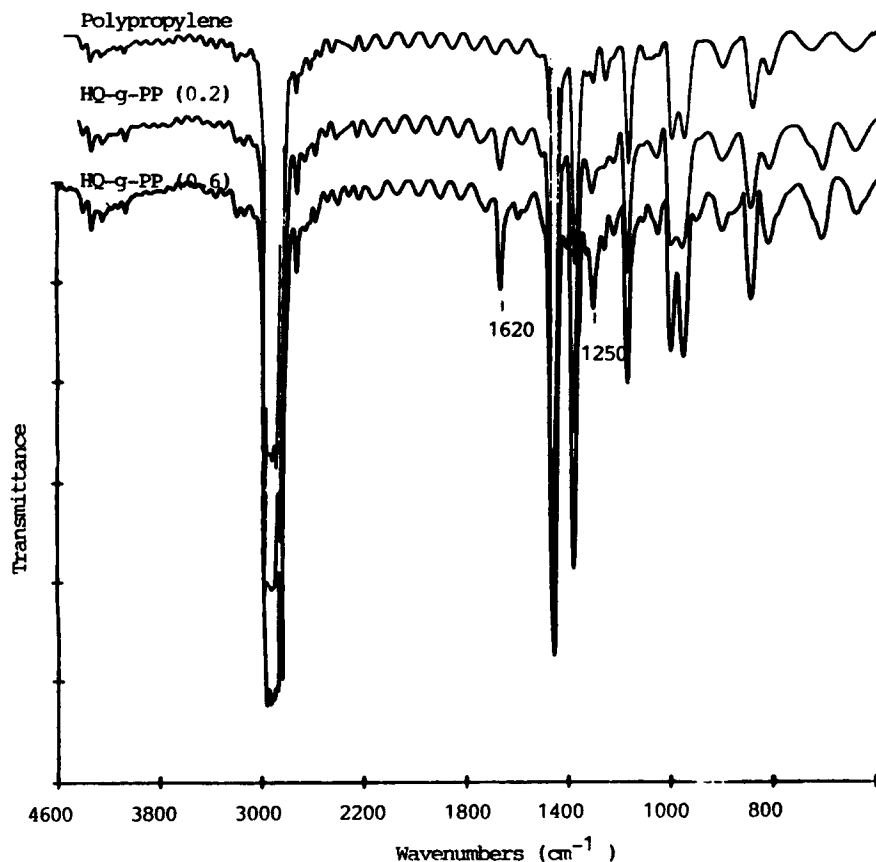


Figure 3 FTIR spectra of polypropylene (control) and HQ-*g*-PP samples. (A) Polypropylene, (B) 2% of graft yield, and (C) 6% of graft yield.

where θ is the contact angle, g the surface tension, subscript s the solid, subscript l the liquid, and superscript h the hydrogen bonding components, and superscript d the dispersion force components (see Table I).

Effects of Reaction Condition

Series of graft reactions were performed to get the effect of BP concentration, HQ concentration, and irradiation time on the graft yield.

RESULTS AND DISCUSSION

BP activated as a triplet state via a singlet state by UV radiation¹² abstracts hydrogen atoms from hydroxyl group of HQ, thus making HQ molecules possess oxyradicals. UV radiation activates the PP backbone chain, and produces polymer radicals.¹³ Therefore, it is expected that the radicals in the backbone of PP and HQ combine with each other,

and then a graft reaction is performed, i.e., free radical recombination reaction. The reaction scheme in Figure 2 represents overall reaction pathways performed in this study.

FTIR spectra of PP and the HQ-*g*-PP samples of different graft degrees are shown in Figure 3. The absorption in the region of 1600 cm^{-1} might be related to the aromatic C=C band of HQ.⁷ Aromatic C—O band around 1250 cm^{-1} , as originally assigned to the C—O stretching of the methoxy groups by Morton et al.⁸ is also shown in FTIR spectra of HQ-*g*-PP. The intensity of these bands increases with the increase in the graft yield.

The reason why the broad band for —OH around 3300 cm^{-1} does not show up may be attributed to the poor resolution of the FTIR for this species.⁹ Therefore, we applied FMIR and identified the band for the —OH group in modified PP.

The FMIR spectrum of typical HQ-*g*-PP surface is shown in Figure 4. OH band around 3300 cm^{-1} and the aromatic C=C band around 1630 cm^{-1} are clearly shown, and there exists a high-intensity band for the aromatic C—O group around 1250 cm^{-1} .

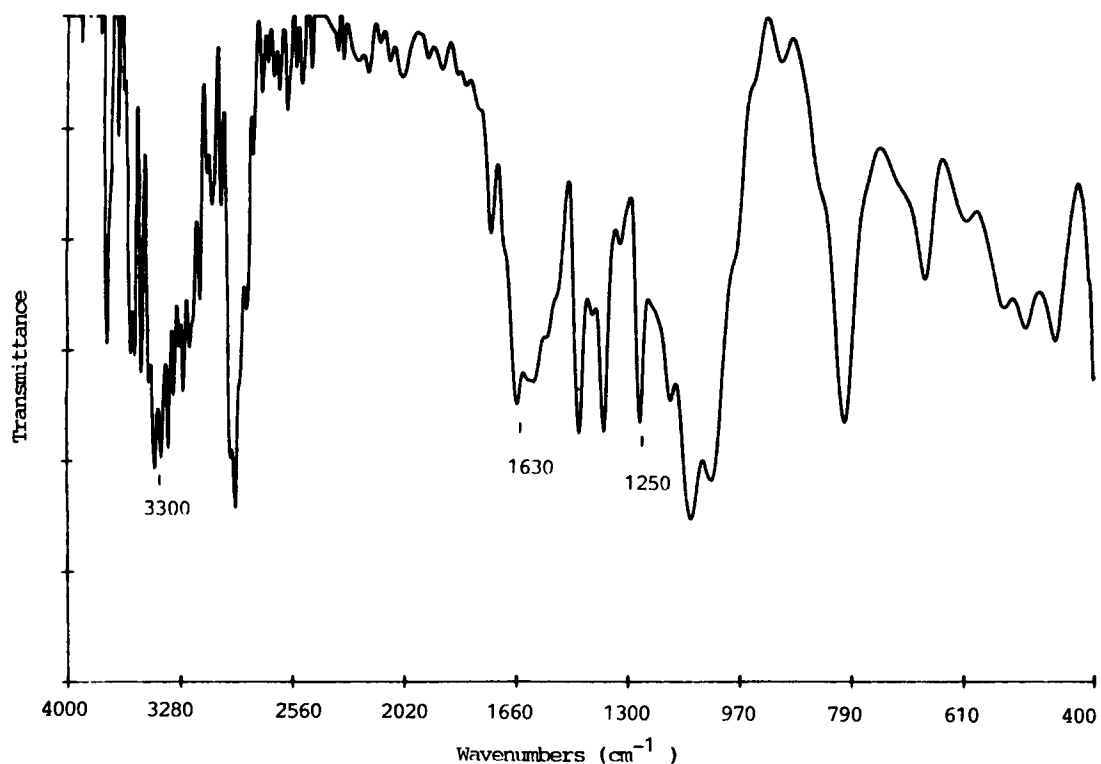


Figure 4 FMR spectrum of HQ-g-PP (6% of graft yield).

Figure 5 represents the general trend of the graft reaction of HQ onto surface of PP film with 3.5 wt % of BP and 40°C of reaction temperature. Graft yield increases up to 3 wt % of HQ concentration in the reaction medium, then reaches its plateau.

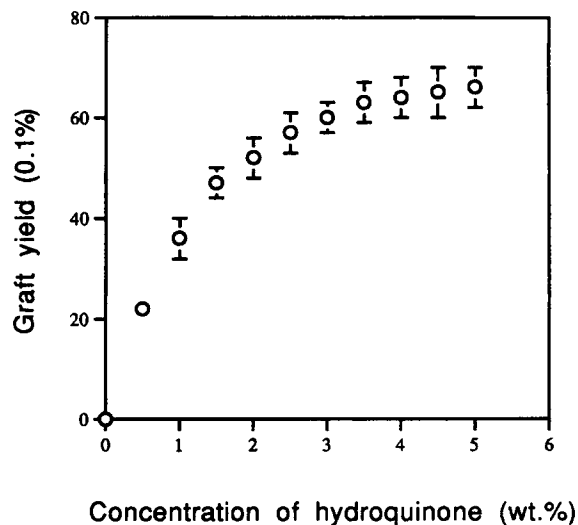


Figure 5 Effect of HQ concentration on graft yield of HQ-g-PP (BP conc.: 4 wt %, temp.: 40°C, irradiation time: 30 min).

The initial increasing trend is due to the increased HQ concentration as shown in the graft reaction of styrene on PP.¹⁰

Graft yield increases with the increase of BP concentration, then slightly decreases as shown in Fig-

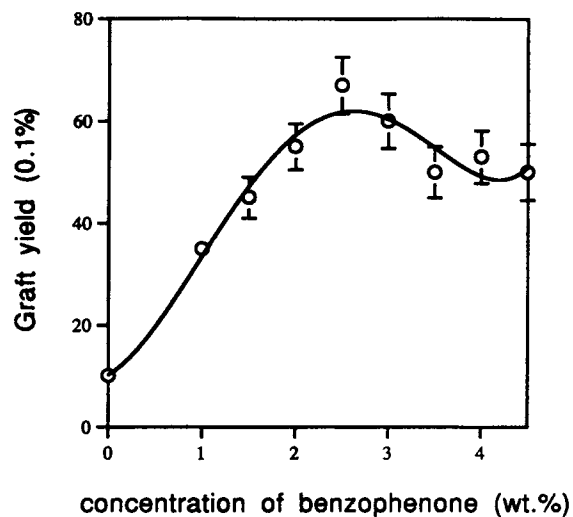


Figure 6 Effect of BP concentration on graft yield of HQ-g-PP (HQ conc.: 3.5 wt %, irradiation time: 60 min, temp.: 40°C).

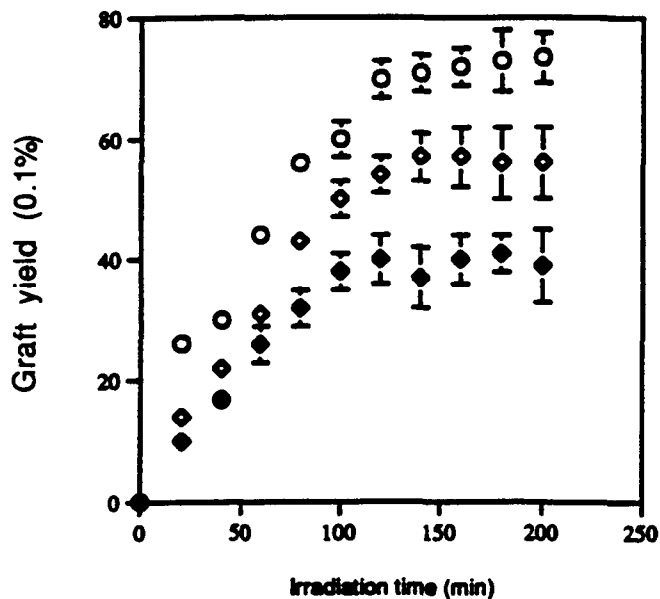


Figure 7 Effect of irradiation time on graft yield of HQ-*g*-PP. BP conc.: 2.5 wt %, temp.: 40°C, HQ conc.: (◆) 1.5 wt %, (◇) 2.5 wt %, and (○) 3.5 wt %.

ure 6. A possible explanation of this phenomenon is that as the concentration of BP is introduced into the reaction system the activation of the PP chain and hydroquinone increases up to an optimum concentration of 2.5 wt %. Further increase in concentration of BP above the optimum value increases the number of activated molecules¹³ which increases the probability of the side reactions such as bimo-

lecular recombination reaction between polypropylene radicals or an increase in reaction between activated HQ molecules.¹¹ The above factors could account for the decrease in the graft ratio with increase in BP concentration. The increase in ESR signal intensity of PP with the addition of BP to a maximum with a decrease in higher concentrations of BP have been shown by Kubata et al.¹³

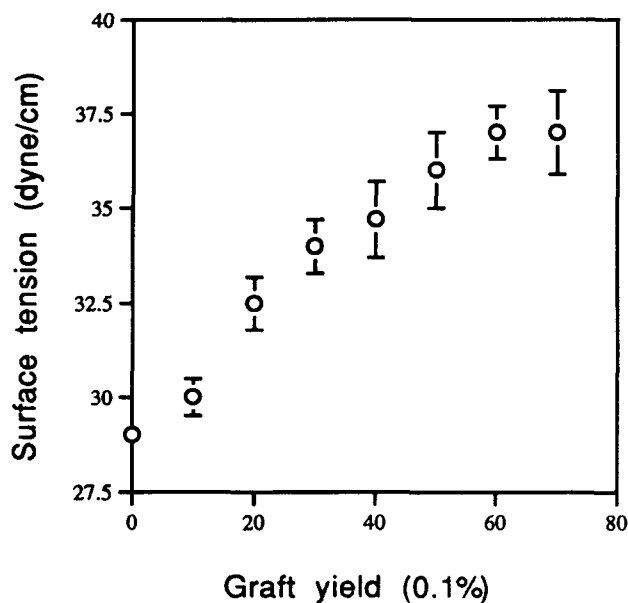


Figure 8 Changes in surface tension with respect to the graft yields of the samples (temp.: 25°C, measured by Erma contact angle meter G-1).

Figure 7 shows the effect of irradiation time on the graft yield of HQ-g-PP films at various HQ quantities. The concentration of BP was fixed to 2.5 wt %, and three different concentration of HQ were introduced. Graft yield increases with an increase of reaction time, before reaching a plateau at 150 min.

Figure 8 represents the change of surface tension of HQ-g-PP with respect to the graft yield. The graft of HQ which is known to be hydrophilic, and soluble for most polar solvents, makes the surface of PP more hydrophilic with increase in graft yield.

CONCLUSION

1. HQ-grafted isotactic PP films can be fabricated using liquid-phase UV irradiation reactor.
2. The graft was confirmed by the appearance of IR bands of aromatic double bonds, aromatic ether, and hydroxyl groups possessed by HQ.
3. It is concluded that the optimal reaction conditions for HQ-g-PP are 3.5 wt % of HQ, 2.5 wt % of BP with respect to the weight of PP film, and 150 min of UV irradiation time.
4. It is concluded that the surface tension of HQ-g-PP increase with increase in graft yield.

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