

Polystyrene Photodegradation with a Novel Titanium Dioxide/ Poly(ethylene oxide)/Methyl Linoleate Paint Photocatalyst System

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ABSTRACT: The photodegradation of a polystyrene (PS) film was performed by a titanium dioxide (TiO₂)/poly(ethylene oxide) (PEO)/methyl linoleate (ML) paint photocatalyst system. The PS surface was catalytically photodegraded by the TiO₂/PEO component, and a conjugated carbon–carbon double bond was partially produced. A crosslinking reaction occurred between the PS carbon–carbon double bond and radical species; as a result, the photodegradation diffusion into the inner region was blocked. The additional ML component certainly blocked the crosslinking reaction and accelerated the photodegradation rate. The fraction of less than 10,000 molecular weight of the 4-h-photodegraded film with the TiO₂/PEO/ML paint was 15.1%, and its photodegradation yield increased four times compared with that with the TiO₂/PEO one. The weight loss values of the photodegraded PS part were 9.9, 10.7, and 11.7% at 4, 8, and 12 h, respectively, and gradually increased with increasing irradiation time. Some part of the film was violently photodegraded by the paint, and its photocatalytic effect lasted. The ML was graft-polymerized into the film, and a phase separation was caused. The photodegradation behavior between the 0.05- and 0.1-mm films was remarkably different; this showed that the diffusion of the ML radical was affected by the film thickness. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3490–3496, 2013

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INTRODUCTION

The commercial market of polymeric materials has been developing for a long time, and extensive efforts have been expended on the stabilization of these materials by scientists and engineers. As a result, polymeric materials have enormous stability and are widely used in our lives. However, the intense use of polymeric materials combined with their enormous stability has created serious problems of plastic waste and has given rise to an intensive interest in new polymer systems, such as photodegradable and/or biodegradable materials.^{1–11} Degradable materials have attracted much attention from the viewpoint of their environmental compatibilities.

Polystyrene (PS) is one of the most useful polymeric materials, and it is widely used in packaging materials. Although PS has many attractive properties, its waste does not decompose in landfills and is not good for the environment. PS is a nonbiodegradable polymer. Generally, large molecules such as PS cannot easily enter the cells of microorganisms. Therefore, PS for microorganisms to metabolize. If PS is spontaneously degraded into low-molecular-weight products, it will become biodegradable. In fact, Motta et al.⁶ reported that PS showed biodegradability by a pro-oxidant. The mechanism of PS biodegradation involves two

stages, abiotic and microbial oxidation, and its biodegradation rate strongly depends on the abiotic oxidation stage initiated by a pro-oxidant. Therefore, pro-oxidant development is very important for the preparation of such biodegradable PSs. A titanium dioxide (TiO₂) photocatalyst has been studied as such a pro-oxidant.^{2,3,9,12} TiO₂ photocatalytically reacts with H₂O in air with exposure to sunshine, and OH· is produced. Because OH· has a high reactivity, the photodegradation of polymeric materials can be initiated by OH· under mild conditions.^{2,3,9,12–14} The loading method of TiO₂ photodegradation catalyst has, however, been confined to melt or solution mixing with polymeric materials. The mixing method has been required because of poor diffusion of the photodegradation initiator, and the use of the mixing-type catalyst has limited application. A novel paint-type TiO₂ photodegradation catalyst has been required for commonly used PS products. In our previous study,⁷ the addition of a poly(ethylene oxide) (PEO) microcapsule containing TiO₂ to polypropylene (PP) was performed. The PEO was photocatalytically degraded by the TiO₂, and then H₂O, radical species (initiator), acid, and aldehyde (accelerator) compounds were produced. Because these products had the ability to facilitate PP photodegradation,^{15,16} the addition of the microcapsule caused the PP

photodegradation rate to increase dramatically.⁷ The TiO₂/PEO photocatalyst system must have been effective against the PS photodegradation because the main-chain structure of PS is the same as that of PP. The photocatalyst system has readily been modified by additional components.^{8,10,11} It seems that the photocatalyst system was able to convert to the paint-type as well.

In this study, the photodegradation of PS films was performed by the painting of a novel TiO₂/PEO/methyl linoleate (ML) photocatalyst system. The performance of the system was evaluated by gel permeation chromatography (GPC) and weight loss measurement. The effect of the ML component on the photodegradation was studied by NMR spectroscopy.

EXPERIMENTAL

Materials

PS was purchased from Sigma-Aldrich Co. (St. Louis, Missouri). The GPC curve was composed of two peaks (see Figure 1). The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n , where M_n is the number-average molecular weight) of the major and minor peaks were 3.6×10^5 and 1.3×10^3 and 3.0 and 1.2, respectively. In this study, the characteristics of the PS molecular weight were studied by division into molecular weight regions that were lower (low molecular weight) and greater than 10,000 (high molecular weight). PEO was purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). The average molecular weight was 5.0×10^5 . TiO₂ (anatase-type, diameter $\approx 5 \mu\text{m}$) and ML were purchased from Wako Pure Chemical Industries, Ltd. These were used without further purification.

Preparation of the PS Film

The PS pellets were molded into the film ($50 \times 50 \times 0.05$ or $50 \times 50 \times 0.1 \text{ mm}^3$) by compression molding at 180°C under 40 MPa for 5 min.

Painting of the TiO₂/PEO and TiO₂/PEO/ML Photocatalyst Systems on the PS Film

The painting conditions on the PS film were as follows: 50 mL of water or 25 mL of water + 25 mL of ML solution containing 10 mg of TiO₂, and 500 mg of PEO was prepared. The aqueous

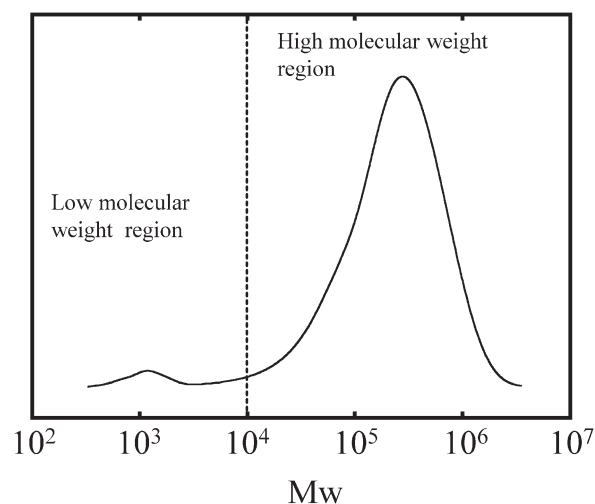


Figure 1. Differential molecular weight distribution curve of the PS film.

solution was painted onto the film surface. The paint amounts were 0.1 and 0.05 g of photocatalyst system/g of film for the 0.05 and 0.1 mm thick films with the same surface ($50 \times 50 \text{ mm}^2$), respectively. In other words, the paint amount of the photocatalyst system was the same per unit area.

Photodegradation Condition

The film was laid on a Petri dish. A 400-W mercury vapor lamp (Toshiba H-400P, Tokyo, Japan, luminance value = 200 cd/cm^2) was used as a UV light source. The distance between the specimens and the lamp was 50 cm. The photodegradation tests were carried out at 30°C.

Degree of Yellowness (ΔYI) Measurement

ΔYI was measured with a Nippon Deshoku ZE 2000 color meter spectrometer (Tokyo, Japan) according to ASTM D 1925 (JIS K7103).

NMR Spectroscopy Measurement

The NMR spectrum was obtained with a JEOL EX-400 spectrometer at 20°C in chloroform d. Tetramethylsilane was added and used as an internal chemical shift reference.

GPC Analysis

The sample in a small vial was dissolved in 5 mL of chloroform, and the obtained sample solution was directly measured by GPC. The molecular weight was determined by GPC (Shimadzu Prominence GPC system, Kyoto, Japan) at 40°C with chloroform as a solvent.

RESULTS AND DISCUSSION

Figure 2 shows the time dependence of ΔYI of the PS film photodegraded with the TiO₂/PEO paint. The ΔYI rapidly increased up to 24 h of irradiation time and then became almost constant. The yellowing was due to the formation of a conjugated carbon-carbon double bond.¹⁷ The formation of the carbon-carbon double bond led to the crosslinking of the PS chains.¹⁸ The crosslinking structure affected the rate of PS photodegradation induced by the TiO₂/PEO paint because it blocked the diffusion of radical species such as OH \cdot . The blocking of the crosslinking reaction certainly led to the acceleration of the photocatalytic conversion reaction to lower compounds of the PS.

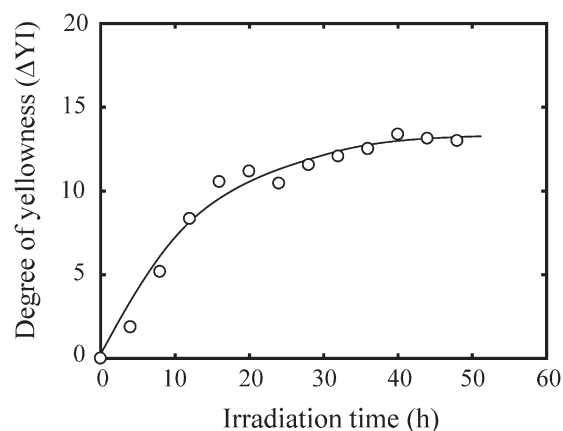


Figure 2. Time dependence of ΔYI of the PS film photodegraded with TiO₂/PEO paint (film thickness = 0.05 mm).

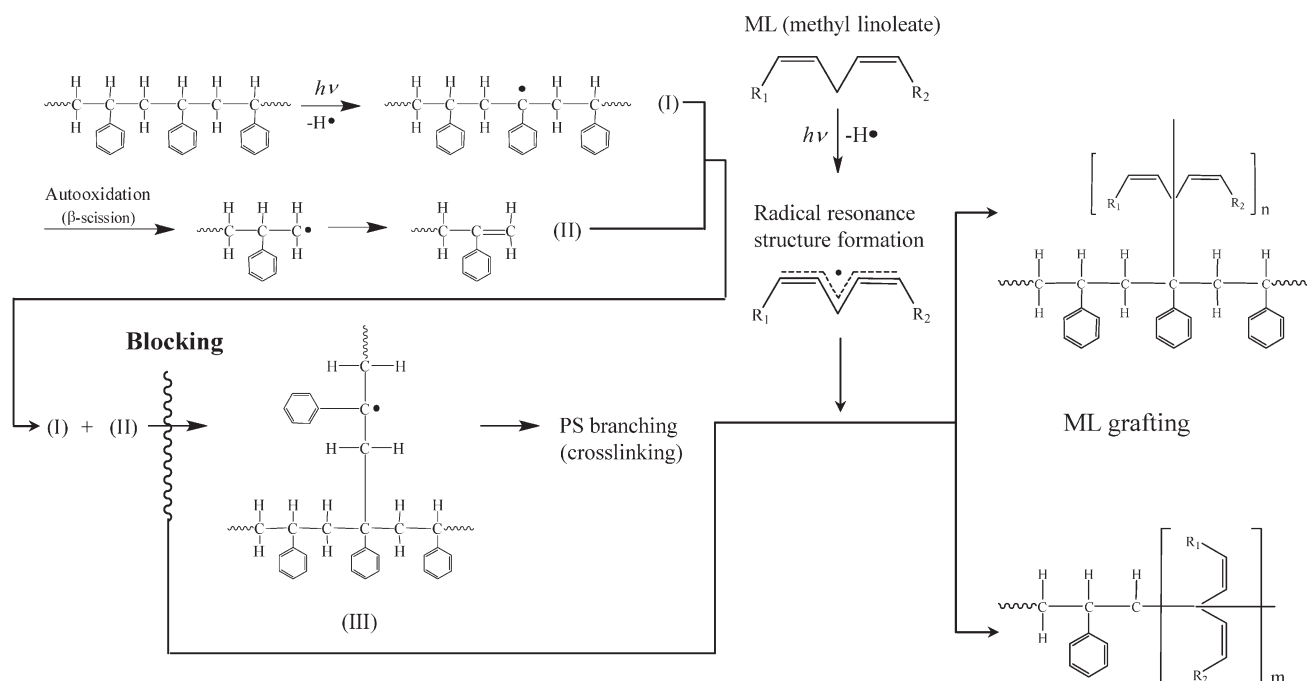


Figure 3. Schematic reaction path induced by the $\text{TiO}_2/\text{PEO}/\text{ML}$ photocatalyst system.

As shown in Figure 3, a crosslinking reaction occurred between the PS large molecules. Therefore, their molecular mobility must have been considerably low. When a small radical molecule with higher molecular mobility was presented in the photodegradation system, it preferentially reacted with the unsaturated and/or radical PS molecules; this led to the blockage of the PS crosslinking reaction. ML is known to be a nonpolar lipid model and has been widely used in antioxidant activity testing.^{19–21} As shown in Figure 3, ML had allyl hydrogens and became a stable radical because of its radical resonance structure. In addition, ML had the compatibility to diffuse into the PS inner part. ML was suitable as a source of such small radical molecules to graft-polymerize with the unsaturated and/or radical PS molecules.

Figure 4 shows the differential molecular weight distribution curves of the pristine PS film and the PS film photodegraded for 4 h. The curves of the photodegraded films both with and without the TiO_2/PEO paint certainly shifted to a higher molecular weight compared with that of the pristine one; this suggested that the PS crosslinking reaction occurred. In contrast, the curve of the photodegraded film with the $\text{TiO}_2/\text{PEO}/\text{ML}$ paint did not show such a shift and did show a drastic increase in the peak intensity in the low-molecular-weight ($<10,000$) region. Figure 5 shows the integral molecular weight distribution curves of the pristine and 4-h-photodegraded PS films. The fraction values of the less than 10,000 molecular weight were 2.5, 2.0, 4.5, and 15.1% for the pristine and 4-h-photodegraded

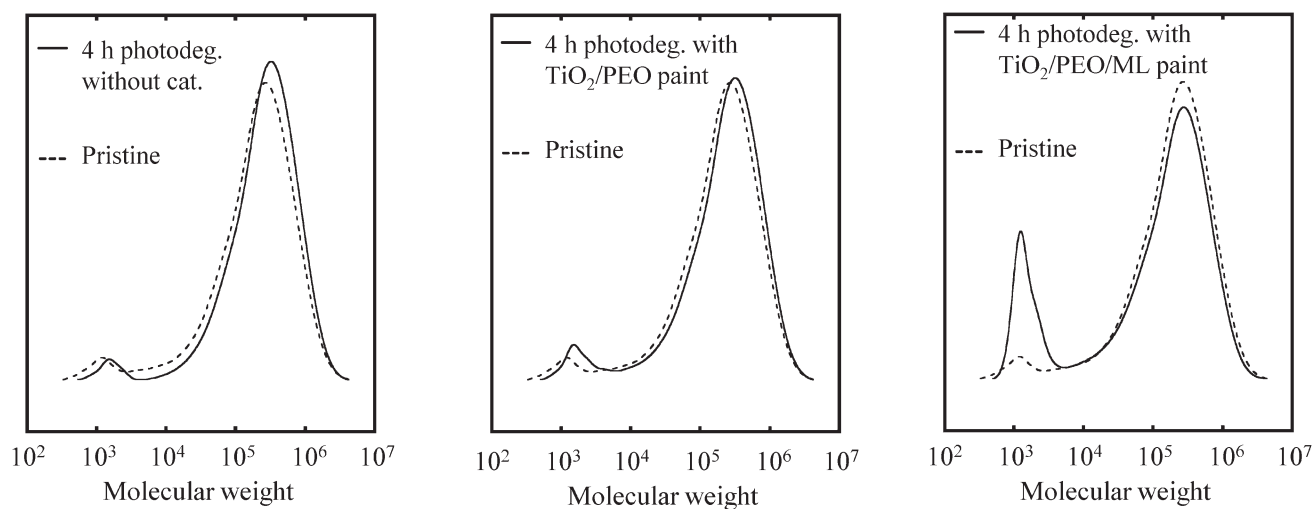


Figure 4. Differential molecular weight distribution curves of the pristine and photodegraded PS films (film thickness = 0.05 mm).

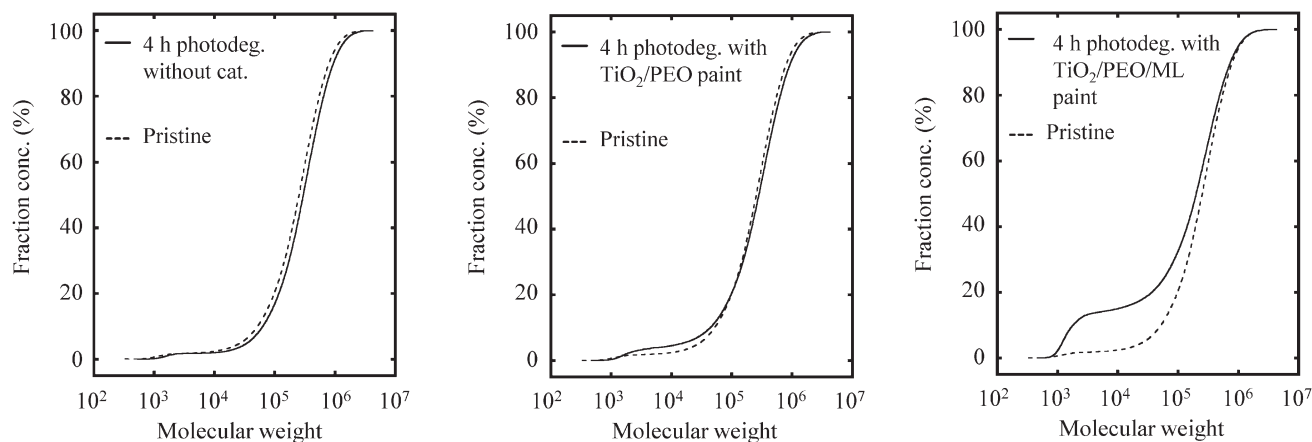


Figure 5. Integral molecular weight distribution curves of the pristine and photodegraded PS films (film thickness = 0.05 mm).

PS films without the photocatalyst and with TiO₂/PEO and TiO₂/PEO/ML paints, respectively. The painting of these photocatalyst systems on the PS film certainly brought about the increment of the low-molecular fraction. In particular, the existence of ML led to a greater increment. Figure 6 shows the irradiation time dependence of the M_w and M_n values in the high-molecular-weight region peak. These values of the photodegraded PS without photocatalyst showed the ups and downs for the irradiation time. Such oscillating behavior was due to competition reaction between the PS chain scission and cross-linking. The M_w and M_n values of the photodegraded PS with the TiO₂/PEO paint showed similar oscillating behaviors. In contrast, these values of the photodegraded PS with the TiO₂/PEO/ML paint decreased with increasing irradiation time; this supported the idea that the ML certainly blocked the PS cross-linking reaction.

Figure 7 shows the irradiation time dependences of the weight loss of the photodegraded TiO₂/PEO/ML paint, PS with the TiO₂/PEO/ML paint, and the theoretical value, where the theoretical value was obtained as follows:

$$\text{Theory value (\%)} = 100 \times [1 - (1 + 0.1 \times (1 - X/100))/1.1]$$

where X is the weight loss (%) of the photodegraded TiO₂/PEO/ML paint. The painted PEO/ML was photocatalytically degraded by TiO₂ on the PS surface, and then, radical species (initiator), acid, and aldehyde (accelerator) compounds were produced.^{15,16,19–21} These products had the ability to facilitate PS photodegradation. The weight loss of the photodegraded paint was about 84% at an irradiation time of 4 h, and most of the PEO/ML components rapidly vaporized from the PS surface. However, some part of the photodegraded components certainly diffused into the PS film and worked as initiators and accelerators for the PS photodegradation. The weight loss values of the photodegraded PS with the paint were 17.6, 18.8, and 19.7% for irradiation times of 4, 8, and 12 h, respectively. The differences between the weight loss values of the photodegraded PS with the paint and the theoretical values for the same irradiation time corresponded to the weight loss values of the net photodegraded PS part. The values obtained from the subtraction were 9.9, 10.7, and 11.7% for irradiation times of 4, 8, and 12 h, respectively, and gradually increased with increasing irradiation time. These results show that some part of the PS matrix was violently photodegraded by the paint photocatalyst system, and the photocatalytic effect lasted during the irradiation.

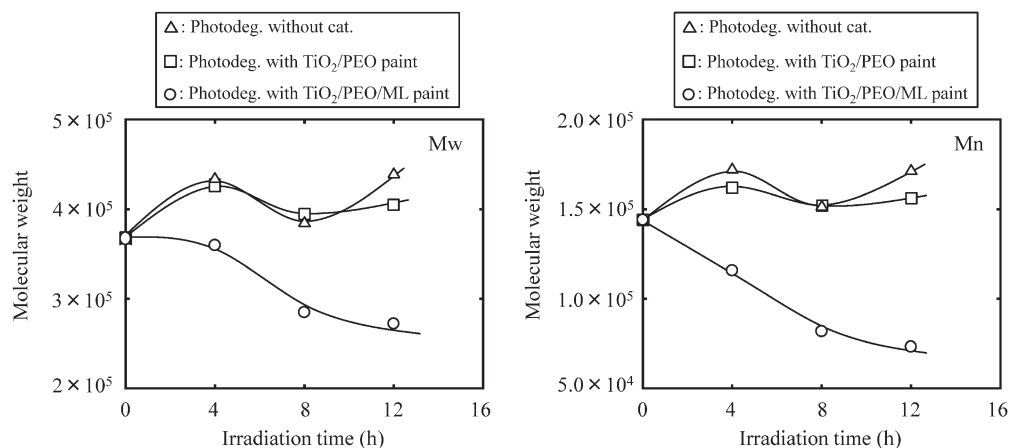


Figure 6. Irradiation time dependences of M_w and M_n in the high-molecular-weight (greater 10^4) region peak (film thickness = 50 mm).

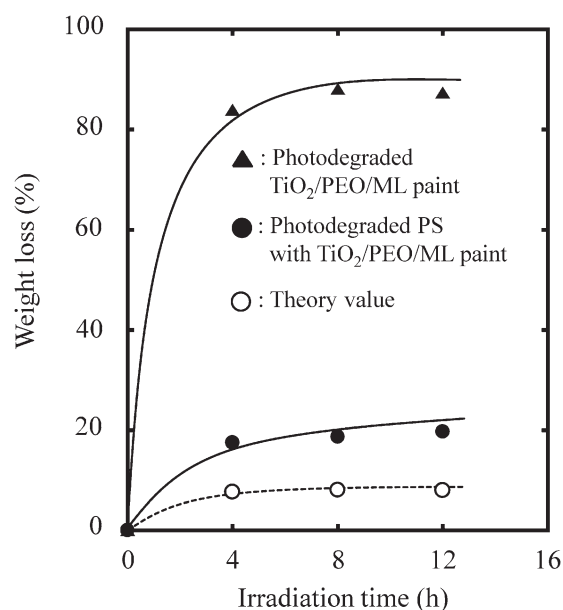
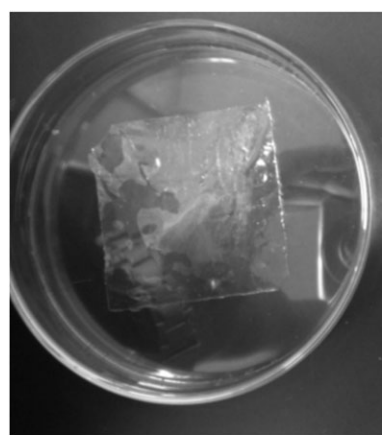


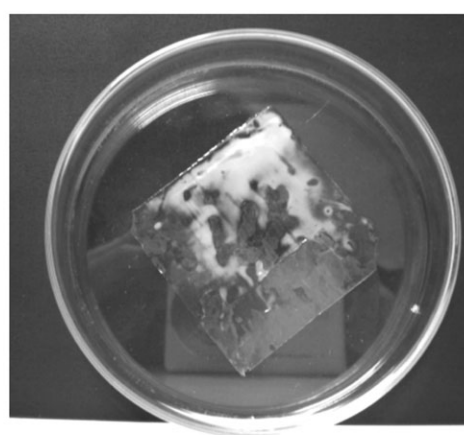
Figure 7. Irradiation time dependences of the weight loss of the photodegraded TiO₂/PEO/ML paint, PS with TiO₂/PEO/ML paint, and theory value (film thickness = 0.05 mm).

Figure 8 shows photographs of the PS films that were undegraded and photodegraded with the TiO₂/PEO/ML paint. The PS painted film showed transparency without irradiation and was whitened after 4 h of irradiation time. The optical transmittance of the whitened part was considerably lower than that of the pure PS one. In addition, the part was composed of not a bubble but a continuous phase. The whitening was caused by the ML graft polymerization. The photodegraded film was plasticized with progression of the photodegradation because of the formation of the low-molecular PS part. Therefore, the graft-polymerized part had considerable mobility and reorganized in the PS matrix. The phase separation brought about the whitened part.

The photodegradation rate of the PS with the TiO₂/PEO/ML paint decreased considerably for the 12 h or more of irradiation.



Irradiation time = 0 h



Irradiation time = 4 h

Figure 8. Photographs of PS films undegraded and photodegraded with the TiO₂/PEO/ML paint (film thickness = 0.05 mm).

tion. The M_w and M_n (the high-molecular-weight region peak) values of the PS photodegraded for 48 h were 6.3×10^4 and 2.3×10^5 , respectively. The decrease in the rate of the molecular weight was only 15% between the samples photodegraded for 12 and 48 h. Such slow photodegradation behavior must have been due to a change in the ML component. Figure 9 shows the ¹H-NMR spectra of the ML and PS photodegraded with the TiO₂/PEO/ML paint for the 48 h. The photodegraded PS spectrum contained some resonances of ML. However, the three resonances assigned to the vinyl (δ 5.5–5.2 ppm) and allyl (δ 2.8–2.6 and 2.1–1.9 ppm) protons were not observed. The loss of the carbon double bond group was due to the oxidation of ML;²² this suggested a loss of ability to block the PS crosslinking reaction. The photodegradation rate was strongly affected by the ML component.

Figure 10 shows the irradiation time dependence of the M_w , M_n in the high-molecular-weight region peak, and fraction of the low-molecular region with different film thicknesses. The M_w and M_n reduction rates of the 0.1-mm PS film were considerably slower than those of the 0.05-mm one. In particular, the film photodegraded for 4 h showed slightly increased M_w and M_n values; this suggested that the crosslinking reaction occurred. It seemed that the ML amount was too small to block the crosslinking reaction. The fraction of the low-molecular region was considerably lower than that of the 0.05-mm film, and the tendency was distinguished at an early stage in addition to the M_w and M_n values. Although the paint amount of the TiO₂/PEO/ML was the same per unit area, the photodegradation behavior between the 0.05- and 0.1-mm films was remarkably different. These results show the diffusion of the radical species, such as the ML radical, was certainly affected by the film thickness, and a greater amount of ML was required with increasing thickness.

CONCLUSIONS

The photodegradation of the PS film was performed by the painting of the TiO₂/PEO/ML photocatalyst system. The PS was catalytically photodegraded by the TiO₂/PEO component, and

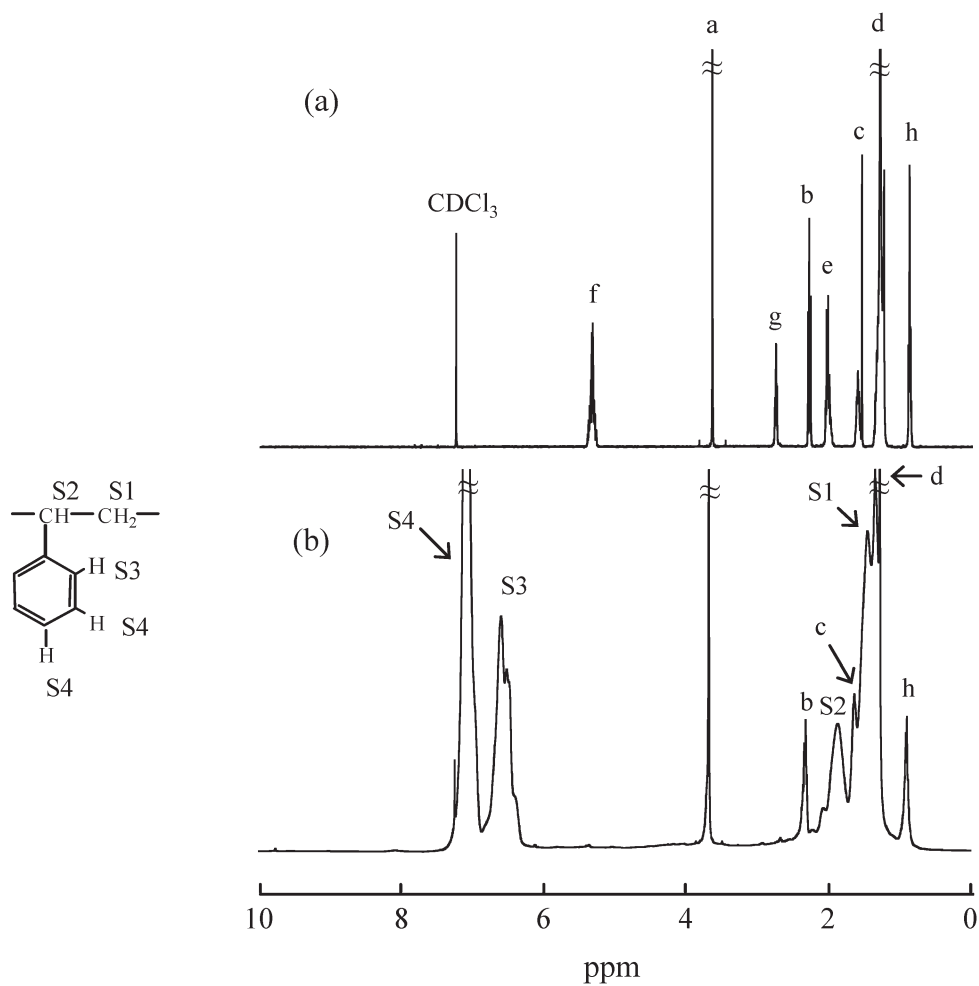
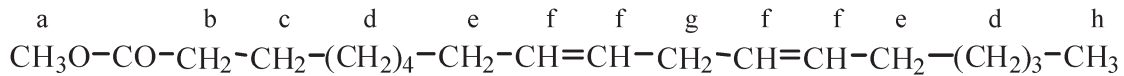


Figure 9. ¹H-NMR spectra of (a) ML and (b) PS photodegraded with TiO₂/PEO/ML paint for 48 h (film thickness = 0.05 mm).

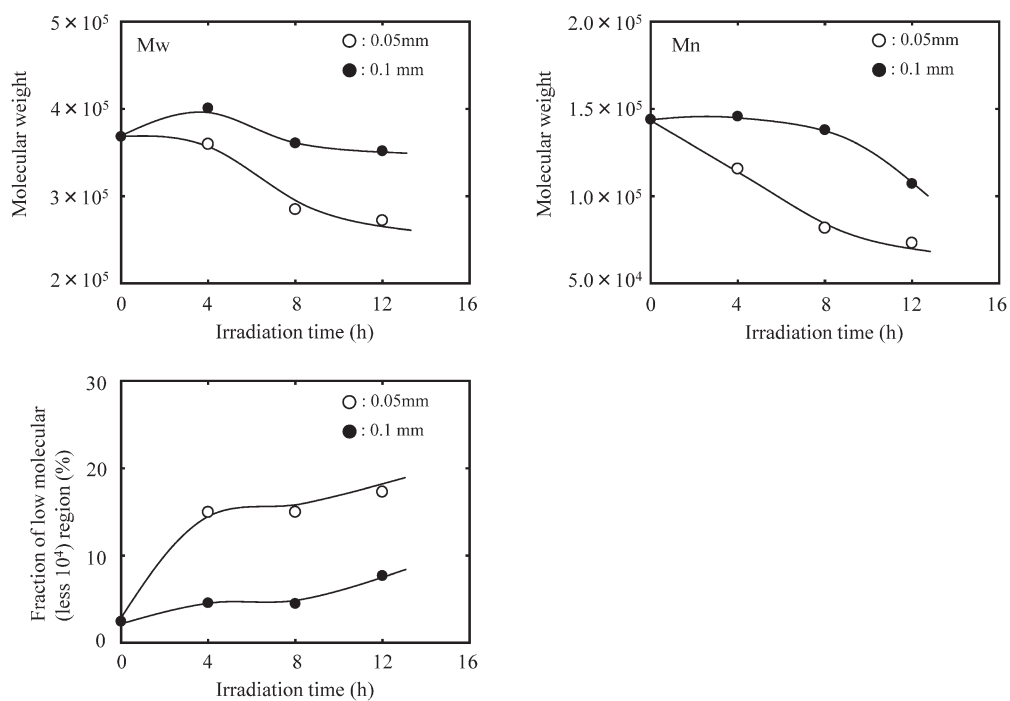


Figure 10. Irradiation time dependences of M_w and M_n in the high-molecular-weight region peak and the fraction of the low-molecular region. Photodegradation was performed with TiO₂/PEO/ML paint.

the conjugated carbon–carbon double bond was partially produced. The crosslinking reaction occurred between the PS carbon–carbon double bond and radical species; as a result, the photodegradation diffusion into the film was blocked. The ML existence certainly blocked the crosslinking reaction and accelerated the photodegradation rate. The fraction of the PS film photodegraded with the TiO₂/PEO/ML paint for 4 h that had a molecular weight of less than 10,000 was 15.1%, and its photodegradation yield increased to approximately four times compared with that photodegraded with the TiO₂/PEO paint. The weight loss values of the photodegraded PS part were 9.9, 10.7, and 11.7% for the films photodegraded for 4, 8, and 12 h, respectively; these gradually increased with increasing irradiation time. Some part of the PS matrix was violently photodegraded by the TiO₂/PEO/ML paint, and its photocatalytic effect lasted. The ML was graft-polymerized onto the PS film, and the phase separation was caused. The photodegradation behavior of the 0.05- and 0.1-mm PS films was remarkably different and showed that the diffusion of the ML radical was certainly affected by the film thickness.

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