

Scission of the Poly(methyl methacrylate-*co*-methacrylic acid) Chain by Excited-State Acridine

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ABSTRACT: A photochemical reaction between acridine and poly(methyl methacrylate-*co*-methacrylic acid) (PMCA) was studied in benzene to build a recyclable polymer photodegradation system. The illumination of acridine in the presence of PMCA with 365-nm light induced the bleaching of acridine and the degradation of PMCA. The average molecular weight of the degraded polymer decreased rapidly for the first 30 min of the photolysis. A nonvolatile product of this reaction was found to have a 2-methyl-2-

propenyl end group. The efficiency of the PMCA scission by this method was 30 times as large as that of poly(methyl methacrylate). These results suggest that an efficient photochemical polymer decomposition system can be built by adding the mixing process of a little methacrylic acid into the synthetic processes of general vinyl polymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1209–1212, 2005

Key words: degradation; photochemistry; recycling

INTRODUCTION

The recovery, reuse, and recycling of plastics are important subjects when one wishes to deal effectively with limited petroleum resources. One of the major energy resources for plastic recycling is still precious fossil fuels. Sunlight is a clean, safe, and almost infinite energy source. If polymers could be efficiently recycled with sunlight energy, the consumption of petroleum resources could be decreased. This approach could mitigate the load to the global environment, such as through the discharge of carbon dioxide. One solution to this problem is the development of photodegradable polymers.¹

The important properties of photodegradable polymers are their degradability and durability. However, it is difficult to develop new polymers that have such opposite properties. To solve such a problem, one must develop a polymer photodegradation system that minimizes the modification of the structure of the existing polymer and causes photodegradation efficiently by suitable processing at an arbitrary time. However, few attempts based on this strategy have been made.²

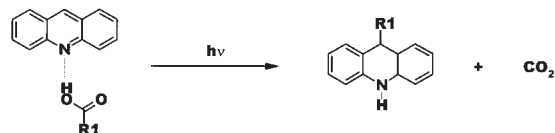
A polymer can be degraded by illumination either directly or with a photosensitizer.^{3–5} Although the direct irradiation by light of a material is the simplest method, the introduction of a photosensitive structure to a polymer makes it less durable. The photosensitization method is the better idea because the decom-

position of a polymer can be started on demand by the addition of a sensitizer. There are several reports about the decomposition of polymers by photosensitization reactions. Torikai et al.⁶ studied the benzophenone-sensitized photodegradation of polystyrene and proposed a mechanism in which hydrogen abstraction of the polymer backbone by excited-state benzophenone caused the degradation of the polymer. Ikeda et al.⁵ studied the benzophenone-sensitized photodegradation of poly- α -methylstyrene by an electron spin resonance technique and proposed that the degradation started at a free radical produced on the polymer backbone.

It has been reported that illumination to acridine in the presence of aliphatic carboxylic acid produced alkylacridane (Scheme 1).^{7–9} Mataga and Tsuno¹⁰ demonstrated that acridine and a carboxyl created an association at the ground state. A photochemical reaction between acridine and carboxyl on a polymer may give a tertiary carbon radical that has been accepted as a precursor of main-chain scission on the polymer chain. The polymer, which has carboxyl moderately on a polymer chain, can be easily prepared by the copolymerization of a monomer having a carboxyl, such as methacrylic acid. Fox et al.¹¹ reported that the influence of methacrylic acid composition on the glass-transition temperature of a poly(methacrylic acid-*co*-acrylonitrile) copolymer was small when the fraction of the acid component was small.

This article describes the polymer photodegradation reaction that occurred by the photochemical reaction of poly(methyl methacrylate-*co*-methacrylic acid) (PMCA) and acridine.

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Scheme 1

EXPERIMENTAL

Materials

Acridine was obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), and was recrystallized from ethanol and dried under reduced pressure. PMCA [methyl methacrylate/methacrylic acid = 1:0.067, number-average molecular weight (M_n) = 16,000] was obtained from Aldrich Chemical Co., Ltd. (Milwaukee, WI). The quantity of carboxyl in this polymer was confirmed by the neutralization titration method. Poly(methyl methacrylate) (PMMA; M_n 's = 7400 and 290,000) and spectroscopic-grade benzene were obtained from Kanto Chemicals Co., Inc. (Tokyo, Japan) and were used as received.

Instruments

A Shimadzu HPLC LC-6A system (Kyoto, Japan), which was equipped with Shim-pack GPC-802 and GPC-804 columns, was used to obtain gel permeation chromatograph (GPC) chromatograms. A Bruker DMX500 instrument (Rheinstetten, Germany) was used to measure $^1\text{H-NMR}$ spectra. Deuterated chloroform was used as a solvent for the measurement. A Shimadzu GC-1700AFW gas chromatograph (Kyoto, Japan) equipped with a J&W Scientific DB-WAX (Tokyo, Japan) $0.25\ \mu\text{m} \times 30\ \text{m} \times 0.25\ \text{mm}$ column was used for the quantitative and qualitative analyses of the pyrolysis products. A Hitachi U-3800 spectrophotometer (Tokyo, Japan) was used to record ultraviolet-visible (UV-vis) spectra.

Photolysis

A 200-mg portion of PMCA or PMMA and a 20-mg portion of acridine were dissolved in 10 mL of benzene and placed in 12-mm Pyrex tubes. Oxygen in the tubes was removed by nitrogen purge for 15 min at 0.1 L/min. The tubes were placed in a 22-mm Pyrex tube, and the spaces between these tubes were filled with acetone to cut ultraviolet light shorter than 350 nm. This reaction tube set was placed in a "merry-go-round" apparatus and was irradiated with a USHIO 450-W (Tokyo, Japan) high-pressure mercury lamp at room temperature. After each irradiation time, the solution was diluted with benzene to 1/100 of the initial concentration, and the absorption spectrum was measured. After irradiation, the solvent was removed from the reaction mixture by a rotary evaporator. The residue was dissolved in 1.5 mL of

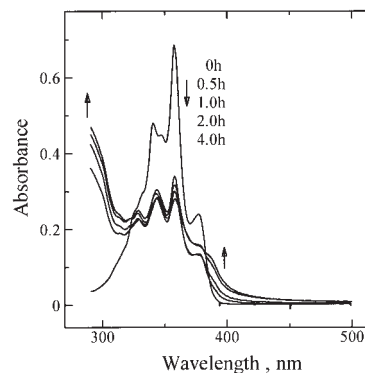


Figure 1 UV-vis absorption spectra of the reaction mixture measured for each photo-irradiation time. Each reaction mixture was diluted with benzene to 1/100 of the initial concentration and measured with a quartz cell with a 1-cm path length.

acetone, and the solution was poured into 10 mL of methanol to remove low-molecular-weight species. A white precipitate was isolated by filtration, dried under reduced pressure, and weighed. The photochemically degraded PMCA was decomposed at 300° under nitrogen, and the decomposition product was analyzed by gas chromatography by comparison of authentic samples.

Comparison of the quantum yield of scission (ϕ_s)

Φ_s for the main-chain scission is given by the following equation:^{5,12}

$$\phi_s = \frac{C}{(M_n)_0} \frac{d[(M_n)_0 / (M_n)_t - 1]}{d(t)} \quad (1)$$

where $(M_n)_0$ is the initial number-average molecular weight, $(M_n)_t$ is the molecular weight at irradiation

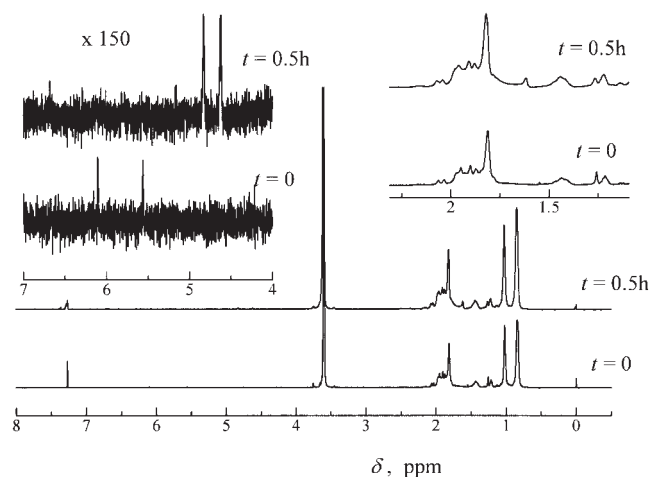


Figure 2 $^1\text{H-NMR}$ spectra of the nonvolatile product obtained by the 30-min illumination of acridine in the presence of PMCA, where δ is the chemical shift.



Scheme 2

time t , I is the intensity of light absorbed by acridine, and C is the concentration of the polymer. This equation gives a relationship between Φ_s and t . Φ_s could be estimated from the initial slope of each plot.

RESULTS AND DISCUSSION

The UV-vis absorption spectra of the solution measured for each photo-irradiation time are shown in Figure 1. The absorption intensity of acridine decreased, and new absorption bands appeared instead. Similar absorption bands on UV-vis spectra have been observed when acridine has been photoreduced.¹³ Neither the logarithmic plot of the absorption intensity to the reaction time nor the reciprocal plot of the intensity to the time were in a linear relationship. At reaction times longer than about 60 min, there were no isosbestic points.

The ¹H-NMR spectra of the copolymer and its photoproducts are shown in Figure 2. After 30 min of illumination, signals of the telechelic end groups of PMCA between 5.5 and 6.2 ppm disappeared, and two new peaks appeared between 4.6 and 4.9 ppm. The same spectral change was observed in the photoreaction of high-molecular-weight PMMA ($M_n = 290,000$) and acridine. These new signals were assigned to olefinic geminal protons of the 2-methyl-2-propenyl (**1b**) group. No other types of olefinic protons were detected under these conditions.

It is generally accepted that a scission-type radical such as **1a** is generated by the reaction shown in Scheme 2. For PMMA and PMCA, **1b** is considered as a feature end group of the product of this type of scission. Manring¹⁴ studied the thermal decomposition of PMMA and reported that the initiation reaction of the random decomposition of PMMA is not the scission of the main chain but the scission of a side

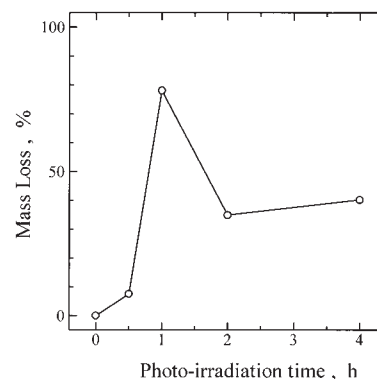


Figure 3 Mass loss of the substance in feed during the photochemical reaction of PMCA and acridine.

group. Fox et al.¹¹ studied the γ -radiolysis of a series of poly(methacrylic acid-co-acrylonitriles) and concluded that the formation of a propagating radical (or scission-type radical) resulted from a β -scission reaction at methacrylic acid/acrylonitrile dyad. In both cases, a tertiary carbon radical arose by the elimination of a substituent. A tertiary carbon radical was also produced during the photoreaction of acridine and PMCA by the elimination reaction of a substituent.

The PMCA scission reaction started by the elimination of substituents. Because the degraded product of the photochemical reaction between acridine and PMMA also had the same end group as the reaction with PMCA, the elimination of an ester group may cause the scission of PMCA. The average molecular weight of the degraded polymers in each reaction time and the molecular weight dispersions are summarized in Table I, and a relationship between the mass loss of the sample and the reaction time is shown in Figure 3. A rapid decrease in the average molecular weight observed for PMCA and the high-molecular-weight PMMA was a feature of the random scission mechanism. Because the degraded polymer had a telechelic end group, the cause of the extremely large mass loss at 60 min of illumination was considered to be the depolymerization of the degraded polymer.¹⁵ The repolymerization of the reactive products by further illumination was considered to be the cause of the decrease in mass loss and the increase in the

TABLE I
Molecular Weight and Polydispersity Index Values of PMCA and PMMA Before and After Irradiation as Determined by GPC

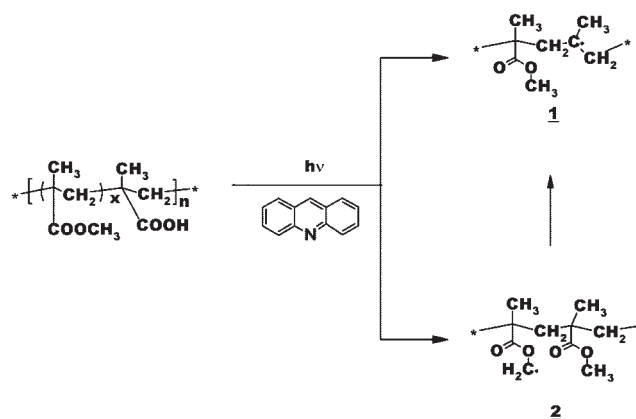
Irradiation time (min)	PMCA		PMMA			
	M_n	M_w/M_n	M_n	M_w/M_n	M_n	M_w/M_n
0	1.6×10^4	1.7	2.9×10^5	1.9	7.4×10^3	1.6
30	2.6×10^3	2.4	3.1×10^4	3.8	6.0×10^3	1.7
60	3.7×10^3	2.1	3.4×10^4	4.1	5.5×10^3	1.7
120	3.7×10^3	2.2	3.7×10^4	3.8	6.0×10^3	1.7
240	6.0×10^3	2.2	3.5×10^4	3.4	6.9×10^3	1.7

M_w = weight-average molecular weight.

average molecular weight. As already described, isobestic points were not observed on the superimposed UV-vis spectra of solutions illuminated for more than 30 min. These results suggest that data obtained for solutions illuminated for 60 min or more were not related to the photochemical reaction of acridine and PMCA directly.

The time dependence of yield of the polymer scission is shown in Figure 4. It is clear that the scission yield for PMCA was larger than that of PMMA: the initial slope of the plot was about 30 times as large as that of PMMA. The influence of solution viscosity, which comes from the difference in a molecular weight, is considered the cause. However, the difference in the initial slope between PMMA of different molecular weights was negligible compared with the difference between PMMA and PMCA. To confirm the disappearance of the carboxyl group, gas chromatograms of pyrolysates of both PMCA and PMCA degraded by 30 min of illumination were compared. The peak corresponding to methacrylic acid was not observed in the pyrolysate of degraded polymer produced by the photoreaction of acridine and PMCA, although it was observed in the gas chromatogram of the pyrolysate of PMCA. These results suggest that the elimination of carboxyl was the major process of polymer chain scission in the photochemical reaction of acridine and PMCA.

As already described, the end group of the photoreaction product of acridine and PMMA was **1b**. The photoreduction of acridine produces an acridanyl radical, which abstracts hydrogen from a substrate.^{16,17} So, radical **2**, in addition to radical **1**, can be generated by the photoreaction of acridine and PMCA (Scheme 3). Ichikawa et al. concluded that intramolecular conversion of radical **2** to **1** induces the degradation of PMMA. Although hydrogen abstraction from PMMA may produce radical **2**, as shown in Scheme 3, the results shown in Figure 4 suggest the contribution of this process to be small in the acridine-assisted photodegradation of PMCA. The association between acridine and the car-



Scheme 3

boxyl group on the polymer chain was considered the cause of the high efficiency of the polymer scission.

CONCLUSIONS

The photochemical reaction of PMCA and acridine produced the product by the main-chain scission of PMCA. In this reaction, the elimination of the carboxyl group of PMCA was induced by the photo-excitation of acridine associated with carboxyl on the polymer chain. The elimination of the carboxyl occurred more effectively than the elimination of the ester group, which was the major substituent in this polymer. An on-demand recyclable photochemical polymer decomposition system can be built by adding the mixture process of a little methacrylic acid into the synthetic processes of ready-made polymers.

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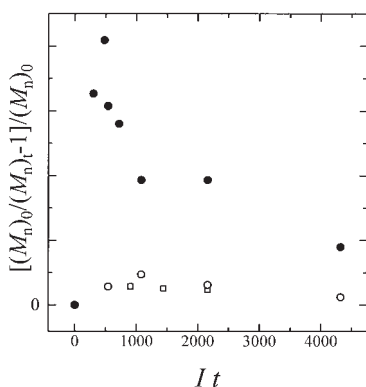


Figure 4 Yield of polymer scission during the photochemical reaction of the polymethacrylates and acridine: (●) PMCA, (□) PMMA ($M_n = 290,000$), and (○) PMMA ($M_n = 7400$).