

Surface Modification of Polypropylene by a Combination of Photooxidation and Photosubstitution Reactions

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SYNOPSIS

An efficient photoprocess has been developed to increase polypropylene surface wettability by insertion of acid, ester, and amide functionalities. A systematic study of polypropylene surface irradiations indicates that photooxidations always precede the photosubstitution reactions that occur at the carbonyl site to form carboxyl, ester, and amide groups. Irradiations with amines to form amide groups always achieved the highest level of wettability improvement without changing bulk morphology. This process may be very beneficial in facilitating the fabrication of composite membranes with hydrophilic barriers on top of a hydrophobic polymeric support such as polypropylene. The high chemical resistance of polypropylene matrix to various solvents makes the partially hydrophilized polypropylene an ideal membrane support when hydrophilic membrane barriers made by interfacial polymerization/crosslinking are needed for a variety of separation applications. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Surface modification of polymers by UV/EB (electron beam) grafting of monomers, such as acrylates, is well documented in the polymeric literature.¹⁻³ However, very few works have dealt with the surface photofunctionalization of polymers (e.g., polyolefins) with small hydrophilic groups (e.g., photochlorination⁴). Recently, it was found in our labs that irradiation of alkylbenzene compounds with various alcohols resulted in substitution of the benzyl hydrogens with alcoholic moieties in a very selective mode.⁵ The alkylbenzenes underwent photosubstitution only at the α position to the aromatic ring, whereas the aliphatic alcohols reacted exclusively at the α position to the hydroxyl group. Similarly, this high selectivity was also observed in the photooxidation of alkylbenzenes.^{6,7} A series of alkylbenzene compounds with up to C₄ open chain alkyl substituents underwent the same course of photoreaction at the α position to the aromatic ring, as no oxidation of the aromatic ring itself was detected under these

circumstances. Based on those studies, we adopted a similar approach to photochemically insert oxygen and nitrogen containing groups on polypropylene films.

This photomodification process seems to be very beneficial in facilitating the fabrication of composite membranes with hydrophilic barriers on top of hydrophobic polymeric support such as polypropylene. Recently, we were engaged in the development of new membranes for the separation of extraction solvents such as furfural and *N*-methyl-pyrilidone (NMP) from diesel fuel extract and raffinate. A well-known type of membrane synthesized previously for our lube oil/solvent separations is the composite membrane that contains a porous matrix and on top of it a dense barrier layer that actually accomplishes the separation. For the diesel/furfural and the diesel/NMP separations the thin barrier layer was made *in situ* by an interfacial crosslinking of a polyimine, or by an interfacial polymerization of an amine with diisocyanate or dicarbonylchloride monomers. The high chemical resistance of polypropylene matrix to NMP, makes the partially hydrophilized polypropylene obtained by our surface modification process an ideal membrane support for the above hydrophilic barriers.

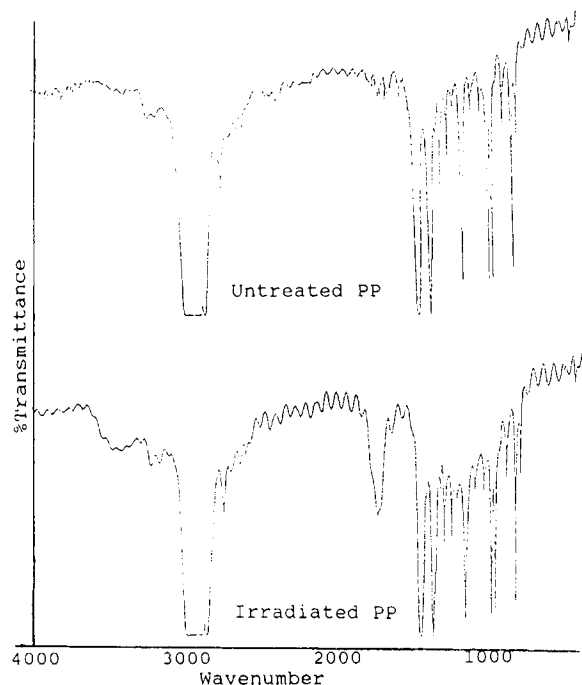


Figure 1 IR analysis of polypropylene irradiated without substituents.

EXPERIMENTAL

Polypropylene films were irradiated in a Rayonet photoreactor containing 16 lamps of 35 W each. The films were soaked prior to irradiation in various alcohols or amines that served as the hydrophilic sub-

stituent donors. The polypropylene surfaces were then exposed to UV irradiation at 185–253 nm under air or nitrogen atmosphere. The samples were analyzed by reflectance FTIR for functionality identification, by X-ray photoelectron spectroscopy (XPS) for elemental analysis of oxygen and nitrogen, and by X-ray diffraction (XRD) for analysis of bulk morphology. Surface wettability was measured by contact angle analysis.

The detailed synthesis of the polymeric membranes are documented elsewhere.^{8,9} A pressure driven flow cell system was used to evaluate membrane performance in separating the diesel/furfural and the diesel/NMP streams. Membrane flux was given in kilogram/square meter/hour (kmh) units and selectivity was expressed as percent diesel rejection {rejection (%) = 100 (feed concn – permeate concn)/feed concn}. Feed and permeate were analyzed by refractive index measurements using calibration curves for each stream.

RESULTS AND DISCUSSION

The two major groups of substituent donors irradiated with the polypropylene films contain the hydroxyl and the amine functionalities. Irradiations with mono- (e.g., methanol) and di- (e.g., ethylene glycol) alcohols indicated that unlike the alkylbenzene compounds, photosubstitutions in polypropylene are always accompanied by photooxidations,

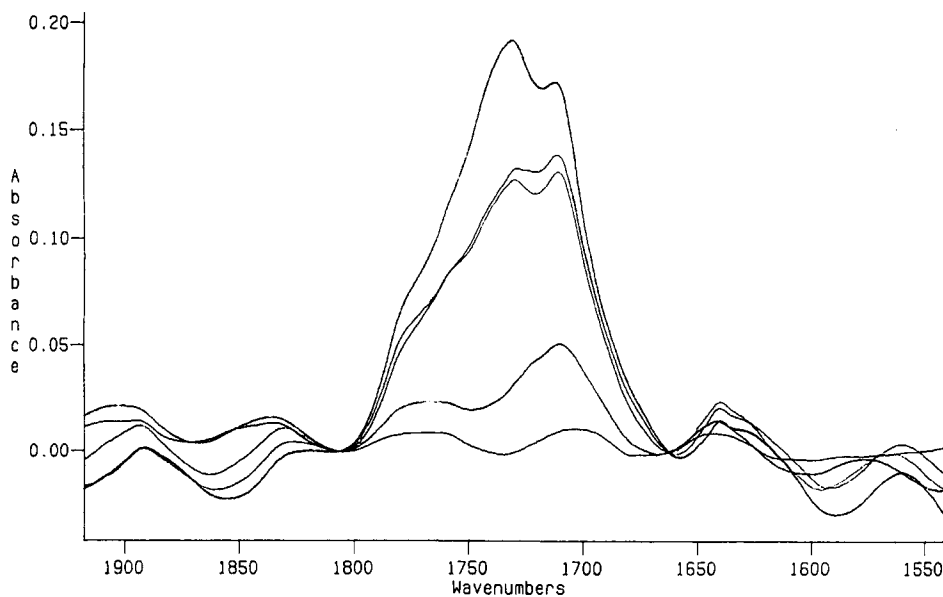


Figure 2 IR analysis of photosubstituted polypropylene with methanol after different intervals of time.

even under nitrogen atmosphere. Photooxidations alone formed carboxylic groups on the polypropylene, as shown by the FTIR of the film before and after irradiation (see Fig. 1).

The IR spectra of a methanol photosubstitution reaction at different intervals of time shows bands at 1710 and 1730 cm^{-1} , which indicates the formation of acid and ester carboxyls, respectively. As the irradiation progressed, the ester groups, which apparently formed by methoxy moieties reacting at the carbonyl site, were growing at a much faster rate (see Fig. 2).

Similar pathways of photosubstitution at carbonyl sites, which followed the preliminary photooxidation, were observed with amine substituents, as IR measurements indicated the formation of amide groups. The absorptions bands at 3264–3287 cm^{-1} in Figure 3 are typical of N—H bands, whereas bands at 1656–1663 cm^{-1} are indicative of CO functionality in an NCO amide group. The position and appearance of these bands are similar to those of *N*-acetyl ethylene diamine, because ethylene diamine (EDA) served as amine donor in our experiments.

XPS measurements of the polypropylene photosubstituted films with amine moieties¹⁰ further supported our structure elucidation, because the nitrogen to oxygen ratios in these samples were always close to the one ratio of the amide (NCO) group (see Table I).

Similar quantities of oxygen insertion was observed with the mono- and di-alcohol's photosub-

Table I XPS and Contact Angle Measurements of Photomodified PP Films

Reactant	% O	% N	N/O Ratio	Contact Angle (°) ^a
—	4	—	—	65
CH ₃ OH	10	—	—	56
HOC ₂ H ₄ OH	11	—	—	56
H ₂ NC ₂ H ₄ NH ₂	9	9.8	1.09	43
(H ₂ NC ₂ H ₄) ₂ NH	11	11	1	49

^a Unreacted polypropylene has a contact angle value of 90°.

stitution reactions on the film surface. However, blank irradiations that resulted only in photooxidation showed a lower amount of oxygen in the polypropylene. Table I also indicates that wettability, expressed in contact angle values, is related to the level of functionalization as well as to the nature of the inserted group. Indeed, some modeling studies performed in our labs on the wettability of polymer surfaces agree quite well with the experimental data.¹¹ The main conclusion derived from our experimental and calculated data is that photosubstitution at carbonyl sites with alcohols or amines, to form ester or amide groups, respectively, always has an advantage over pure processes of photooxidation or photosubstitution in improving wettability.

A series of irradiations under strictly inert conditions of nitrogen atmosphere, showed that photooxidations always occurred, even with minor

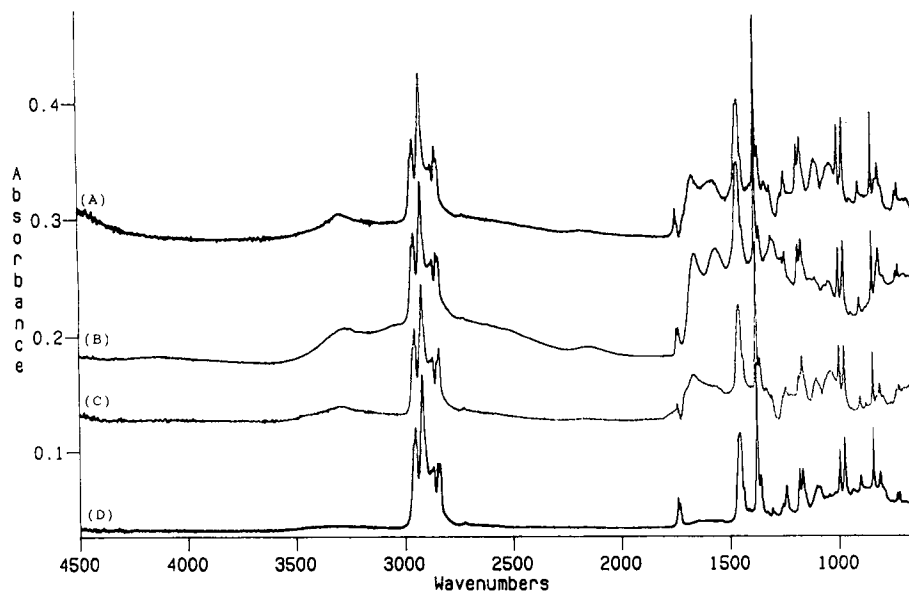


Figure 3 IR analysis of photosubstituted polypropylene with amines: (A) and (C) H₂NC₂H₄NH₂, (B) (H₂NC₂H₄)₂NH, (D) untreated polypropylene.

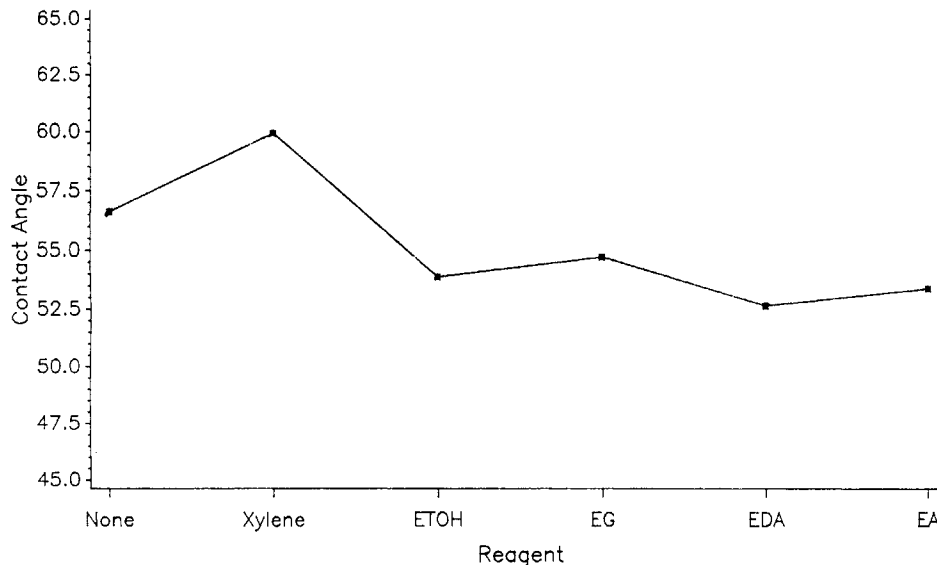


Figure 4 Statistical study of the significance of the substituent factor.

amounts of oxygen, which is apparently absorbed on the film surface. This fact may indicate that the only way to eliminate photooxidation is to irradiate the polypropylene films in a vacuum chamber. Practically, it would be difficult to avoid photooxidations in a large scale process, but our data demonstrates it has no merit because a combination of photooxidation and photosubstitution always results in the highest improvement of surface wettability.

To thoroughly evaluate the experimental factors that affect this photomodification process, a statis-

tical scheme was designed based on our preliminary data. A 6×2^4 factorial design was used in which the reagent factor was investigated at the six following levels: blank (none), xylene, ethanol (EtOH), ethylene glycol (EG), ethylenediamine (EDA), and ethanolamine (EA). The other four factors have two levels each, and the whole scheme involved 96 experiments with three measurements of contact angle for each case. The interpretations of the statistical data further support most of our previous conclusions. As can be seen in Figure 4, the contact angle

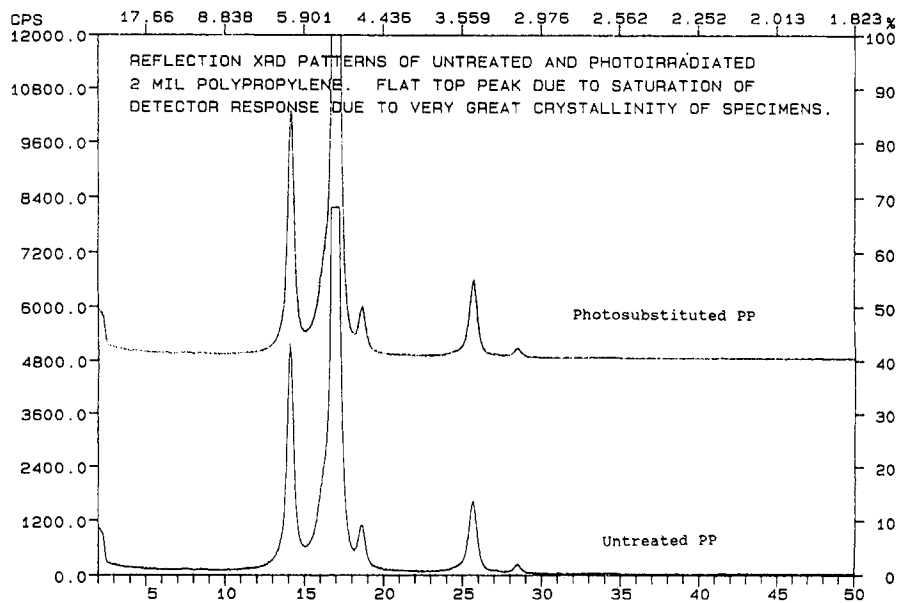


Figure 5 XRD analysis of: (A) photosubstituted polypropylene with methanol and (B) untreated polypropylene.

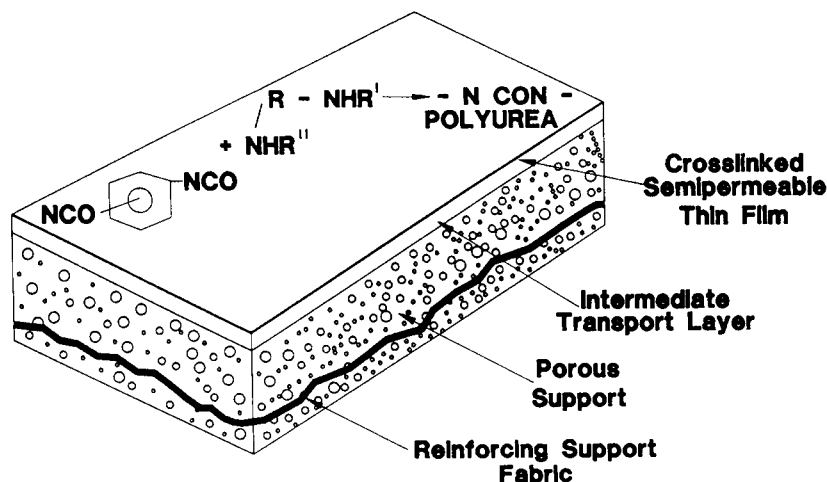


Figure 6 A composite membrane for diesel/solvent separation.

readings for the neutral reagent xylene were significantly higher than those of the other hydroxyl and amine substituents, whereas the values for EDA photosubstitutions were significantly lower.

The fact that blank irradiations with no reagents resulted in better wettability than xylene under certain conditions, may indicate the existence of a screening phenomenon responsible for light absorption and dissipation by the top solvent layer. To avoid such a screening obstacle, more accurate procedures to form thinner solvent layers on top of the polypropylene substrate would be required.

To assure that only surface modifications occurred during our irradiations, XRD analysis was conducted on several of the photosubstituted samples. The diffraction patterns in Figure 5 of the highly crystallized polypropylene films exhibit the same features for an irradiated and a nonirradiated sample, indicating that no change in bulk morphology occurred as a result of the surface photomodification process.

Finally, this process may be very beneficial in facilitating the fabrication of composite membranes with hydrophilic barriers on top of a hydrophobic polymeric support such as polypropylene. In our

recent studies,^{8,9,12} it was found that hydrophilic membrane barriers synthesized by interfacial polymerization or crosslinking on top of a polymeric support are very effective in removal of extracting solvents (e.g., furfural, NMP) from diesel fuel. The composite membrane developed for this application contains barriers formed by polymerization/crosslinking of an amine/polyimine with various diisocyanate/dicarbonylchlorides, to form urea ($-\text{NCON}-$) or amide ($-\text{CON}-$) bonds, respectively (see Fig. 6).

The evaluations of these membranes in separating a 4 : 1 furfural/diesel feed showed excellent selectivity and very good flux (see Table II). In the second stream of 1 : 4 furfural/diesel the membranes showed excellent selectivity and fair flux.

A similar study was also performed on the separation of 1 : 2 and 1 : 3 NMP/diesel streams. Because the development of a membrane support with good chemical stability for NMP had not been completed at this time, only symmetric films of the above chemistry were fabricated. The evaluation results showed excellent selectivity of 99.9% diesel rejection with a good chemical resistance of the barrier films toward NMP. The high chemical resistance of polypropylene toward a variety of strong and reactive solvents, such as NMP, makes the partially surface hydrophilized polypropylene matrix an ideal support for the hydrophilic barriers that are needed in this application.

Table II Membrane Separation of Furfural/Diesel Streams

Feed Ratio Furfural/Diesel	Rejection (%)	Flux (kmh)
4 : 1	99.9	38.5
4 : 1	99.9	53.9
1 : 4	99.9	6.4
1 : 4	99.9	6.9

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