JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 2767–2773 (1971)

# Effect of Wavelength Region on Photo-Induced Graft Copolymerization onto Cellulose

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

## Synopsis

The effect of wavelength region of ultraviolet light was examined on the unsensitized photo-induced graft copolymerization of methyl methacrylate onto cellulose. When the quartz tube system was compared to the glass tube system, there was no induction period of copolymerization, the rate of reaction was a little larger, the homopolymerization of methyl methacrylate was increased causing interference with graft copolymerization, and the depolymerization of grafts and the scission reaction of cellulose chains occurred easily. The number of grafts was hardly improved by varying the reaction conditions, and the copolymers obtained generally exhibited low per cent grafting and contained grafts with lower degree of polymerization.

## INTRODUCTION

In a previous paper[1] we have reported on photo-induced graft copolymerization of methyl methacrylate (MMA) onto cellulose using glass tubes as a reaction vessel. Since ultraviolet light (UV) of wavelength below approximately 300 m$\mu$ is hardly transmitted when hard glass tubes are used,[2,3] an induction period of copolymerization, a relatively slow rate of reaction, and grafts with higher molecular weight were observed as the characteristics of copolymerization. Of course, the use of sensitizer had some effects on the reaction, but the high activity of graft copolymerization was not attained. Similar effects were observed when ceric ion[4,5] and hydrogen peroxide[6] were used with UV irradiation. It is well known that UV of lower wavelength has a strong breaking energy and participates in the deterioration of high polymeric substances. In the same manner, it is thought to have some effect on photo-induced graft copolymerization. In the unsensitized photo-induced graft copolymerization of styrene onto nylon 6, Ishibashi and Tamaki[3] reported on the effect of UV wavelength on the graft copolymerization.

In the present paper, the graft copolymerization of MMA onto cellulose in quartz tubes was examined in the absence of photosensitizer while special attention was paid to the initiation reaction, and the results were compared with those for a glass tube system in the previous paper[1] in order to clarify the effect of wavelength on the initiation behavior.

## EXPERIMENTAL

### Graft Copolymerization

Graft copolymerization was carried out at 40°C for a given time under nitrogen by irradiating the reaction tubes containing a given amount of cellulose, a commercial dissolving pulp, 2.5 ml of MMA, and 40 ml of distilled water with ultraviolet light. As reaction vessels, quartz tubes and hard glass tubes approximately 1 mm thick were used. It is well known that glass limits the transmission of light below approximately 300 mμ, while quartz extends the wavelength region to approximately 200 mμ.[2,3] As UV light source, a Toshiba mercury lamp for photochemical use (H-400P) was used, and the irradiation was carried out on the system in a reaction vessel at a distance of approximately 11 cm from the light source. After being washed with water, the polymerization products were extracted with acetone to remove the homopolymer. The per cent grafting, the per cent homopolymer, and the number of grafts were calculated as described in the previous papers.[1,6,7]

Grafted copolymer was treated with 72% sulfuric acid, and the poly(MMA) of the grafts was isolated. Weight-average molecular weight of grafts was determined from the viscosity of the acetone solution at 25°C.[8]

### Degree of Polymerization (DP) of Cellulose

After the systems of graft copolymerization conditions in which monomer was absent were replaced by nitrogen, irradiation with UV was carried out at 40°C for a given duration. The irradiated cellulose sample was washed with water, dried, and a sample for the measurement of DP was obtained. Weight-average DP of sample was determined from the viscosity of cupriethylenediamine solution at 25°C.[9]

## RESULTS AND DISCUSSION

### Graft Copolymerization in Quartz Tubes

The results of graft copolymerization on various amounts of cellulose using quartz tubes are shown in Figure 1. The formation of grafted polymers generally increased up to a reaction time of approximately 40 min, at which time the highest values were obtained. In some systems, the values rather decreased after that time period. It was definitely observed that in the initial stage of reaction, the amount of grafted polymers formed increased with increase in the amount of cellulose. These results seem to indicate that cellulose participates directly in the initiation of graft copolymerization; similar facts were also observed for the glass tube system of the previous paper.[1] However, attention should be paid to the induction period, which is almost absent in the copolymerization, and to the peculiar reaction time dependence of the formation of grafted polymers. The homopolymerization of MMA was also readily initiated even in the absence of cellulose, and a remarkable amount of homopolymer resulted.

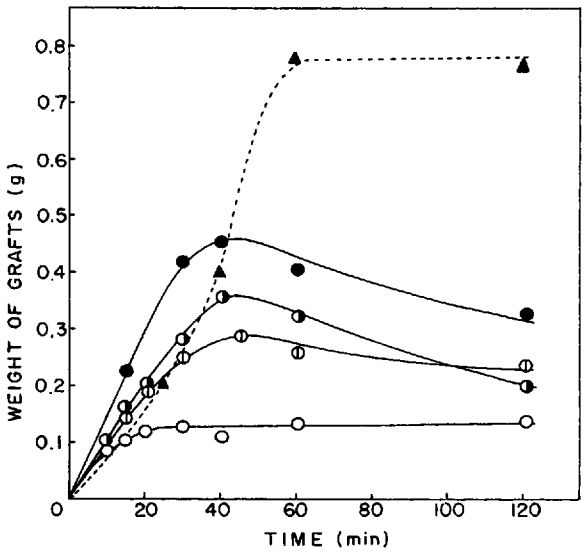


Fig. 1. Graft copolymerization in the system using quartz tube. Amount of cellulose (g): (▲) 0; (○) 0.25; (◑) 0.50; (◑) 0.75; (●) 1.00. Temperature, 40°C; amount of monomer, 2.5 ml; total volume of system, 42.5 ml.

As for the relationship between the average molecular weights of grafts and homopolymers formed in the present systems, it was observed that the average molecular weights of grafts were generally larger than those of homopolymers and more easily affected by the reaction time, as shown in Figure 2. Moreover, there was a definite tendency to obtain a greater average molecular weight for both polymers with increased amount of cellulose used in the system. However, it was observed that the average molecular weight of grafts was inversely proportional to the amount of cellulose[1] when glass tubes were used. Therefore, a definite contrast exists between the different vessels in the relation between the amount of cellulose to molecular weight of grafts.

For the reaction in quartz tubes, it should be taken into consideration, from the relations in Figure 1, that ultraviolet light works somewhat to depolymerize the poly(MMA) being formed in the reaction system as well as to introduce grafts, and as a result the average molecular weight of the grafts is lowered. This influence is apparently well demonstrated as the reaction time dependence of the average molecular weight for each system in Figure 2. This type of depolymerization by UV was observed for polystyrene by Ishibashi and Tamaki[3] and for poly(MMA) by Fox and Price.[10] On the other hand, the reason why the molecular weight of grafts or homopolymers increases with the increased amount of cellulose in the system could be explained by a decreased termination reaction, which is inversely proportional to the amount of cellulose in the present system. This effect might be assumed to increase as the polymerization proceeds more inside the cellulose fibers; namely, it seems to indicate that, in the quartz tube system, the shorter wavelength component of UV acts

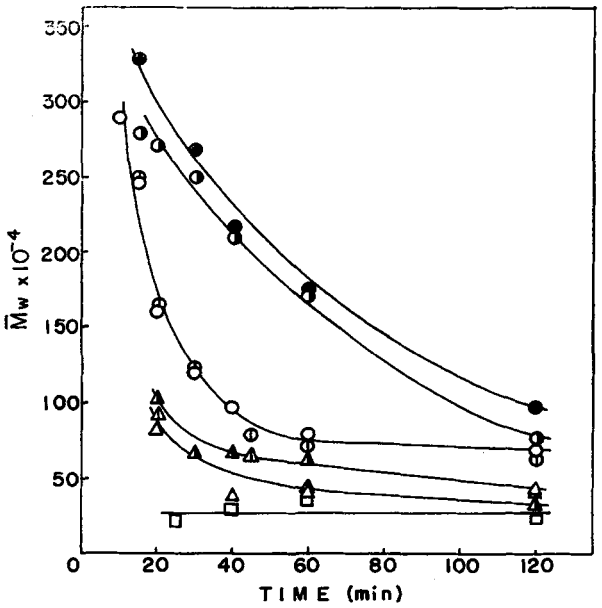


Fig. 2. Changes in average molecular weights of grafts and homopolymers with time. Amount of cellulose (g): grafts—(○) 0.25; (◑) 0.50; (◑) 0.75; (●) 1.00. Homopolymer—(□) 0; (△) 0.25; (▲) 0.50; (▲) 0.75.

more inside the cellulose fibers and that radicals are formed at this site. It is thought that the termination reaction of propagating radicals is apt to be suppressed because of their limited mobility. The difference in wavelength region is considered as the sole cause of the different tendency in the previous paper.[1] In the previous paper it was also observed that the formation of grafts was almost confined to the surface of the fibers in the glass tube systems. Probably, the difference in wavelength has an effect on the location of the grafting sites, yielding complicated results.

## Comparison with Graft Copolymerization in Glass Tubes

In order to clarify the character of the initiation system in which UV irradiation was carried out employing quartz tubes, comparisons with results in glass tubes were undertaken. Part of the data is quoted from the previous paper,[1] and the same copolymerization conditions are selected for both systems except for the vessels used.

Figure 3 shows comparisons of per cent grafting and per cent homopolymer formed. The copolymerization reaction in glass tubes was accompanied by an induction period and proceeded gradually to attain approximately 120% of the per cent grafting. The reaction in quartz tubes attained approximately 40% of the per cent grafting after a shorter period, a value considerably lower than that in glass tubes. This is attributed to a higher activity of homopolymerization of MMA in quartz tubes, even in the absence of cellulose. On the contrary, no formation of

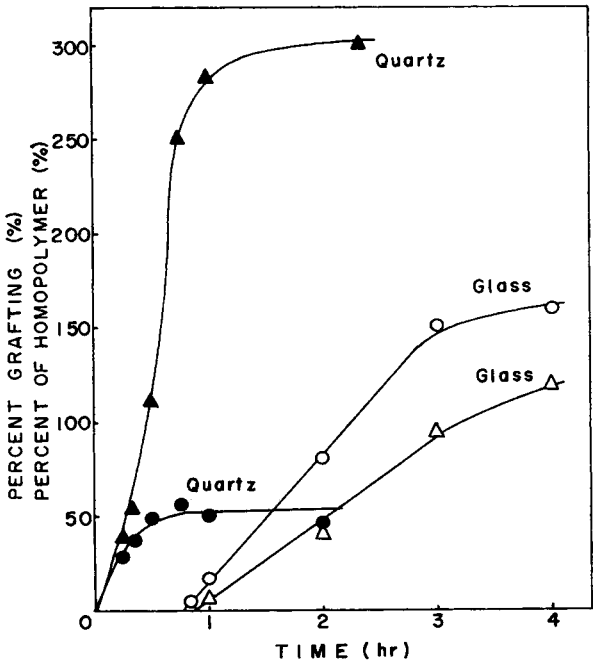


Fig. 3. Comparison of per cent grafting and per cent homopolymer. Amount of cellulose, 0.50 g; amount of monomer, 2.5 ml; total volume of system, 42.5 ml; temperature, 40°C: (○), (●) per cent grafting; (△), (▲) per cent homopolymer.

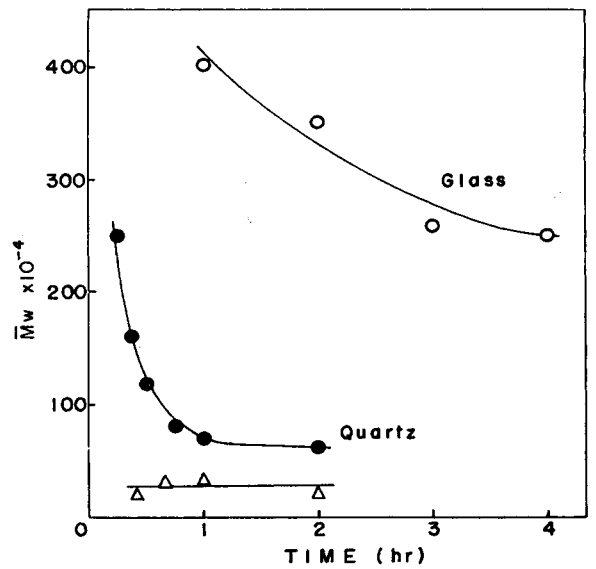


Fig. 4. Changes in average molecular weight of grafts with time: (△) in the absence of cellulose sample. Polymerization conditions same as those in Fig. 3.

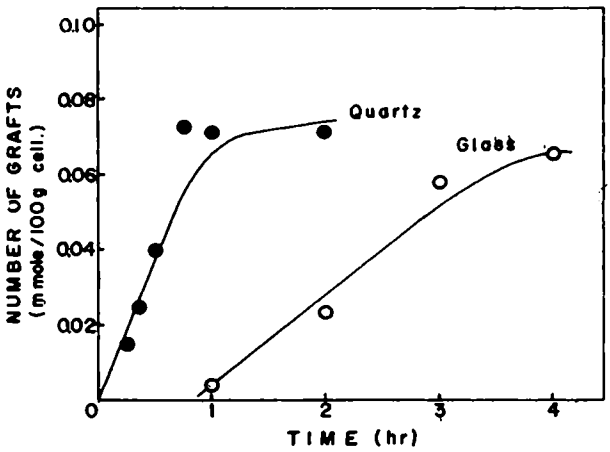


Fig. 5. Changes in number of grafts in copolymers with time. Polymerization conditions same as those in Fig. 3.

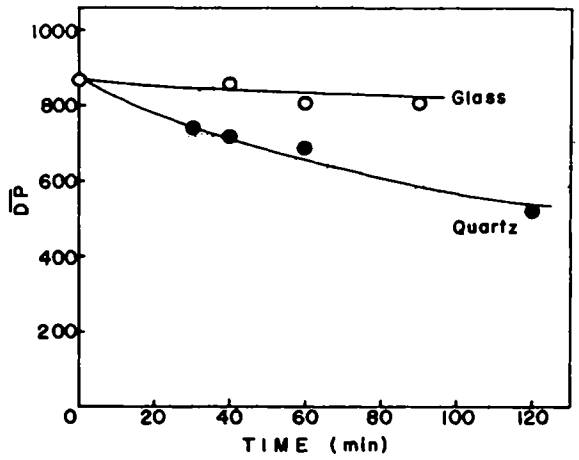


Fig. 6. Changes in degree of polymerization of cellulose with time. Amount of cellulose, 0.50 g; total volume of system, 42.5 ml; reaction temperature, 40°C; nitrogen atmosphere.

homopolymer was observed in glass tubes even after 4 hr of reaction under the same conditions. However, the formation of a fair amount of homopolymer could not be avoided in the systems containing cellulose with either glass or quartz vessel.

The relationships between the average molecular weight of grafts and the reaction time of both systems are compared in Figure 4. The average molecular weight decreased with the reaction time for either system. However, a remarkable difference was observed between the systems. Namely, in glass tubes, the average molecular weight did not decrease to less than half of the initial value even after several hours, whereas in

quartz tubes it did decrease to less than half within 1 hr. This difference probably has a remarkable effect on the properties of grafted cellulose.

The number of grafts is compared for both systems in Figure 5. Although the rate of formation of grafts was different in each system, almost the same number of grafts was ultimately obtained for both systems. Accordingly, it is concluded that a substantial difference in the number of grafts is not found between the systems. However, as mentioned above, a remarkable difference was noticed in the average molecular weight between the two systems. It is also very interesting that there was no ultimately significant difference in the number of grafts between both systems, even though the quartz tube system resulted in grafts of shorter length within a shorter period of time as compared to the glass tube system.

As it is known that DP of cellulose is generally lowered by UV irradiation,[11–14] the changes in average DP of cellulose in both systems are compared in Figure 6. As expected, the effect of wavelength of UV is evident; namely, the decrease in average DP of cellulose was larger for the quartz tube system than for the glass tube system, as in the case of grafts.

Thus, when quartz tubes were used, the reactive lower wavelength region of UV acted to contribute to the homopolymerization of MMA and to the hindrance of copolymerization, including the depolymerization of grafts and the scission reaction of cellulose chains, whereas it did not effect any improvement in the number of grafts. In the glass tube system, on the contrary, this hindering action was fairly suppressed.

Similar differences in polymerization behavior due to reaction tubes have been reported by Ishibashi and Tamaki.[3] It is believed that we encountered almost the same characteristics of the UV wavelength region in the irradiation of cellulosic materials.

The authors wish to acknowledge the contribution of Mr. Toshiro Yamashita for the experimental work.

## References

1. Y. Ogiwara and H. Kubota, *J. Polym. Sci. A-1*, in press.
2. S. Fujii, *Kobunshi*, **5**, 46 (1956).
3. H. Ishibashi and H. Tamaki, *Kobunshi Kagaku*, **24**, 171 (1967).
4. Y. Ogiwara, H. Kubota, and Y. Ogiwara, *J. Polym. Sci. A-1*, **6**, 3119 (1968).
5. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **14**, 2611 (1970).
6. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **14**, 2879 (1970).
7. Y. Ogiwara and H. Kubota, *J. Appl. Polym. Sci.*, **14**, 817 (1970).
8. S. Chinai, J. Matlack, and A. Resink, *J. Polym. Sci.*, **17**, 391 (1955).
9. E. H. Immergut, B. G. Rånby, and H. F. Mark, *Ind. Eng. Chem.*, **45**, 483 (1953).
10. R. B. Fox and T. R. Price, *J. Appl. Polym. Sci.*, **11**, 2373 (1967).
11. C. Kujirai, *Sen-i Gakkaishi*, **21**, 183 (1965).
12. E. H. Daruwalla, A. P. D'Silva, and A. C. Mehta, *Text. Res. J.*, **37**, 147 (1967).
13. R. L. Desai, *Pulp Pap. Mag. Can.*, **69**, T322 (1968).
14. R. L. Desai and J. A. Shields, *Makromol. Chem.*, **122**, 134 (1969).

Received April 27, 1971
Revised June 30, 1971