

Syntheses and Properties of Photodegradable Polystyrene-Containing Carbonyl Group

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ABSTRACT: The copolymerizations of styrene (St) and methyl vinyl ketone (MVK) or phenyl vinyl ketone (PVK) were carried out in benzene by using azobisisobutyronitrile (AIBN). The synthesized copolymers, poly(St-co-MVK) and poly(St-co-PVK), were identified by infrared (IR) spectroscopy. Under the presence of oxygen, the copolymers containing carbonyl group after UV irradiation showed photodegradable properties that caused by Norrish Type II reaction. The new IR characteristic peaks, such as carbonyl and vinyl groups of the photooxidized copolymers, increased by increasing UV irradiation time. In the photodegradation property, the color differences of the synthesized copolymers were higher than those of polystyrene with increasing UV irradiation time, which was caused by the inherent photodegradable property of carbonyl unit in copolymers. The average molecular weights of samples after UV irradiation for 300 h decreased, as compared with polymers before irradiation. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1237–1242, 1998

Key words: photodegradable polymer; mechanism of photodegradation; color differences of polymers; UV irradiated polymers; average molecular weights

INTRODUCTION

The photodegradable polymers containing oxygen moiety, such as hydroperoxide, peroxide, and various carbonyl groups, have been the main subject of numerous investigations.^{1–7} It was known that one of the most useful methods for obtaining the photodegradable polymer is to incorporate the carbonyl group into copolymer,⁸ which will be able to absorb UV light.

The aim of this work is to synthesize a new photodegradable copolymer-containing carbonyl group by the solution polymerization method. In this study, poly(St-co-MVK) and poly(St-co-PVK) were synthesized from the reaction of styrene (St) and methyl vinyl ketone (MVK) or

phenyl vinyl ketone (PVK) by using azobisisobutyronitrile as an initiator. The structures of the synthesized copolymers were identified by infrared (IR) spectra. The photooxidation, photodegradation, changes of molecular weight, and morphology of the copolymer according to the UV irradiation were also investigated.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK; Aldrich Chemical Co.) and styrene (St; Junsei Chem.) were purified by washing successively with 5% aqueous sodium hydroxide, drying over anhydrous CaCl₂, and distilling under vacuum. PVK was prepared from chloropropiophenone and purified, as described previously.⁹ Azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from methanol. Benzene, tetra-

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Table I The Feed Ratios, Conversions, and Mole Fractions of MVK or PVK in Copolymers

Feed Ratio (wt %)		Conversion (%)	Mole Fraction (%) of Vinyl Ketones in Copolymers ^a	
			MVK	PVK
St : MVK	75 : 25	38	28	—
St : MVK	50 : 50	47	46	—
St : MVK	25 : 75	63	63	—
St : PVK	75 : 25	42	—	44
St : PVK	50 : 50	66	—	58
St : PVK	25 : 75	92	—	66

^a The mole fractions were determined by a UV spectrophotometer.

hydrofuran (THF), dimethylformamide (DMF), acetone, and *n*-hexane were distilled prior to use.

Syntheses of Copolymers

Given amounts of St, MVK, and PVK were dissolved in 100 mL benzene, and the solution was poured into a polymerization tube with 1 wt % of AIBN. After charging with purified nitrogen, the tube was sealed; and the polymerizations were carried out in the various monomer concentrations of 25–75% for 60 h at 60 ± 0.05°C, as shown in Table I. The polymer solution obtained was precipitated in excess methanol, filtered out, and then dried in a vacuum oven until kept at a constant weight. All preparations of the polymers were performed in the dark surroundings. Table I is listed the feed ratios of monomers, conversions, and mole fractions of MVK and PVK in copolymers.

Measurements

Infrared Spectroscopy

The structures of poly(St-*co*-MVK) and poly(St-*co*-PVK) were identified by an infrared (IR) spectrophotometer (Perkin–Elmer 1330). The photooxidation trends of the copolymers were determined by the changes of the IR characteristic peaks due to carbonyl stretching vibration and vinyl out of plane peaks after UV irradiation by using a Fadeo-Meter.

Gel Permeation Chromatography

The average molecular weights of copolymers were determined by gel permeation chromatogra-

phy (GPC) (Waters–Water 244) that was calibrated with polystyrene standards. The eluent was used as THF.

Photodegradation Properties

The photodegradation was determined by a Fadeo-Meter (Atlas) and a color difference meter (ND-101 DP). The prepared film specimens were casted from benzene solutions (ca. 3 wt %) on a nonyellowing, urethane-coated hiding paper. The films were slowly dried at room temperature and then kept under vacuum until they reached a constant weight. The cross-sectional area of the films was 5 × 10 cm³, with a thickness of 35 μm. The color difference values (ΔE) of the films after exposing to UV were calculated by the Hunter–Schofield equation.¹⁰

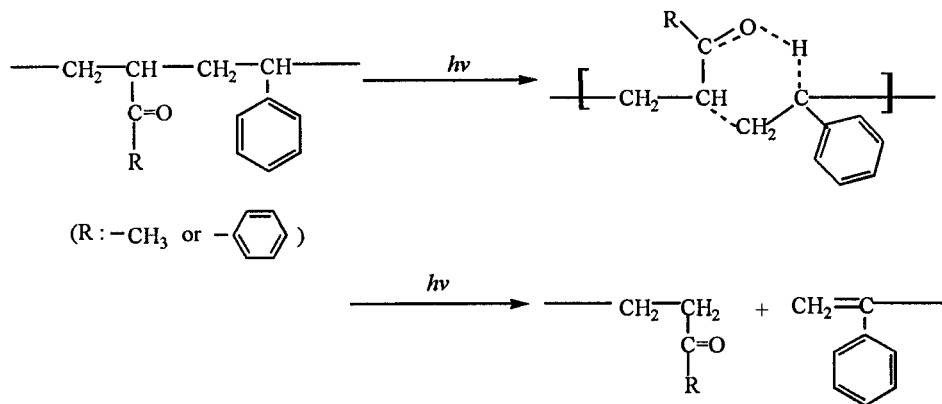
Scanning Electron Microscopy

The morphologies of the copolymers were analyzed by a scanning electron microscopy (SEM) instrument (JEOL JSM35-CF). In the examination of copolymer surfaces, the samples before and after UV irradiation were metallized by gold coating prior to the installation in the SEM chamber.

RESULTS AND DISCUSSION

Characterization

The structures of the synthesized copolymers were identified by IR spectra. In the poly(St-*co*-MVK) spectrum, several characteristic peaks appeared at 3010 (aromatic C—H bond; stretching



Scheme 1

vibration), 2980 (aliphatic C—H; stretching vibration), 1710 (C=O bond; stretching vibration), 1350 (CH₃; bending), and 680–730 cm⁻¹ (aromatic =C—H bond; out-of-plane vibration), respectively. In the poly(St-co-PVK) spectrum, several characteristic peaks are identified at the same ranges of poly(St-co-MVK), together with the carbonyl stretching vibration at 1680 cm⁻¹ due to PVK moiety.

Photodegradation Properties

Photooxidation in Oxygen

Polymers containing carbonyl group have shown to undergo mainly Norrish Type I and II mecha-

nisms.^{11,12} In the presence of carbonyl group at the side chain directly bound to the main chain, only the Norrish Type II causes direct cleavage of the polymer. Therefore, the changes of IR characteristic peaks at 908, 1700, and 1720 cm⁻¹, respectively, can be assigned to vinyl and carbonyl groups of the synthesized copolymers. The main chain dissociation in copolymers may be represented as Scheme 1.

The characteristic peaks in the IR spectrum by photooxidation of poly(St-co-MVK) under oxygen atmosphere are shown in Figure 1. Initially, the carbonyl absorption bands decrease at 1700 cm⁻¹, but the new carbonyl peak begins to increase according to the photooxidation at 1720 cm⁻¹ after

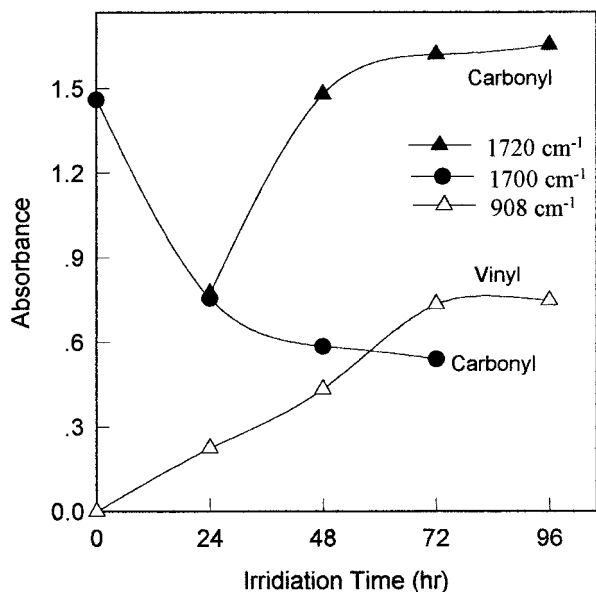


Figure 1 The changes of IR characteristic peaks versus UV exposure time in an oxygen atmosphere for poly(St-co-MVK).

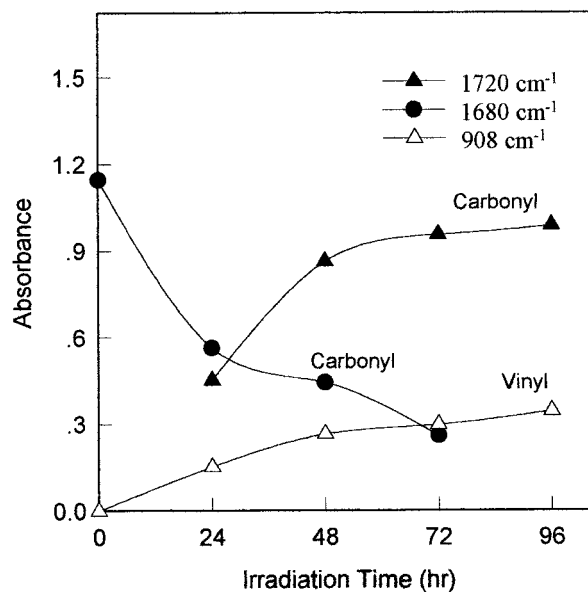


Figure 2 The changes of IR characteristic peaks versus UV exposure time in an oxygen atmosphere for poly(St-co-PVK).

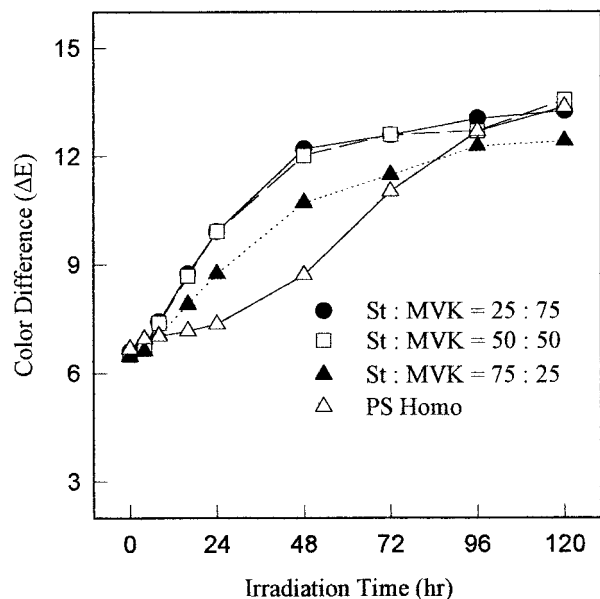


Figure 3 Plot of color differences versus irradiation time for poly(St-co-MVK).

24 h UV irradiation; also, the IR characteristic peak of the terminal vinyl out-of-plane vibration increases with an increase in the UV irradiation time at 908 cm^{-1} . These results may be attributed to the breakage of polymer main chains due to the Norrish Type II mechanism, as shown in Scheme 1. In the photodegradation of poly(St-co-PVK), Figure 2 shows the IR characteristic peaks at 1680 , 1720 , and 908 cm^{-1} , respectively. The pho-

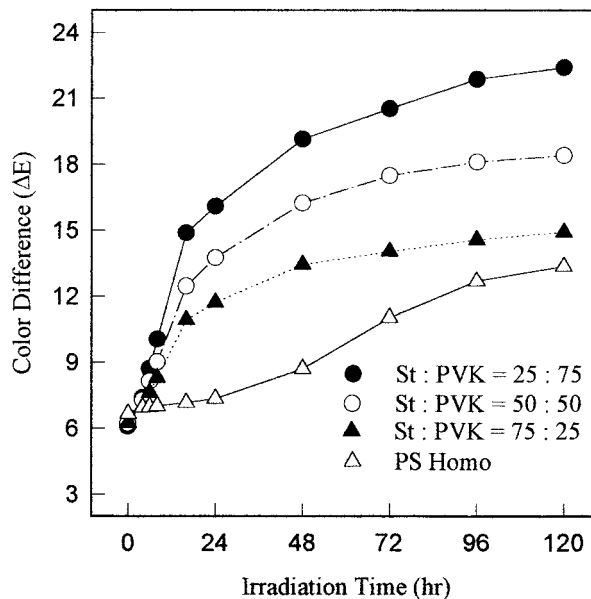


Figure 4 Plot of color differences versus irradiation time for poly(St-co-PVK).

tooxidation property has the same trends, such as poly(St-co-MVK).

Photodegradation

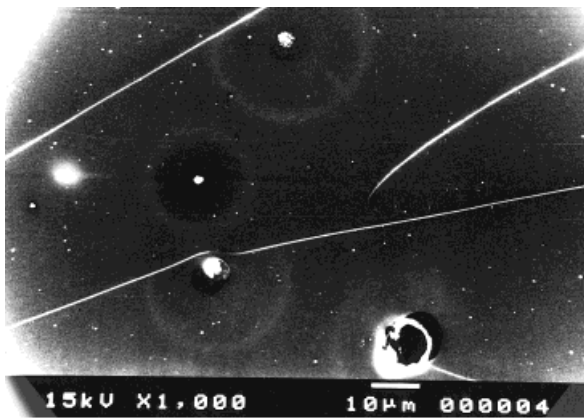
Figures 3 and 4 show the photodegradations of poly(St-co-MVK) and poly(St-co-PVK), respectively, and the values are semiquantitatively expressed in terms of color difference (ΔE) with the National Bureau of Standards Unit.¹³ The copoly-

Table II The Changes of Average Molecular Weights According to UV Irradiation Time

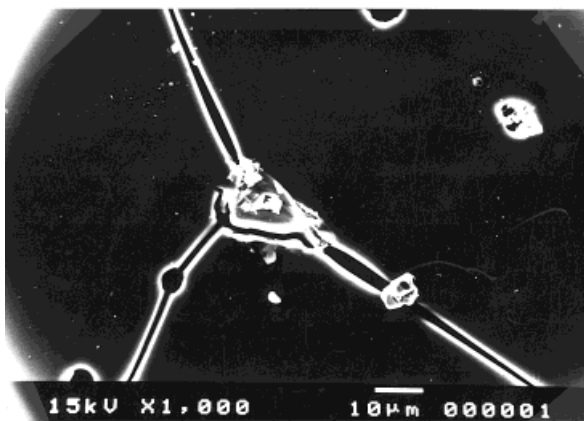
Samples	UV Irradiation Time (313 nm)	Feed Ratio (wt %)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
Poly(St-co-MVK)	0 h ^a	75 : 25	22,200	40,800	1.8
Poly(St-co-MVK)	0 h ^a	50 : 50	24,800	47,500	1.9
Poly(St-co-MVK)	0 h ^a	25 : 75	26,600	55,300	2.1
Poly(St-co-MVK)	300 h ^b	75 : 25	1,600	5,400	3.4
Poly(St-co-MVK)	300 h ^b	50 : 50	1,800	6,200	3.4
Poly(St-co-MVK)	300 h ^b	25 : 75	1,500	3,400	2.3
Poly(St-co-PVK)	0 h	75 : 25	29,000	53,600	1.8
Poly(St-co-PVK)	0 h	50 : 50	35,400	60,000	1.7
Poly(St-co-PVK)	0 h	25 : 75	31,800	58,200	1.8
Poly(St-co-PVK)	300 h	75 : 25	1,500	3,400	2.3
Poly(St-co-PVK)	300 h	50 : 50	2,400	6,100	2.5
Poly(St-co-PVK)	300 h	25 : 75	2,400	6,300	2.6

^a 0 h: polymers before UV irradiation.

^b 300 h: polymers after 300 h UV irradiation.



(A) before UV irradiation (×1,000)



(B) after UV irradiation (×1,000)

Figure 5 Scanning electron micrographs of poly(St-co-MVK) before and after UV irradiation: (A) before UV irradiation (×1000); (B) after UV irradiation (×1000).

mers are evaluated by a Fade-o-Meter in the range from 0 to 120 h. The photodegradable property of poly(St-co-PVK) is much higher than poly(St-co-MVK) at 48 h UV irradiation. This may be attributed to the electron withdrawing effect due to the phenyl group in PVK. The photodegradations of copolymers increase with an increase in the carbonyl moiety; and the color differences exhibit much higher values than that of polystyrene, depending on the increasing irradiation time. The higher photodegradation properties of copolymers may be related to the inherent photodegradable property due to the carbonyl groups in MVK and PVK units of polymers.

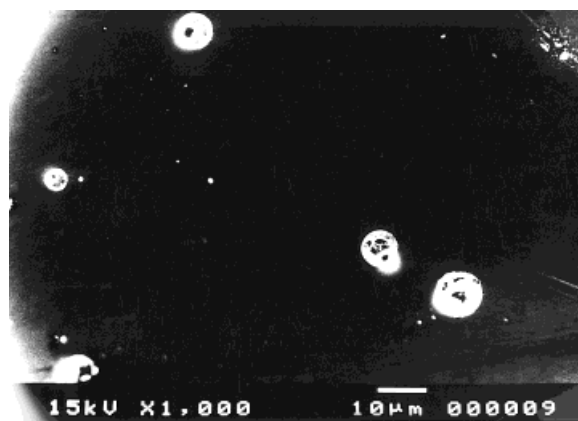
The Changes of Average Molecular Weights

The changes of the average molecular weights in photooxidized copolymers produced as a conse-

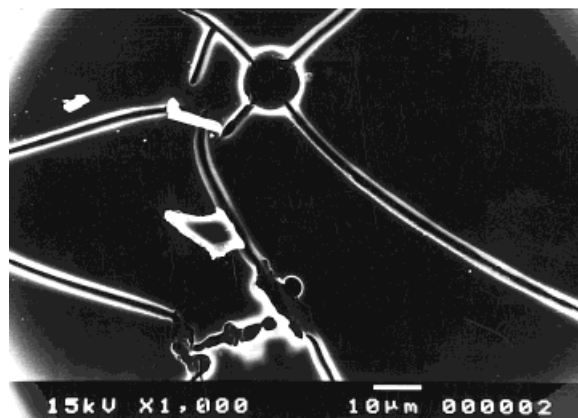
quence of the main chain dissociation by the Norrish Type II reaction were identified by GPC, as shown in Table II. The number-average molecular weights of poly(St-co-MVK) after UV irradiation for 300 h are in the range of 1500–1800 compared with 22,200–26,600 of those before irradiation. In the poly(St-co-PVK), the number-average molecular weights after irradiation are in the range of 1500–2400 compared with 29,000–35,400 before irradiation. The polydispersity indices of both copolymers show the values from 2.3 to 3.4. It is shown that the copolymers after UV irradiation have lower molecular weights with broad molecular weight distributions according to the polymer main chain dissociation, as shown in schemes of photooxidation.

Morphology

In the morphology of samples analyzed by SEM, the film surfaces of copolymers undertaken by UV



(A) before UV irradiation (×1,000)



(B) after UV irradiation (×1,000)

Figure 6 Scanning electron micrographs of poly(St-co-PVK) before and after UV irradiation: (A) before UV irradiation (×1000); (B) after UV irradiation (×1000).

irradiation are shown in Figures 5 and 6. The micrographs of poly(St-co-MVK) and poly(St-co-PVK) after irradiation show the extensive surface crack compared with those before irradiation, which may be ascribed to the photodegradation. This results are consistent with photooxidation and photodegradation results.

CONCLUSIONS

The copolymers, poly(St-co-MVK) and poly(St-co-PVK), were synthesized from the reactions of St and MVK or PVK using AIBN as an initiator by radical polymerization. The photooxidation, photodegradation, change of average molecular weight, and morphology according to UV irradiation were investigated. The important results are summarized as follows:

1. In the IR characteristic peaks of copolymers by UV irradiation under an oxygen atmosphere, initially, the carbonyl absorption bands decreased at 1700 cm^{-1} ; but the new carbonyl peak at 1720 cm^{-1} increased with an increase in the UV irradiation time.
2. In the terminal vinyl out-of-plane vibration, the IR characteristic peak increased with an increase in the UV irradiation time at 908 cm^{-1} .
3. The photodegradations of copolymers increased with an increase in the carbonyl moieties by the MVK and PVK units in copolymers.
4. The number-average molecular weights of copolymers after UV irradiation were in the range of 1500–2400 compared with 22,200–35,400 of those before irradiation.
5. The micrographs of poly(St-co-MVK) and poly(St-co-PVK) after irradiation showed the extensive surface crack compared with those before irradiation.

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