

Photopolymerization of Methyl Methacrylate in the Presence of Saccharide

HITOSHI KUBOTA and YOSHITAKA OGIWARA, *Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan*, and KEI MATSUZAKI, *Department of Engineering Chemistry, Faculty of Engineering, University of Tokyo, Tokyo 113, Japan*

Synopsis

Photopolymerization of methyl methacrylate (MMA) in aqueous solution of saccharide was investigated. Glucose, cellobiose, maltose, and fructose accelerated the photopolymerization in the hard glass system, but α -methyl-*D*-glucoside was inactive. On the other hand, no remarkable effect of saccharide except fructose was observed in the quartz glass system. A conversion in the hard glass system increased with irradiation time and with concentration of saccharide, which showed the effect in the order of ketose > aldose > nonreducing saccharide. Scission of glucosidic bonds and decomposition of reducing groups of saccharide molecule took place in the quartz glass system, but there was no reduction in the reducing power of saccharide in the hard glass system. By studying the ESR of the photoirradiated system containing saccharide, MMA, and water, no radical of saccharide was found in hard glass systems, but an increase in growing radical of MMA was clearly observed in systems with the coexistence of ketose and aldose, while α -methyl-*D*-glucoside was inactive. It is believed, therefore, that both ketose and aldose contribute effectively to initiate the photopolymerization without any change in their own structures. On the other hand, reducing groups of saccharide play a very important role in the sensitizing action of the initiation.

INTRODUCTION

It is known that changes of optical rotation and reducing properties of saccharide are generally observed when saccharide solutions are irradiated with ultraviolet light. It is also considered¹ that monosaccharides are photolyzed to give carbon oxide, carbon dioxide, and hydrogen as final products through intermediate products such as acids and fragments containing fewer carbon atoms, and a scission reaction of glucosidic bonds occurs for di- to polysaccharides. The authors observed an easier formation of radicals in cellobiose than that in glucose comparing the ESR spectrum² of photoirradiated samples. The high activity of cellobiose toward light might be attributed to glucosidic bonds in the molecule.

In the present paper, photoirradiations were carried out in an aqueous solution of saccharide containing methyl methacrylate (MMA). The photopolymerization of MMA in the presence of various saccharides was examined relating to the characteristics of saccharides under irradiation conditions.

EXPERIMENTAL

Photopolymerization

Saccharides of commercial grade were used. MMA, styrene, and acrylonitrile were purified by distillation under reduced pressure. Acrylamide was purified by recrystallization. Methacrylic acid esters other than MMA were passed through columns of activated alumina to remove inhibitors. Methanol, acetone, and dioxane were distilled before being used.

A reaction tube containing 20 ml aqueous solution of saccharide with or without organic solvent was flushed with nitrogen. Monomer, 2 ml, was injected into the system, and polymerization was carried out by irradiating with light at 40°C for a given time. Irradiations with a high-pressure mercury lamp were conducted in a Riko rotary photochemical reactor RH 400-10W, around which reaction tubes were set to rotate. Polymerization products were poured into a large amount of methanol, filtered, washed with methanol, and dried under vacuum.

The molecular weight of poly(MMA) was determined from viscosity³ in acetone solution at 25°C.

Determination of Reducing Power of Saccharide

Irradiation was carried out at 45°C in air atmosphere with a Toshiba high-pressure mercury lamp H400-P (400 W) while placing the reaction tube containing 50 ml aqueous solution of saccharide at a distance of approximately 10 cm from the light source. Reducing power of saccharide was determined according to Somogyi's method. Namely, a flask containing 5 ml aqueous solution of saccharide, to which 5 ml alkaline cupric salt solution containing known amounts of KI and KIO₃ was added, was kept in a boiling water bath for 15 min. After being cooled, 2*N* sulfuric acid was added to it, then titrated with 1/200*N* sodium thiosulfate using starch as indicator. Reducing power was expressed as the value calculated in terms of mg of glucose.

Measurement of ESR Spectrum

A hard glass tube (5-mm diameter) filled with known amounts of saccharide, water, and MMA and flushed with nitrogen was exposed to a high-pressure mercury lamp H400-P at 77°K for 120 min. All ESR measurements were made at 77°K with a Japan Electron Optics Laboratory JES-ME-X instrument. Resonance spectra were observed with x-band and 100 kcps field modulation.

RESULTS AND DISCUSSION

Photopolymerization in Aqueous Solution

Results of photopolymerization of MMA in the presence of various saccharides are shown in Table I. The Photopolymerization in the hard glass system even without saccharide initiated to some extent, however, the conversion showed increase by the additions of glucose, cellobiose, maltose, and

TABLE I
Photopolymerization^a of MMA in Aqueous Solution of Saccharide

Saccharide	Hard glass, 60 min		Quartz glass, 30 min	
	Conversion, %	$\bar{M} \times 10^{-5}$	Conversion, %	$\bar{M} \times 10^{-5}$
None	2.9	8.42	6.5	1.23
α -Methyl- <i>d</i> -glucoside	2.4	8.60	6.7	1.18
Glucose	5.2	6.00	7.2	1.18
Fructose	18.0	6.90	12.4	1.30
Maltose	5.7	6.41	—	—
Cellobiose	5.3	6.20	7.5	1.19
Sucrose	4.6	7.10	7.0	1.13

^a Conditions: 40°C, 1 mmole/l. aqueous saccharide.

fructose, with the exception of α -methyl-*d*-glucoside. On the other hand, in the quartz glass system, no notable effect of saccharide was observed on the polymerization excepting fructose. This seems to be originating from the activated initiation of MMA itself caused by light shorter than 300 nm in the quartz glass system. The hard glass system resulted in poly(MMA) of higher molecular weight as compared to the quartz glass system. Ketose and aldose also worked to reduce the molecular weight in the hard glass system.

Table II shows results of the photopolymerization of various monomers in the presence of fructose, proving the most effective additive in case of MMA. The photopolymerization of various monomers other than MMA was accelerated by the addition of fructose, but the conversions for styrene and acrylonitrile were very low, while for acrylamide it was fairly high. The conversion of methacrylic ester monomers decreased with increase in bulkiness of the alkyl substituent in the order methyl > ethyl > isopropyl > *n*-butyl. Thus, fructose was found to act effectively in the photopolymerization of various vinyl monomers.

In the photopolymerization of MMA in the hard glass system, the conversion increased with irradiation time, showing a steep increase at 90 or 120 min in each system (Table III). This phenomenon is believed to be caused by a gel effect. The conversion increased generally with increasing concentration

TABLE II
Photopolymerization^a of Vinyl Monomers in Aqueous Solution of Fructose

Monomer	Irradiation time, min	Conversion, %	
		Without fructose	With fructose
Methyl methacrylate	60	2.9	18.0
	90	13.2	22.0
Ethyl methacrylate	90	9.0	19.6
Isopropyl methacrylate	90	8.7	11.7
<i>n</i> -Butyl methacrylate	{ 90	0	1.5
	{ 180	15.4	25.1
Styrene	150	0	0.6
Acrylonitrile	150	0	6.8
Acrylamide	60	27.9	70.3

^a Conditions: 40°C, hard glass system, 1 mmole/l. aqueous fructose.

TABLE III
Effect of Irradiation Time on Photopolymerization^a of MMA in
Aqueous Solution of Saccharide

Saccharide	Irradiation time, min	Conversion, %
None	30	2.0
	45	2.3
	60	2.9
	90	13.2
Glucose	30	3.5
	60	5.2
	90	33.0
	120	37.1
Fructose	30	9.8
	60	18.0
	90	22.0
	120	55.3
Cellobiose	30	3.2
	60	5.3
	90	7.2
	120	27.2

^a Conditions: 40°C, 1 mmole/l. aqueous saccharide.

of saccharide, but the value for sucrose was kept low and constant irrespective of the amount used (Table IV). The conversion in the system using saccharides can be said to be of the order ketose > aldose > nonreducing saccharide.

From above, both ketose and aldose were found to accelerate the photopolymerization of MMA. It is concluded, therefore, that the reducing properties of saccharide play an important role in the polymerization initiated by saccharide and light. Okimoto et al.⁴ observed that polymerization was accelerated by adding aldose and ketose to the ferric ion-sensitized photopolymerization of acrylonitrile in aqueous media.

Photopolymerization in Organic Solvent-Water Solution

Tables V and VI show results of the photopolymerization of MMA in the system using organic solvent-water solution. The system became completely

TABLE IV
Effect of Concentration of Saccharide on Photopolymerization^a of MMA

Concn. of saccharide, mmole/l.	Conversion, %			
	Fructose	Glucose	Cellobiose	Sucrose
0	2.9	2.9	2.9	2.9
0.5	9.6	4.7	4.2	4.5
1.0	18.0	5.2	5.3	4.6
5.0	26.5	8.6	8.4	4.5
10.0	40.0	12.5	12.0	4.7

^a Conditions: 40°C, 60 min, hard glass system.

TABLE V
Photopolymerization^a of MMA in Methanol–Water Solution

Concn. of methanol, vol-%	Conversion, %	
	Without glucose	With glucose
0	3.8	12.5
25	32.0	33.8
50	68.2	60.8
75	47.3	46.2
100	7.1	7.6

^a Conditions: 40°C, 60 min, hard glass system, 10 mmole/l. glucose.

homogeneous in the range of 50 to 75 vol-% concentration of organic solvent. The reaction was highly activated by methanol–water solution, showing a maximum conversion at approximately 50 vol-% methanol (Table V). However, glucose hardly contributed to improve the conversion in such a system. Effects of saccharide on the photopolymerization in various organic solvent–water solutions are shown in Table VI. In general, the conversions in acetone– and dioxane–water solutions were very low, suggesting low activities of initiation. No saccharide was observed to improve the conversion in the homogeneous systems. Thus, saccharides were proved to have little effect on the photopolymerization in which solubility of MMA was increased by employing organic solvent.

Changes of Reducing Power of Saccharide

The reducing power of various saccharides under photoirradiation was investigated, and the results are shown in Figure 1. No change in reducing power of any saccharide was observed in the hard glass system. In the quartz glass system, however, glucose, fructose, and cellobiose lost their reducing powers by photoirradiation, while sucrose was exceptionally observed to increase the reducing power to some extent. By paper-chromatographic analysis,² a certain amount of glucose was detected in the photoirradiated quartz glass system of disaccharide. Accordingly, it is considered that sucrose is photolyzed to give glucose and fructose, indicating the reducing power. Thus, it is shown that light of wavelength shorter than 300 nm contributes to

TABLE VI
Photopolymerization of MMA in Organic Solvent–Water Solution^a

Saccharide	Conversion, %		
	Methanol	Acetone	Dioxane
None	43.6	1.9	1.0
Glucose	45.8	2.1	1.3
Fructose	49.2	4.3	3.0
Cellobiose	48.9	2.4	1.2
Sucrose	41.1	1.9	1.0

^a Conditions: polymerization time, 60 min for methanol; 120 min for acetone and dioxane; temperature, 20°C; concentration of saccharide, 10 mmole/l.; concentration of organic solvent, 50 vol-%.

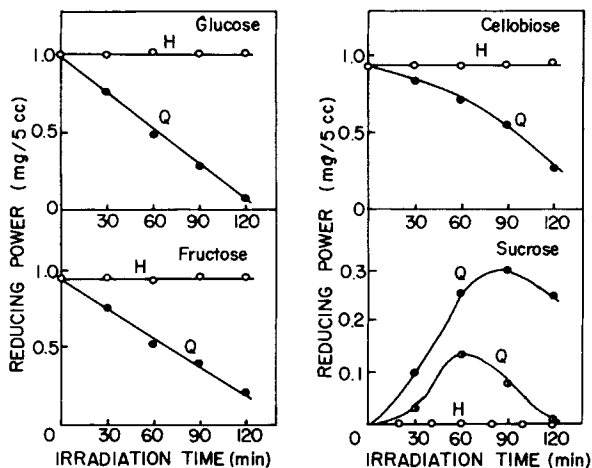


Fig. 1. Changes in reducing power of saccharide by photoirradiation: H, hard glass; Q, quartz glass. Photoirradiation was carried out at 45°C in air atmosphere.

both scission of glucosidic bonds as well as to decomposition of reducing groups of saccharides. However, no change of the reducing power of saccharide was observed in the hard glass system, demonstrating difficult decomposition of saccharide under the irradiated light.

ESR Study

In order to clarify radical species formed in the photopolymerization system in the presence of saccharide, the hard glass tube containing saccharide, MMA, and water was exposed to light from a high-pressure mercury lamp at

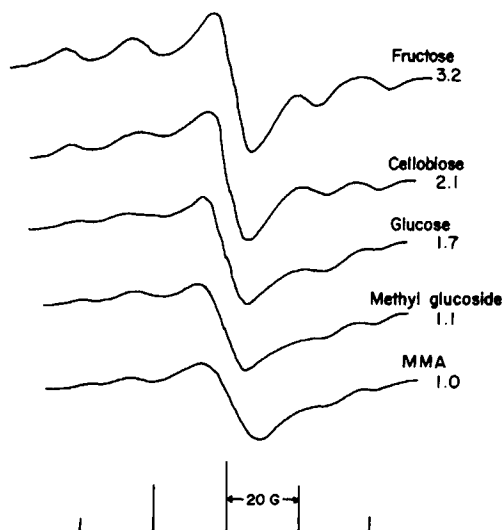


Fig. 2. ESR spectra of photoirradiated system containing saccharide, MMA, and water. Photoirradiation was carried out at 77°K for 120 min in the hard glass system. Number represents relative signal intensity of the spectrum.

77°K, and ESR spectra measured at the same temperature are shown in Figure 2. The spectra of each system exhibited five lines corresponding to a growing radical of MMA.⁵⁻⁹ No ESR spectrum was observed on saccharide only irradiated under the same condition. The relative signal intensity of the spectrum increased with the additions of fructose, cellobiose, and glucose to the system of photoinitiation, but α -methyl-*D*-glucoside was inactive. Thus, it is true that photoinduced growing radical of MMA was accelerated with ketose and aldose, however, the radicals from saccharide itself were not detected under the present irradiation conditions. Accordingly, saccharides are supposed to contribute to the initiation without any photodecomposition. Namely, the acceleration of photopolymerization might originate in the sensitizing action of ketose and aldose involving an energy transfer, where the reducing group seems to be related closely to it.

Preirradiated Fructose

The photopolymerization of MMA employing fructose, whose reducing group was decomposed beforehand by preirradiation and has a depressed reducing power, was examined. The results are shown in Table VII. First, aqueous solutions of fructose with depressed reducing power were prepared by photoirradiation using the quartz glass tube. After adding 2 ml MMA to the solutions, the photopolymerization was carried out in the hard glass system at 40°C for 90 min. Increases in conversion were distinctly observed for the preirradiated fructose in air atmosphere, however, only a small change in the conversion was observed for the preirradiated fructose under nitrogen.

Peroxide formed in the preirradiated solutions was measured iodometrically. A fair amount of peroxide was found in the preirradiated solutions under air, while only a little was found under nitrogen. The formation of peroxide by glucose, cellobiose, and sucrose was also observed and the amounts formed by 60-min irradiation in the quartz glass system were 0.11, 0.10, and 0.05 mmole/l., respectively. Phillips and Moody¹⁰ reported that hydrogen peroxide is formed during the irradiation of aqueous solution of glucose in oxygen with ultraviolet light. The formation of hydrogen peroxide was also observed

TABLE VII
Photopolymerization of MMA in Preirradiated Aqueous Solution of Fructose^a

Irradiation time, min	Preirradiation ^b		Formation of peroxide, mmole/l.		Conversion ^c , %	
	Reducing power, mmole/l.					
	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
0	1	1	0	0	22.0	22.0
30	0.75	0.87	0.08	0.01	26.7	24.5
60	0.49	0.74	0.13	0.02	29.6	25.4
90	0.27	0.59	0.18	0.03	33.6	25.1
120	0.02	0.36	0.23	0.02	37.3	25.5

^a Concentration of fructose, 1 mmole/l.

^b Preirradiation, 45°C; quartz glass system.

^c Conditions, 40°C; 90 min, hard glass system.

for γ -ray-irradiated monosaccharides^{11,12} and disaccharide,¹³ in their aqueous solutions. So, the peroxide formed in the present system is sure to be hydrogen peroxide. It is believed, therefore, that the ability of the preirradiated aqueous solution of fructose to accelerate the photopolymerization of MMA is ascribed to the sensitizing action of hydrogen peroxide produced in the system. It is well known that hydrogen peroxide is easily decomposed by photoirradiation and the resultant hydroxyl radical¹⁴⁻¹⁸ can initiate the polymerization of vinyl monomers. On the other hand, the formation of hydrogen peroxide in aqueous solution of fructose was not observed in the hard glass system. Accordingly, the preirradiation to aqueous solution of fructose in the hard glass system hardly accelerated the photopolymerization of MMA.

In conclusions, it can be said that decomposition of reducing group, scission of glucosidic bonds, and formation of hydrogen peroxide take place in photoirradiated aqueous solutions of saccharides in the quartz glass system, but saccharides are hardly decomposed in the hard glass system. A more detailed study of the photochemistry of saccharide including the formation of hydrogen peroxide are now underway based on this preliminary investigation.

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