

Photoinduced Graft Polymerization of Styrene onto Polypropylene Substrates

YUHUA LI, JOSEPH M. DESIMONE, CHI-DUEN POON, EDWARD T. SAMULSKI

Department of Chemistry, CB# 3290, Venable and Kenan Laboratories, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290

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ABSTRACT: The photochemical grafting of styrene onto polypropylene (PP) using benzophenone (BP) and benzoin ethyl ether (BEE) as photosensitizers is described. The effects of various parameters (such as monomer and photosensitizer concentration, reaction time, and solvent) on percent grafting were studied. We found that BP is a very efficient photosensitizer for the grafting of styrene onto PP surfaces. Unlike BEE, BP does not initiate nongrafting homopolymerization reactions in solution which compete with grafting reactions. This is advantageous over other photosensitizers since homopolymer formed in solution can interfere with the grafting reaction as well complicate sample preparation and purification. The graft copolymers obtained using both BP and BEE were characterized by high resolution $^1\text{H-NMR}$, optical microscopy and swelling studies. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 883–889, 1997

Key words: photochemical grafting; styrene; polypropylene; benzophenone; benzoin ethyl ether

INTRODUCTION

Photochemical grafting is known to be a useful technique for the modification and functionalization of polymeric materials. This approach has been utilized in a wide range of fields such as surface modification of polymers,^{1–5} immobilization of enzymes,⁶ photostabilization of PP,⁷ and synthesis of biocompatible materials.⁸ The technique involves the initiation of the polymerization of vinyl monomers at reactive sites generated on solid polymer surfaces using photoirradiation methods. The photosensitizers most commonly used for grafting are aromatic ketones. The initiation mechanism of these photosensitizers can be

classified into two types: hydrogen abstracting, and photofragmenting. Benzophenone (BP) is typical of the former type and benzoin and its derivatives are involved in the latter. Both kinds of photosensitizers have been successfully used for photografting a variety of vinyl monomers onto polymer surfaces. However, for the photografting of styrene onto polypropylene (PP), while benzoin ethyl ether (BEE) has been found to be an efficient photosensitizer, BP has been reported to be unsuccessful.^{9–11} In the irradiation conditions used in this study, in contrast to what has been reported, we have found that BP was a very effective photosensitizer to initiate the grafting of styrene onto PP substrates. Moreover, we have found that BP behaves quite differently from other common photosensitizers such as BEE and its derivatives.

Most studies on the surface modifications of polymeric materials by graft polymerization have focused on the efficiency of the graft polymerization process. Little, if any, attention has been paid

Correspondence to: J. M. DeSimone and E. T. Samulski.
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to the characterization of the grafted polymer chains. It is reasonable to think that photosensitizers which can generate reactive sites on the surface of a polymer substrate could also create radicals on the growing grafted polymer chains which can lead to chain branching and/or crosslinking. While crosslinking in grafted polymer chains is desirable in a number of applications, it limits the application of the polymers as reagents and substrates for solid phase and combinatorial chemistry because the crosslinked density ultimately defines the accessibility of functional groups on the grafted surface. For example, it has been determined that when acrylic acid is grafted onto PP substrates under different conditions, samples can have variable degrees of grafting. However, when such samples are used as substrates for solid phase peptide synthesis, the peptide loading is not proportional to the percent of grafting. Surprisingly, the substrate with lower percent grafting gave a higher peptide loading than that with a much higher percent grafting.¹²

Herein we report an efficient procedure for graft polymerization of styrene onto PP substrates using BP and BEE as photosensitizers and methanol as a solvent. The graft polymerization was carried out by photoirradiation of a methanol solution of styrene containing a photosensitizer (BP or BEE) in the presence of polymer substrates. The effects of various parameters, such as photosensitizer and monomer concentration, reaction time, and solvent, on percent grafting were studied. The morphology of the polystyrene (PS) grafts on the PP surface was examined with optical microscopy. The graft polymers obtained from these two systems were characterized by high resolution ¹H-NMR, and swelling studies.

EXPERIMENTAL

Materials

PP substrates were supplied by Glaxo-Wellcome, Inc. (RTP, NC). These substrates were prepared by injection-molding techniques and had the form of pins and crowns.¹³ The PP substrates were prepared by the following steps: (1) a 0.1% Alconox detergent wash for 15 min; (2) rinsing 3 times in deionized water for 15 min each rinse; (3) rinsing with acetone twice; and (4) drying in a vacuum oven at 60°C to constant weight. Styrene (99%) was obtained from Aldrich (Milwaukee, WI) and was deinhibited by passing it through a column

containing alumina. BP (99%), BEE (99%) and PS standard with $M_w = 65,000$ g/mol (Aldrich) were used as received. 1,4-dioxane-d₈ (99%) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). All other chemicals were reagent grade and used as received.

Grafting Reactions

The grafting experiments were performed in Pyrex glass tubes. The photosensitizer, BEE (or BP), and the solvent were added first, followed by H₂SO₄ and CuSO₄ to reach the final concentrations of 0.2M and 5×10^{-3} M, respectively (which have been reported to enhance grafting and to suppress nongrafting homopolymerization reactions in solution¹¹), then monomer to a total volume of 15 mL. Accurately weighed PP substrates (usually 15 pieces, ~ 170 mg/piece) were fully immersed in the monomer solution. The reaction mixture was purged by bubbling with argon gas for 10 min to remove oxygen, and the tubes were sealed. For the irradiation, the tubes were positioned on a rotating frame in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company, Branford, CT) equipped with 16 ultraviolet (UV) bulbs; each bulb is 15W with a wavelength of 350 nm. The distance between UV source and tubes was about 3 cm.

After irradiation for a selected time period, each series of PP substrates was quickly removed from the monomer solution and extracted for at least 72 h in benzene to remove nongrafted homopolymer. The PP substrates were then washed in acetone and dried at 60°C under vacuum to a constant weight.

The degree of nongrafting homopolymerization was evaluated in the following manner. After irradiation, the grafting solution was poured into methanol (100 mL) to precipitate nongrafted homopolymer, if any. The homopolymer which adhered to the polymer substrates and the tube was dissolved in benzene (20 mL), and the benzene solution was added to the methanol in a beaker along with benzene extraction solution of the grafted substrate. The beaker was heated to coagulate all polymer. The mixture was cooled. The formed precipitate was recovered by decanting off the supernatant, washed 3 times with methanol, and dried at 60°C under vacuum to a constant weight. Percent grafting and degree of nongrafting homopolymerization were calculated by the following equations:

$$\text{Percent grafting (\%)} = \frac{W_g}{W_{pp}} \times 100 \quad (1)$$

Degree of homopolymerization (%)

$$= \frac{W_h}{W_g + W_h} \times 100 \quad (2)$$

where W_{pp} is the original weight of PP substrates, W_g is the weight difference between the extracted PP substrates after grafting with styrene and the PP substrates before grafting, and W_h is the weight of the ungrafted homopolymers which formed in the medium during the grafting process.

Swelling Experiments

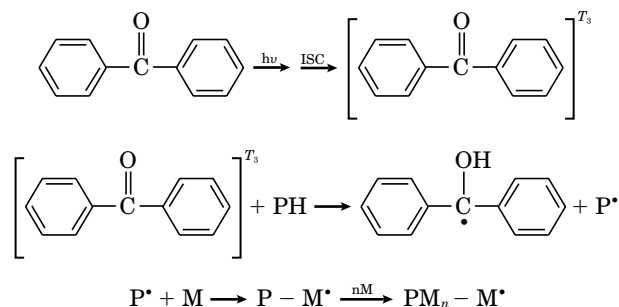
The accurately weighed samples were immersed in toluene and equilibrated at 25°C for various time intervals. The swollen samples were removed from the solvent, wiped dry on the surface with absorbent paper, and weighed in a capped vial as a function of time, then extrapolated to the time equal to zero to obtain the weight of the swollen substrate. All experiments were performed in duplicate and the swelling ratios of the PS grafts were calculated using the following equation:

$$\text{Swelling ratio} = \frac{\Delta W_{(t=t)} - \Delta W_{(t=0)}}{\Delta W_{(t=0)}} \quad (3)$$

where $\Delta W_{(t=0)}$ is the initial weight of PS grafts on PP substrates, e.g., the weight difference between the styrene-grafted PP substrate and the original one; and $\Delta W_{(t=t)}$ is the weight of PS grafts on PP substrates (corrected from swelling of PP substrate) at various swelling times.

NMR Analysis

A PS standard with $M_w = 65,000$ g/mol (Aldrich) was chosen as a model linear polymer for comparison with the grafted materials. PS grafts from the BEE system were stripped off the PP surface with a razor after the grafted surface was first swollen with toluene. The swollen PS-grafted surface from the BP system was also carefully removed with a razor. The removed PS-grafted phases were swollen in 1,4-dioxane- d_8 (99%) for $^1\text{H-NMR}$ studies. All the nuclear magnetic resonance (NMR) experiments were performed using a Bruker AMX 300



spectrometer. In order to obtain accurate peak integration data, the pulse recycle delay was set to 30 s, which is longer than $5 \times T_1$ of the samples under study.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The photochemical grafting of vinyl monomers onto polymer surfaces can be achieved using a photosensitizer such as BP or BEE. (See scheme above as shown by Allmer et al. in ref. 3.) Irradiation of BP with UV light at a wavelength of 350 nm efficiently gives the triplet excited state via intersystem crossing (ISC) from the initially formed singlet state. BP triplets are effective in abstracting hydrogen atoms from polymer surfaces to generate macroradicals that can initiate graft polymerization.³ However, it has been reported by others that when BP was used to initiate the grafting of styrene onto polyethylene and PP, no grafts were obtained and no satisfactory explanation has yet been reached.^{9,10} On the contrary, we have found that a BP is a very effective photosensitizer for the initiation of the grafting polymerization of styrene onto PP substrate, and the graft polymers obtained with BP are quite different from those with other photosensitizers.

The results in Figure 1 show the effect of monomer concentration in methanol on percent grafting using BP and BEE as photosensitizers. The percent grafting obtained using BP as a photosensitizer increased with an increase of monomer concentration, reaching a maximum in grafting efficiency at a monomer concentration of 3.9M, at which point a steady decline in grafting efficiency was observed with increasing monomer concentration. These results are similar to those obtained using BEE as a photosensitizer, which showed a maximum at monomer concentration of

2.6M. The maxima observed in both cases have been attributed to the Trommsdorff effect of methanol.^{10,11,14} The swellability of the PP substrates is proportional to the concentration of styrene in methanol. At low monomer concentrations, the rates of propagation and chain initiation increase with increasing monomer concentration. The termination rate is low because the mobility of the polymer radical is very small in the less-swollen matrix. High monomer concentrations tend to increase the rate of the propagation reaction, but this effect is overcome by the greatly increased termination rate of the more mobile chains in the swollen matrix. Thus there is a monomer concentration at which the grafting rate is a maximum.

BP is not only a very effective photosensitizer for grafting of styrene onto a PP substrate but also quite useful because it does not initiate nongrafting homopolymerization of styrene in solution (Fig. 2). The BP triplet turns into benzhydryl radical after abstracting a hydrogen atom from the polymer surfaces. The benzhydryl radical is apparently too bulky to initiate polymerization of styrene by itself, therefore it only participates in termination reactions. When BEE is used as a photosensitizer to initiate the grafting of styrene onto a PP substrate, a significant amount of unde-

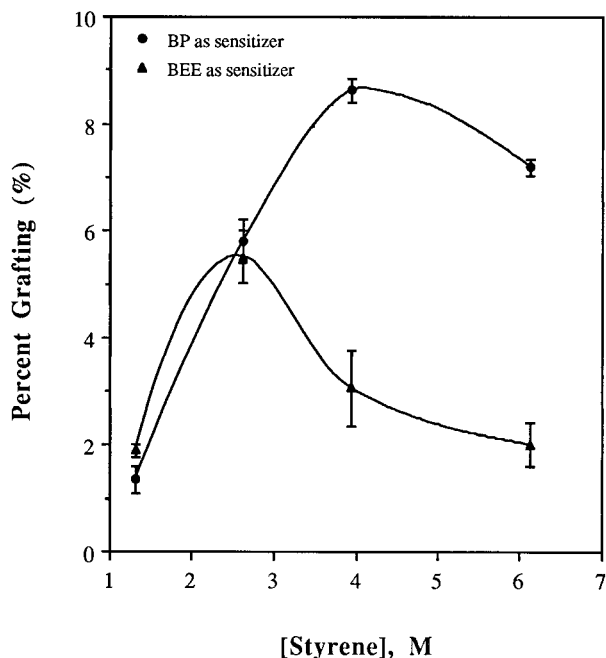


Figure 1 Effect of monomer concentration on graft polymerization of styrene onto PP substrates. Concentration of photosensitizer: $5.5 \times 10^{-2}M$; irradiation time: 6 h.

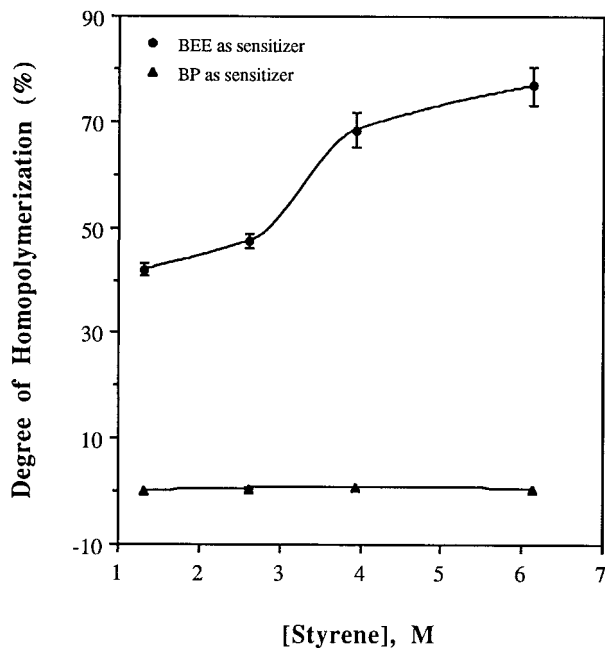


Figure 2 Effect of monomer concentration on nongrafting homopolymerization in photografting of styrene onto PP substrates. Concentration of photosensitizer: $5.5 \times 10^{-2}M$; irradiation time: 6 h.

sired nongrafting homopolymerization in solution occurs. The radicals derived from the direct decomposition of BEE can both initiate the nongrafting homopolymerization of styrene monomer in solution and abstract hydrogen atoms from polymer surfaces to generate macroradicals which can initiate the graft polymerization of styrene. In this system, the nongrafting homopolymerization reaction will compete with grafting reactions; and as such, homopolymer formation is appreciable, which results in difficulty in purifying the grafted materials.

Effect of Irradiation Time

Figure 3 shows the effect of irradiation time on the percent grafting of styrene onto PP substrates using BP as a photosensitizer. The percent grafting increased with an increase in the irradiation time and proceeded much faster at longer irradiation times. In this system, nongrafting reactions were not observed to compete with the desired graft polymerization. The longer the irradiation, the more radicals were generated on the PP surface. However, because the grafted chain mobility is low, chain-end radicals have a low probability of being in position to effect termination. In turn,

the number of reactive sites on the surface increased with the increase in the irradiation time. Because the small monomer molecules still diffuse to the active chain ends even as the termination rate is low, there is a marked increase in polymerization rate. When BEE was used as a photosensitizer, a similar phenomenon was observed. However, the BEE-sensitized reaction system was difficult to study because of the formation of the nongrafted homopolymer which precipitates out of solution when methanol is used as the medium.

Effect of Photosensitizer Concentration

The effect of the concentration of the photosensitizer on the percent grafting of styrene onto the PP substrates is shown in Figure 4. Both BEE and BP were found to be effective photosensitizers for the initiation of the graft polymerization of styrene onto PP substrates. The percent grafting using BP as a photosensitizer is higher than that using BEE under the same grafting conditions. The maximum amount of grafting was obtained when the photosensitizer concentration was about $2.75 \times 10^{-2} M$ in both cases.

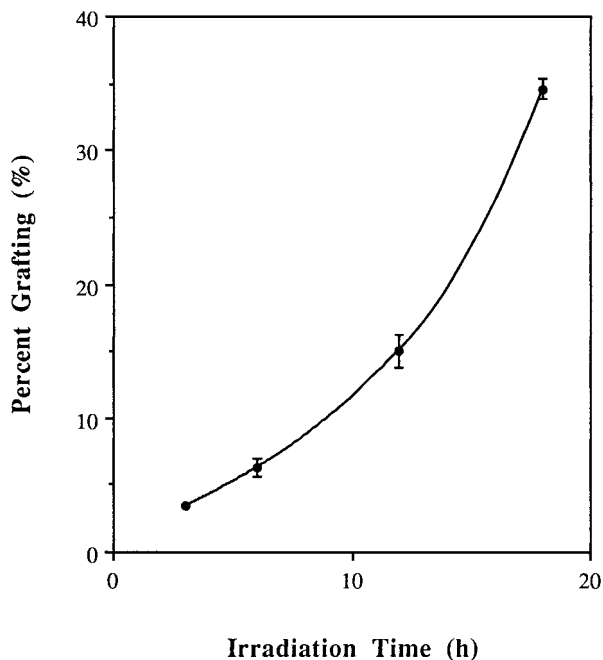


Figure 3 Effect of irradiation time on graft polymerization of styrene onto PP substrates. Concentrations of styrene: $2.6 M$; concentration of BP: $5.5 \times 10^{-2} M$.

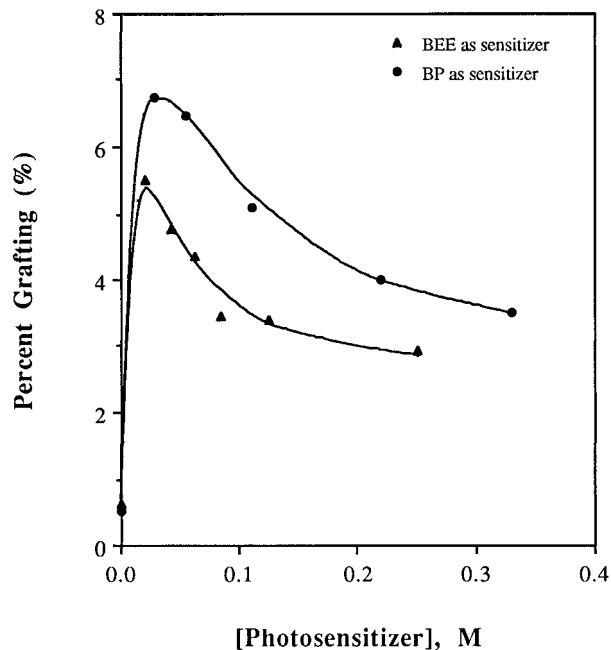


Figure 4 Effect of photosensitizer concentration on graft polymerization of styrene onto PP substrates. Concentrations of styrene: $2.6 M$; irradiation time: 6 h.

Swelling Studies

When extracting the PP substrates with benzene to remove ungrafted PS homopolymer after irradiation, we observed a significant difference between the grafted PP substrates obtained using BP and BEE as photosensitizers. The grafted surface on the PP substrate from the BEE system became a highly swollen, transparent, "gel-like" layer on the PP surface when soaked in benzene and could be easily stripped off the surface with a razor. The grafted layer of PS on the PP substrate obtained from the BP system was very dense and could not be highly swollen with benzene. The difference between the grafted surfaces obtained using BEE and BP as photosensitizers is apparently a result of different degrees of crosslinking of the grafted PS chains. Since both BEE and BP can initiate the graft polymerization of styrene on PP surfaces, they are also capable of generating active sites onto previously grafted chains, leading to branching and a dense network.

The distribution and swellability of the grafted PS surface on the PP substrates was studied by optical microscopy. The photographs in Figure 5 show clear phase-separation lines between the grafted PS surface phase and the PP substrates. The swelling capacity of the grafted surfaces on substrates obtained with both initiating systems

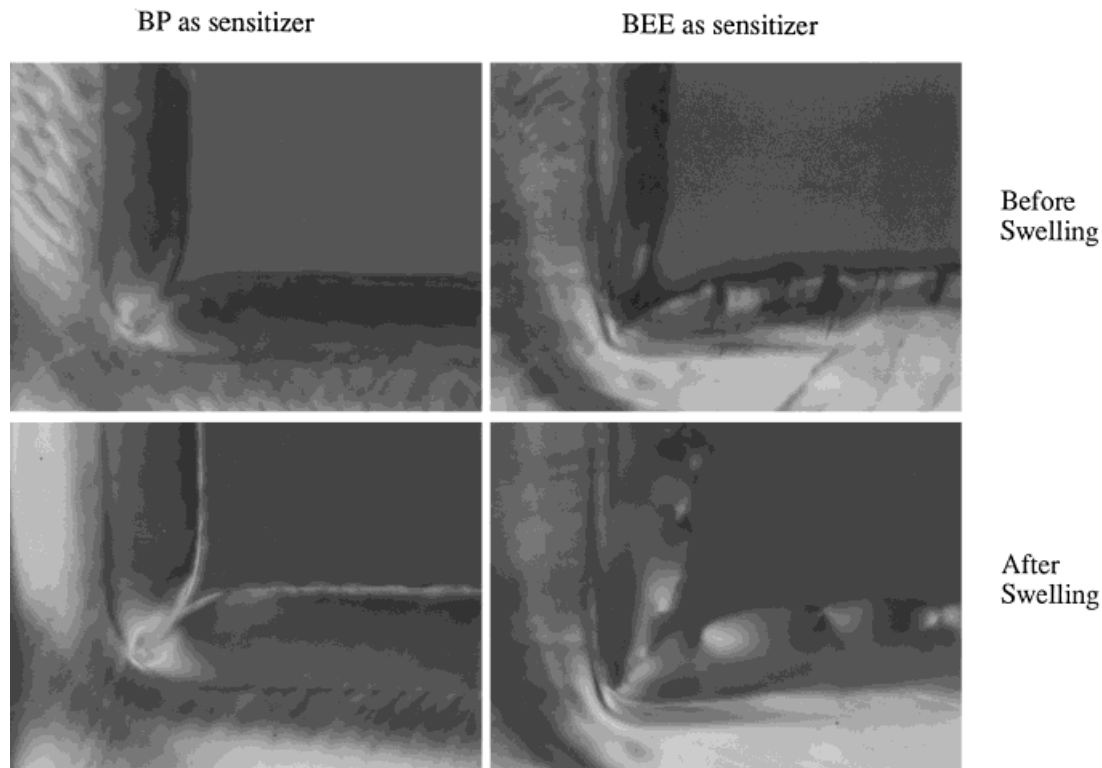


Figure 5 Microphotographs of cross sections of the PS-grafted PP substrates obtained using BP and BEE as photosensitizers before and after swelling with toluene at 25°C.

were also examined under the optical microscope (Fig. 5). After soaking in toluene for 1 h, the dimension of the swollen surface from BEE was almost twice the thickness whereas the grafted phase from the BP system was much less swollen. The surface morphology was also observed to be a function of the initiating system. The grafted surfaces from the BP system were uniform and had a smooth surface, whereas the grafted surfaces obtained from the BEE system were not uniform and were found to have a rough surface, even after swelling.

The degree of swelling of the PS-grafted phase with toluene for both initiating systems is shown in Figure 6. As expected from the optical micrographs, the degree of swelling of the grafted phase obtained using the BEE as a photosensitizer is much higher than the one obtained using BP at the same weight-percent grafting. This indicates that the degree of branching and/or crosslinking is higher in the grafted surfaces obtained using BP than in those obtained using BEE. The time required to attain equilibrium is much shorter for the grafted surface obtained using BEE (1 h) relative to those obtained using BP (7 h). The slow swelling rate is a result of the low diffusion rate of the solvent molecules as the

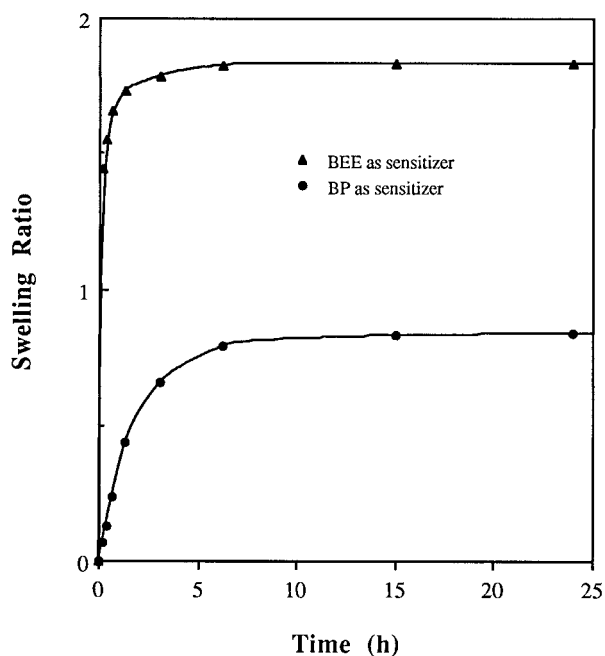


Figure 6 Swelling of the grafted PS surfaces on PP substrates with toluene at 25°C.

degree of branching and/or crosslinking increases. This difference in swelling can play an important role in their application to solid phase and/or combinatorial syntheses because rapid and reproducible reaction steps are crucial to a viable substrate system.

NMR Analysis

The branching and/or crosslinking of the grafted PS surfaces was further studied by $^1\text{H-NMR}$ spectroscopy. Linear PS has a 5 : 3 ratio of aromatic protons to aliphatic (backbone) protons. If the grafted PS chains begin to branch (leading to network formation) then this ratio will decrease because grafting would consume tertiary hydrogen atoms along the polymer backbone. A linear PS standard with $M_w = 65,000$ g/mol was chosen as an NMR reference. The grafted PS phases were removed with a razor from the PP substrate surfaces. All of these samples were put into the 1,4-dioxane- d_8 in different NMR tubes. The linear PS standard dissolves instantly. Some of the grafted phases from the BEE system clearly dissolved, but the majority of the excised PS grafts swelled to clear gels dispersed in the medium. The grafted surfaces obtained from the BP system swelled only slightly upon the addition of 1,4-dioxane- d_8 and ultimately floated on the top of the solvent. A spherical glass insert filled with 1,4-dioxane- d_8 was used to place the PS grafts into the right position in the NMR tube in order to obtain an accurate NMR spectrum.

The data shown in Table I indicates that the abundance of methine hydrogens on the polymer backbone decreased relative to PS standard when BEE was used; this was also the case, but to a more significant degree, when BP was used. This indicates that the degree of branching and/or crosslinking in the grafted surfaces obtained using BP is higher than that obtained with BEE, which is consistent with the swelling experiments.

CONCLUSIONS

We have demonstrated that BP is a very effective photosensitizer for the grafting of styrene onto PP substrates. More importantly, BP only initiates the grafting of styrene onto the substrates and does not lead to nongrafting homopolymerization of styrene. This is advantageous over other photosensitizers such as BEE and its derivatives, which produce a significant amount of nongrafted homo-

Table I Ratio of Aromatic Protons to Aliphatic Protons of the Polystyrenes (PS) Obtained Using Different Polymerization Methods

Sample	Ratio of Aromatic Protons to Aliphatic Protons
PS (standard)	5 : 3.0
PS (BEE)	5 : 2.9
PS (BP)	5 : 2.6

polymer in solution. The swelling studies and the high resolution $^1\text{H-NMR}$ analysis indicate that the PS-grafted surface obtained using BP as the photosensitizer has a higher degree of branching and/or crosslinking than that obtained using BEE. This difference in grafting needs to be considered when accessibility to functional groups on grafted substrates is important, such as in solid phase and combinatorial chemistry.

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