

Tributylborane-Initiated Grafting of Methyl Methacrylate onto Chitin

KUNIHARU KOJIMA, MASAKO YOSHIKUNI, and TOMINORI SUZUKI, *Department of Applied Chemistry, Faculty of Engineering, Chiba University, Chiba 280, Japan*

Synopsis

The grafting of methyl methacrylate (MMA) onto chitin initiated by tributylborane (TBB) was investigated at ordinary temperature. It was found that water was essential to the grafting. No grafting was observed in the usual organic solvents such as *n*-hexane, tetrahydrofuran, and cyclohexanone. The total conversion and the percentage and efficiency of grafting increased with increasing chitin content. The extent of homopolymer formation also increased with increasing chitin content. The optimum concentrations of TBB and MMA for the grafting were determined. Activation energies were estimated to be about 22.8 and 27.4 kcal/mole for the grafting and homopolymerization, respectively. On the basis of these results the mechanism of the grafting onto chitin was discussed.

INTRODUCTION

Chitin, a polysaccharide consisting of β -2-acetoamido-2-deoxy-D-glucose units, is one of the principal ingredients of the carapaces, crusts, and shells of the *Crustacea*, such as crabs, lobsters, prawns, and shrimps. Since the total production of all the *Crustacea* in nature is estimated to be on the order of several billion tons, the utilization of chitin is believed to be of importance for the welfare of mankind. Recently, a new interest in this natural polymer has been aroused—chitin is expected to give better performance in chromatography than ordinary substituted cellulose derivatives, as it can act as a good, solid chelating agent.

However, only a small number of studies on the utilization of chitin have appeared in the literature.¹ Matsushima et al. hydrolyzed chitin to D-glucose derivatives to use it as food, and they found an enzyme capable of selectively hydrolyzing chitin. Yaku and Yamashita² claimed a patent for the preparation of chitin films. Iwakura et al.³ studied the effects of deacetylation on the properties of chitin.

Since we developed a method for grafting of vinyl monomers onto natural products, such as blood components (blood and hemoglobin),^{4,5} fibers (cotton, silk, and wool),⁶⁻⁸ and proteins (albumin and casein)⁹ at ordinary temperature using tri-*n*-butylborane (TBB) as an initiator, we applied this method to the modification of chitin.

EXPERIMENTAL

Materials

Commercial fine-powdered chitin (Wako Pure Chemical, Ltd.; N = 6.32%, isolated by the method of Hackman¹⁰ from the shell of crabs) was purified by extraction with acetone in a Soxhlet apparatus for 24 hr, followed by washing with methanol and drying under reduced pressure. Methyl methacrylate (MMA) was purified in the usual manner,¹¹ bp 42°C/102 mm Hg (46°C/100 mm Hg, d_4^{20} 0.9365). TBB was used after distillation in a dry box under nitrogen atmosphere, bp 108–110°C/20 mm Hg (112°C/25 mm Hg).¹²

Grafting

A mixture of 1.0 g chitin and 15 ml water was placed in a 60-ml tube with a ground-glass stopper and allowed to stand at room temperature for 15 hr. To this were added 5 ml MMA and 0.05 ml TBB. The mixture was shaken for 2 hr in a shaking apparatus thermostatted at 37°C. The grafting was stopped by pouring the mixture into 200 ml methanol. The precipitates were filtered, washed with methanol, and dried at 60°C in vacuo to constant weight. The dried precipitates were extracted with acetone in a Soxhlet apparatus for 48 hr to remove the homopolymer of MMA. The homopolymer was reprecipitated in methanol. Both the acetone-insoluble residue and the homopolymer were dried at 50°C in vacuo to constant weights.

Calculation

Total conversion, the percentage of grafting, and the efficiency of grafting were calculated as follows:

total conversion (%) =

$$\frac{\text{weights of poly(MMA) grafted and homopolymer}}{\text{weight of MMA charged}} \times 100$$

$$\text{percentage of grafting (\%)} = \frac{\text{weight of poly(MMA) grafted}}{\text{weight of MMA charged}} \times 100$$

efficiency of grafting (%) =

$$\frac{\text{weight of poly(MMA) grafted}}{\text{weights of poly(MMA) grafted and homopolymer}} \times 100$$

Viscosity Measurement

The intrinsic viscosity of the homopolymer was determined at 25°C by a Ubbelohde-type viscometer in chloroform, and its molecular weight was estimated from the following equation¹³:

$$[\eta] = 0.48 \times 10^{-4} \bar{M}^{0.8} \quad (\text{dl/g, } 25^\circ\text{C})$$

RESULTS AND DISCUSSION

Effects of Media

Table I shows the dependence of grafting on the type of medium. When the grafting procedures were performed in organic solvents, such as benzene, *n*-hexane, and dimethylformamide (DMF), graft polymers were not obtained. Even a homopolymerization did not occur in DMF. This indicated that the presence of water is essential to the grafting. Similar results have been obtained in TBB-initiated grafting of MAA onto cotton,⁶ silk,⁷ and wool.⁸

Reaction Time

Figure 1 presents the relationship between reaction time and the grafting. As the reaction time became longer the total conversion increased initially, but after about 4 hr it reached 90% or more. The homopolymerization was apparently accelerated by the presence of chitin. The percentage of grafting also increased with increasing grafting time up to 32% and then stayed constant. The efficiency of grafting reached 98% in the initial stage but decreased with increasing grafting time down to 30%. These results indicate that the grafting predominantly occurred in the initial stage but that the number of grafting sites was few.

TABLE I
Effect of Media on Grafting^a

Medium	Total yield, g	Total conversion, %	Percentage of grafting, %	Efficiency of grafting, %
Benzene	1.28	5.8	—	—
<i>n</i> -Hexane	1.64	13.3	—	—
DMF	0.98	—	—	—
Water	1.96	19.9	5.0	25.2

^a Grafting conditions: MMA, 5 ml; chitin, 1.0 g; medium, 15.0 ml; TBB, 0.05 ml; temp., 37°C; time, 2 hr.

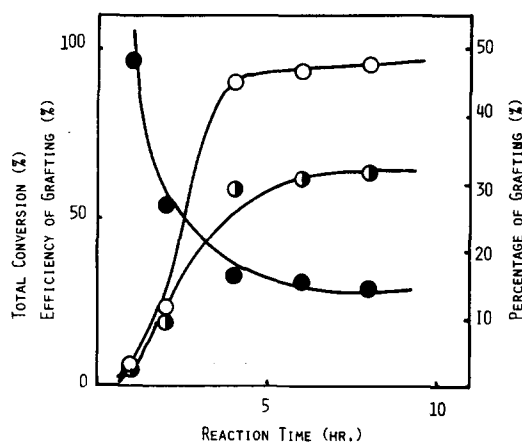


Fig. 1. Effect of reaction time. Chitin, 1.0 g; MMA, 5 ml; water, 15 ml; TBB, 0.05 ml; at 37°C: (O) total conversion; (●) percentage of grafting; (●) efficiency of grafting.

Chitin Content

While the amounts of monomer, water, and TBB were kept constant, the grafting of MMA with various amounts of chitin in the range 0.5 to 1.5 g/20 ml was carried out at 37°C for 2 hr. The results are shown in Figure 2. The total conversion and the percentage and efficiency of the grafting all increased linearly with increasing chitin content. From these results chitin seems to play an important role in the initiation of grafting: active sites of grafting were created by the interaction of chitin and TBB, most likely via complex formation. Homopolymer conversion also increased with increasing chitin content.

Initiator Concentration

Figure 3 shows the effect of initiator concentration on the grafting. The total conversion and the percentage of grafting reached maxima at 0.1 ml/20 ml (0.4 vol-%) of the initiator concentration. Similar tendencies have been observed

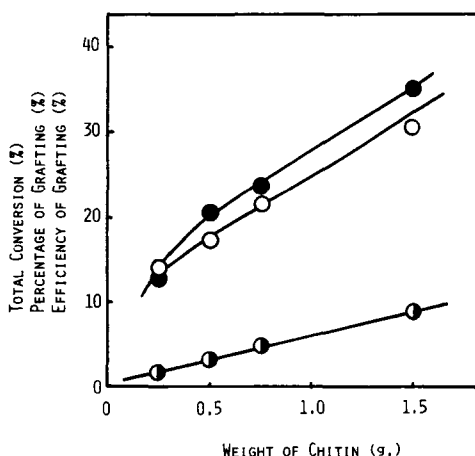


Fig. 2. Effect of chitin content. MMA, 5 ml; water, 15 ml; TBB, 0.05 ml; temp., 37°C; time, 2 hr: (○) total conversion; (◐) percentage of grafting; (●) efficiency of grafting.

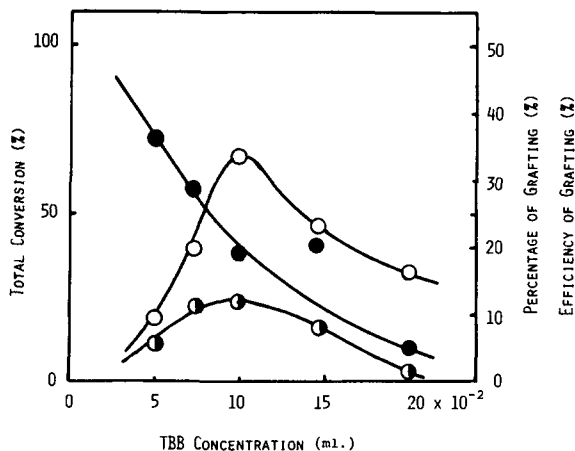


Fig. 3. Effect of TBB concentration. MMA, 10 ml; water, 15 ml; chitin, 1.0 g; temp., 37°C; time, 2 hr: (○) total conversion; (◐) percentage of grafting; (●) efficiency of grafting.

in TBB-initiated grafting onto various backbone polymers; these tendencies have been explained by the assumption that both TBB radicals and radicals formed on backbone polymer are wasted by recombination and other termination processes. However, the efficiency of grafting decreased continuously with increasing initiator concentration. It could be interpreted by assuming that initiator concentration influenced more the rate of homopolymerization than that of grafting. Active sites of grafting may be formed only on its surface in the initial stage.

Monomer Concentration

Figure 4 illustrates the dependence of the grafting on the monomer concentration. The total conversion and the percentage of grafting decreased with increasing monomer concentration, while the efficiency of grafting increased initially and then reached a plateau.

Reaction Temperature

As Figure 5 shows, the reaction temperature influenced the total conversion more than the percentage of grafting, which increased with increasing temperature. The efficiency of grafting decreased as the polymerization temperature was raised. Activation energies were estimated to be 22.8 and 27.4 kcal/mole in grafting and homopolymerization, respectively.

Average Molecular Weight of Homopolymer

It is possible that grafting sites on chitin are formed by radical chain transfer. If so, it is expected that the average molecular weight of homopolymers initiated by this system decreases with increasing chitin content. Figure 6 illustrates the influence of chitin content on the average molecular weight of homopolymer. It is apparent that the molecular weight of homopolymer increases with increasing chitin content. This result indicates that the formation of grafting sites on chitin is independent of the chain transfer by macroradicals.

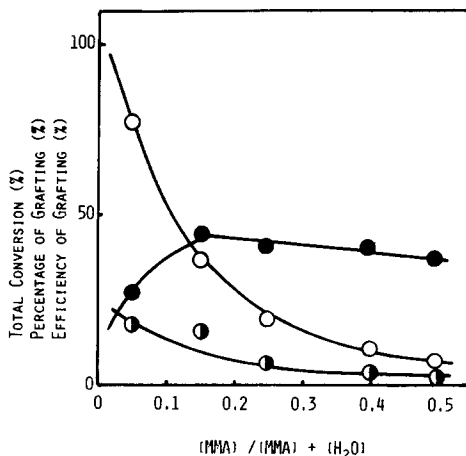


Fig. 4. Effect of MMA concentration. Chitin, 1.0 g; MMA + water, 20 ml; TBB, 0.05 ml; temp., 37°C; time, 2 hr: (○) total conversion; (◐) percentage of grafting; (●) efficiency of grafting.

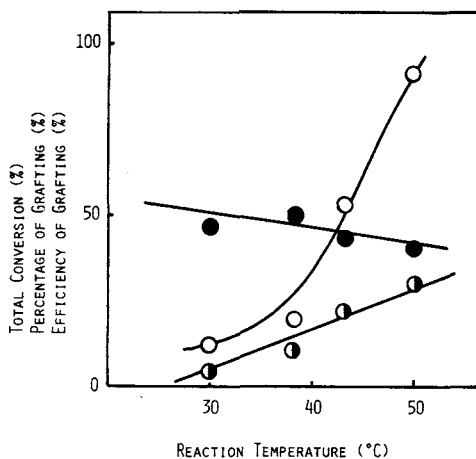


Fig. 5. Effect of reaction temperature. Chitin, 1.0 g; MMA, 5 ml; water, 15 ml; TBB, 0.05 ml; time, 2 hr: (○) total conversion; (◐) percentage of grafting; (●) efficiency of grafting.

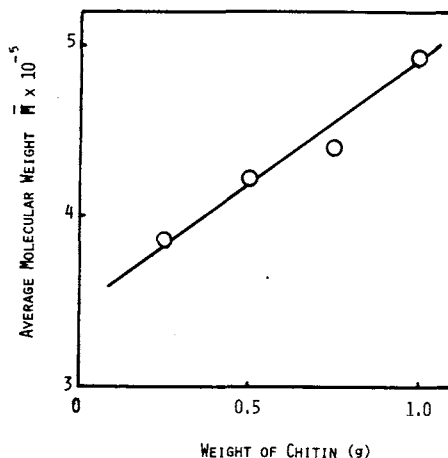


Fig. 6. Relationship between average molecular weight of homopolymer and chitin content.

Scanning Electron Microscope

The scanning electron microscope of grafted fibers is shown in Figure 7. When viewed in a scanning electron microscope, the grafted chitin powder appears to have a different structure from the ordinary chitin powder.

Reaction Mechanism

It is well known that the alkylborane-initiated polymerization of vinyl monomers in the presence of oxygen proceeds via radical mechanism. Since the TBB-initiated grafting onto chitin was carried out in the presence of oxygen, the grafting is assumed to involve free radicals. This assumption is supported by the fact that free radical polymerization is, in general, less sensitive to water than ionic polymerization. The presence of water is essential to the grafting. No grafting occurred in the usual organic solvents, although TBB can initiate polymerization of MMA in these organic solvents. As mentioned above, it seems

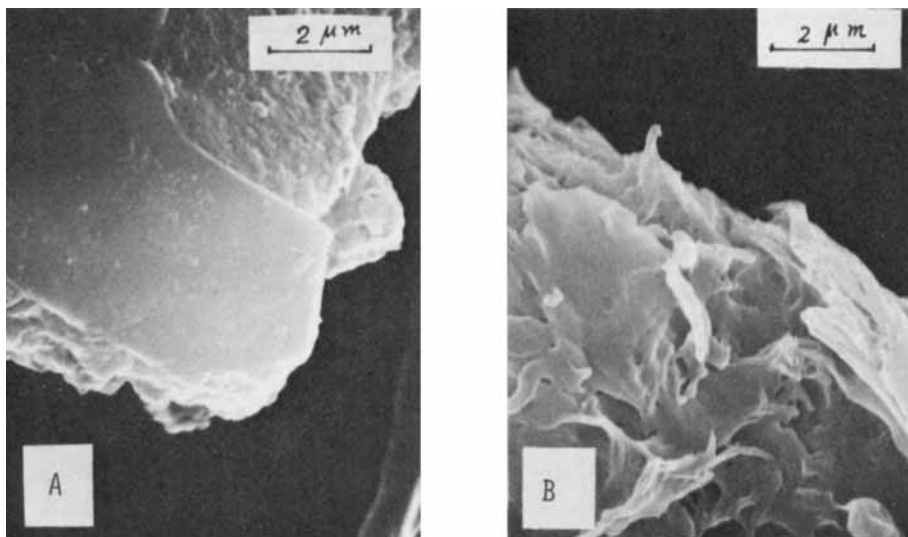


Fig. 7. Scanning electron micrograph: (a) Chitin; (b) chitin-*g*-poly(MMA).

that the grafting sites on chitin are formed by a reaction between TBB, chitin, and water. Since grafting onto chitin was more efficient than that onto cellulose, hydrophilic groups may play an important role in grafting, most likely via the formation of complexes between TBB and these groups. As in our previous papers, the grafting was assumed to proceed via free-radical mechanism in three steps—(1) solvation of water to chitin, (2) formation of the complex from solvated chitin and TBB, and (3) graft initiation by free radicals from the complex.

The authors are grateful to Dr. Susumu Iwabuchi and Dr. Takayuki Nakahira for helpful discussions.

References

1. R. A. A. Muzzarelli, *Natural Chelating Polymer*, Pergamon, New York, 1973, p. 83.
2. T. Yaku and I. Yamashita, Jpn. Pat. 7319231 (1973).
3. T. Sannan, K. Kurita, and Y. Iwakura, *Makromol. Chem.*, **176**, 1191 (1975); *ibid.*, **177**, 3589 (1976); *ibid.*, **178**, 2939, 3197 (1977).
4. K. Kojima, S. Iwabuchi, and K. Kojima, *J. Polym. Sci. A-1*, **9**, 3213 (1971).
5. K. Kojima, S. Iwabuchi, and K. Kojima, *Bull. Chem. Soc. Jpn.*, **44**, 1891 (1971).
6. K. Kojima, S. Iwabuchi, K. Murakami, K. Kojima, and F. Ichikawa, *J. Appl. Polym. Sci.*, **16**, 1139 (1972).
7. K. Kojima, T. Suzuki, S. Iwabuchi, and N. Tarumi, *Nippon Kagaku-Kaishi*, 1943 (1972).
8. K. Kojima, K. Arita, K. Otuka, and M. Yoshikumi, *J. Fac. Eng. Chiba Univ.*, **29**, 239 (1978).
9. K. Kojima, S. Iwabuchi, K. Kojima, and N. Tarumi, *J. Polym. Sci.*, **B-9**, 25 (1971).
10. R. H. Hackman, *Aust. J. Biol. Sci.*, **7**, 168 (1954).
11. S. Kanbara, *Monomer Synthesis*, Kyoritus Publishing, Tokyo, 1958, p. 143.
12. Callery Chemical Co, PA, 16024 *Technical Bulletin C-310*, 1959.
13. J. Bishoff and V. Desreux, *J. Polym. Sci.*, **10**, 437 (1953).

Received January 2, 1979

Revised March 8, 1979