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Modification of chitin by ceric salt-initiated graft polymerisation — preparation of poly(methyl methacrylate)-grafted chitin derivatives that swell in organic solvents

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Graft copolymerisation of methyl methacrylate (MMA) onto chitin initiated with cerium(IV) ammonium nitrate was carried out in a suspension system. The influences of the reaction time, initiator concentration, temperature and the molar ratio of MMA added to chitin unit on the graft polymerisation were studied. Solubility of the highly grafted chitin derivatives in various solvent systems changed significantly, and a gel-like mass swelling in organic solvents was obtained. A fine film could be made from the gel-like material. Calorimetric measurement for the copolymers shows a glass transition temperature of about 130°C, and the enthalpy change of endothermic decomposition is much lower than chitin itself.

INTRODUCTION

Chitin is a natural polysaccharide which has a structural resemblance and abundance close to that of cellulose. Applications of chitin include the full spectra from commodity chemicals to lucrative speciality chemicals for medicals and high-technology fields (Prudden *et al.*, 1970). Since chitin is insoluble in aqueous solutions and common organic solvents due to its strong crystalline structure, chemical modifications for improving the solubility of chitin have been receiving steadily increasing attention (Sannan *et al.*, 1975).

Recently, graft polymerisation on chitin has been employed as an important technique for changing its physical and chemical properties. For example, graft copolymerisation of methyl methacrylate (MMA) onto chitin using a tributylborane initiator (Kojima *et al.*, 1979), and styrene onto chitin by a radiation method (Shigeno *et al.*, 1982) have been reported. Besides these initiation systems, ceric(IV) salt, which has been widely used as the initiator in the graft copolymerisation of cellulose (Mcdowall *et al.*, 1984), was also found to be an effective initiator in the graft copolymerisation of chitin (Kurita *et al.*, 1991). Graft polymerisation of MMA onto cellulose has been studied in detail; however, the grafted cellulose derivates were insoluble in all solvents tried, with a lower water sorbancy than cellulose itself (Ide & Takayama, 1961).

This paper reports on the preparation of the poly(methyl methacrylate) (PMMA)-grafted chitin derivatives initiated with ceric salt, and its structures and properties are discussed. It was found that a swollen gel of the chitin derivatives in organic solvents was obtained when the grafting yield reached as high as 600% under certain reaction conditions. A fine film could be made from the gel-like mass by pressing.

EXPERIMENT

Materials

Chitin (crab shell, Nippon Suisan Co. Ltd, Japan) was purified by Hackman's method (Hackman, 1954) and powdered (120 mesh pass) before use. Cerium(IV) ammonium nitrate and nitric acid (Wako Pure Chemical Industries Ltd) were used without further purification. MMA (purchased also from Wako) was purified by distillation under reduced pressure.

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Graft copolymerisation

Graft copolymerisation was carried out under a nitrogen atmosphere in a flask. Polymer yield and grafting yield are defined as follows.

Polymer yield (%) = weight of consumed MMA/weight of MMA used × 100
Grafting yield (%) = weight of grafted MMA/weight of chitin used × 100

These values were determined by gravimetry. A typical polymerisation procedure is described as follows. Into a nitrogen-substituted flask, chitin powder and nitrogen-substituted distilled water were added and the mixture was stirred at 50°C for 12 h to make a fine suspension. After the mixture was cooled to 30°C, a given amount of MMA was added and stirred for 5 min. Then, the initiator solution, which was prepared by dissolving 5·48 g of cerium(IV) ammonium nitrate in 100 ml of 1 M HNO_3, was added to start the graft polymerisation. The reaction was stopped by pouring the reaction mixture into large amount of methanol. The precipitate was filtered, washed with distilled water and methanol exhaustively, and then dried *in vacuo*. Non-grafted PMMA was removed by Soxhlet extraction with acetone for more than 22 h until no extractable homopolymer remained. The purified graft copolymer was dried under vacuum.

Measurements

The degree of swelling was measured by a simple gravimetry method. the powdered sample (0·2 g) was immersed in 20 ml of solvent at 20°C for 7 days. The wet polymer was collected by centrifugation at 3000 rpm for 10 min, followed by absorbing the surface solvent with a filter paper. The degree of swelling was calculated by the ratio of the amount of solvent involved in the swollen material to the amount of dry polymer.

PMMA chains grafted on chitin were isolated from grafted copolymer by hydrolysis with 20 M H_2SO_4 at 60°C for 30 min (Takahashi *et al.*, 1989). The crude product from the hydrolysate was dissolved in acetone and purified by reprecipitation. The intrinsic viscosity ($[\eta]$) was measured in acetone with a Ubbelohde-type viscometer at 25°C. The weight-average molecular weight ($\overline{M}_w$) of grafted PMMA chains was calculated by the following equation (Chinai *et al.*, 1955):

$$[\eta]_{25} = 9{\cdot}6 \times 10^{-3} \overline{M}_w^{0{\cdot}69}$$

The apparent number of grafted PMMA chains was evaluated according to the degree of grafting yield per 100 g of chitin and the molecular weight of the grafted PMMA chains.

Infrared (IR) spectra were recorded for potassium bromide discs by a Nicolet 5DXB Fourier-transform IR (FTIR) spectrometer. The thermal analysis was performed by a Mettler thermoanalyser TC11 TA4000 with a differential scanning calorimeter (DSC) in DSC 20 cell. Heating was made in the range from 50 to 450°C, at a rate of 10°C/min.

RESULTS AND DISCUSSION

Graft polymerisation

Figure 1 shows the polymer yields and grafting yields at various reaction times. A large increase in the polymer yield and grafting yield occurs at a rather early stage. However, when the reaction time is longer than 1 h, the rate of increase becomes slower. Similar results were also reported in the case of the graft copolymerisation on cellulose initiated with Ce(IV) salt (Mansour & Nagaty, 1979). The fact that the grafting yield increases with the reaction time indicates that the radicals generated on the chitin chain, which initiated the graft polymerisation, increased during the reaction.

The decline in the increases of polymer yield and grafting yield after the reaction time of 1 h would be caused by the exhaustion of monomer and initiator, which will result in the difficulty to maintain a suitable ratio of monomer and initiator during the polymerisation. Effect of the ratio of monomer and initiator concentration ([M]/[I]) on polymer and grafting yields is shown in Fig. 2. As shown in the figure, the yields increase remarkably at low [M]/[I] value up to ~ 47, followed by the gradual decrease at high [M]/[I] values. A most suitable ratio to give the best polymer yield and grafting yield is about 47, and the grafting yield as high as 250% could be achieved.

The reaction temperature also influenced the graft

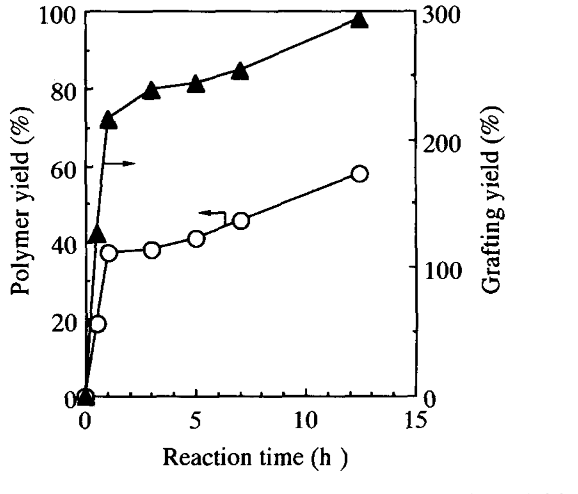

Fig. 1. Time courses of polymer yield and grafting yield. ○, Polymer yield; ▲, grafting yield. Chitin, 0·50 g; water, 220 ml; [MMA] = 1·99 × 10^{-1} M; [I] = 4·25 × 10^{-3} M; [HNO_3] = 3·83 × 10^{-2} M; T = 30°C.

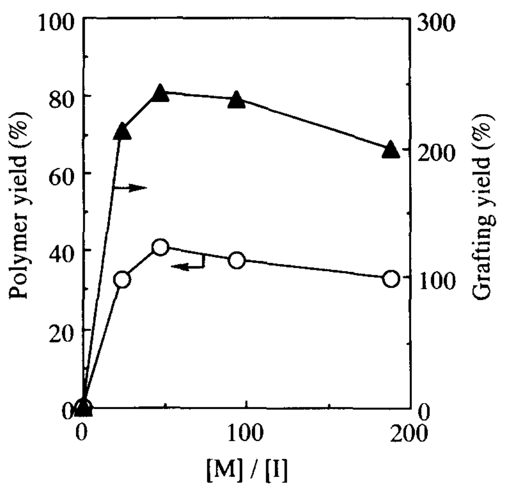

Fig. 2. Effect of the ratio of monomer and initiator concentration on polymer yield and grafting yield. ○, Polymer yield; ▲, grafting yield. Chitin, 0·50 g; water, 220 ml; [MMA] = 1·99 × 10^{-1} M; [HNO_3] = 3·83 × 10^{-2} M; *T* = 30°C; *t* = 5 h.

copolymerisation. The polymer yields and grafting yields obtained at different temperature are shown in Fig. 3. Below 40°C, both polymer yield and grafting yield increase gradually with employing the higher reaction temperature. On the other hand, when the temperature is higher than 40°C, both of them rather decreased with elevating temperature. There is an optimum temperature for the graft copolymerisation at which the polymer yield and grafting yield reach their maxima. The increase in the polymer yield and grafting yield with temperature may be due to a variety of temperature-dependent factors such as diffusion, adsorption of monomer onto chitin, and changes in the rates of initiation, propagation, termination and homopolymerisation. The decrease in the polymer yield and grafting yield at higher temperature may be attributed to the instability of the initiator and an increased rate of termination.

The dependences of the molecular weight and the number of the grafted PMMA chains on the reaction temperature are shown in Fig. 4. The molecular weight of PMMA grafted on chitin molecule increased with a rise in temperature up to 30°C, and then reached constant value about 2 × 10^6. The number of the grafted PMMA chains depends on the temperature significantly. The grafting sites on chitin are increased with a rise in temperature up to 40°C at the maximum of about 0·15 mmol/100 g.

Figure 5 shows the polymer yields and grafting yields obtained at various molar ratio of MMA and

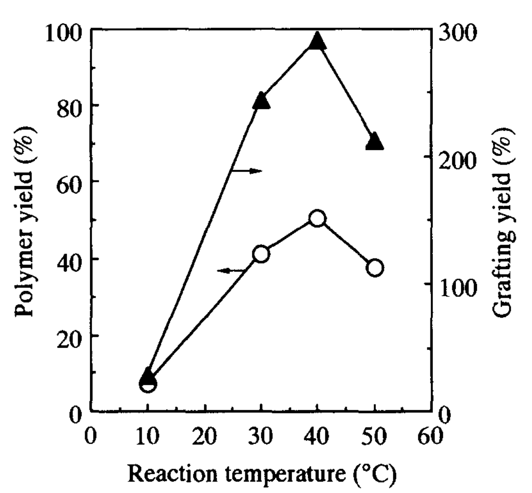

Fig. 3. Influence of reaction temperature on polymer yield and grafting yield. ○, Polymer yield; ▲, grafting yield. Chitin, 0·50 g; water, 220 ml; [MMA] = 1·99 × 10^{-1} M [I] = 4·25 × 10^{-3} M; {HNO_3] = 3·83 × 10^{-2} M; *t* = 5 h.

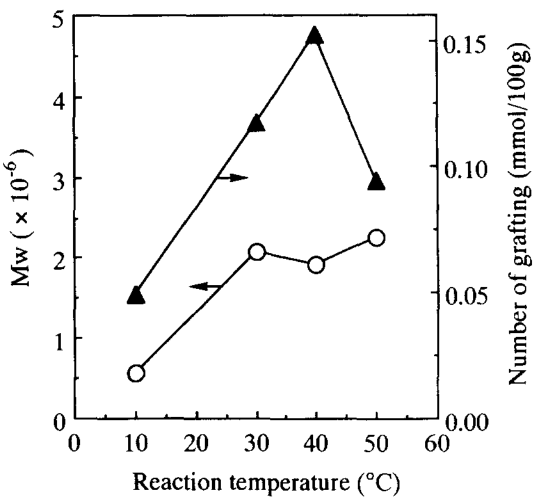

Fig. 4. Effect of reaction temperature on the molecular weight and the number of grafted PMMA chains. ○, Weight-average molecular weight; ▲, number of grafted PMMA chains.

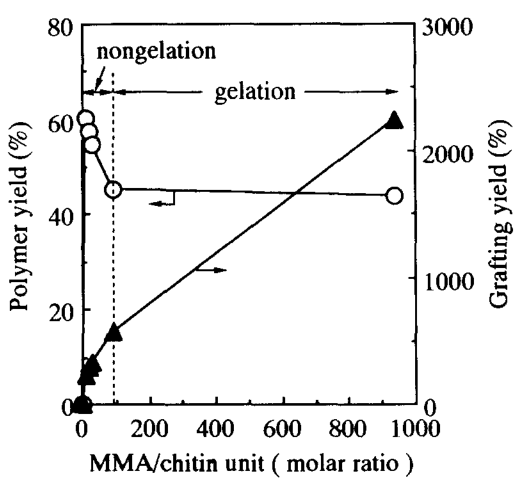

Fig. 5. Influence of molar ratio of MMA and chitin unit on polymer yield and grafting yield. ○, Polymer yield; ▲, grafting yield. Water, 220 ml; [MMA] = 1·99 × 10^{-1} M; [I] = 4·25 × 10^{-3} M; {HNO_3} = 3·83 × 10^{-2} M; *T* = 30°C; *t* = 12·5 h.

chitin residue. As can be seen in Fig. 5, the polymer yield decreases with the molar ratio of MMA and chitin unit when the ratio is less than 95. Above this ratio, the polymer yield reached a constant value about 45%. On the other hand, the grafting yield increases steadily with an increase in the MMA/chitin unit ratio.

When the grafting yield is higher than 600%, the grafted chitin shows a gel-like property which swells in organic solvents such as acetone, chloroform and benzene. It is also interesting that the swollen gel, when it was centrifuged at low temperature and pressed on a glass plate followed by drying, gave a fine thin film. According to the changes in IR spectra for the samples after grafting, as discussed later, the hydrogen bonds between chitin chains are broken in the PMMA-grafted chitin derivative. This may be the main factor of the large solubility change by the grafting.

Characterisation of grafted chitin derivatives

Solubility behaviour is an essential factor for characterisation of the grafted chitin derivatives. Solubility change was found to depend on the grafting yield as shown in Fig. 6. When the grafting yield is lower than 400%, the graft copolymers are resistant to *N*,*N*-dimethylformamide (DMF) than chitin itself. However, above the grafting yield of 400%, the degree of swelling increased drastically, and took constant value at 12, and the copolymer became a swollen transparent gel with the pale yellow green. Even with a second reprecipitation with methanol, the swellabilities are retained well when the grafting yield is below 600% as shown in Fig. 6. On the other hand, when the grafting yield is higher than 600%, the gelation by swelling is unstable. The degree of swelling decreases with the repetition of swelling–reprecipitation cycle. The same phenomena are also observed in the other solvents such as methyl ethyl ketone and toluene. The behaviours of swelling in various organic solvents are summarised in Table 1 for the copolymer with 620% grafting yield. DMF seems to be the best swelling solvent, suggesting that the copolymer has good affinity to this solvent. Besides these common organic solvents, grafted chitin derivative also swell in the solvents for chitin such as dimethylacetamide including a small amount of lithium chloride (Austin, 1977) forming clear gels.

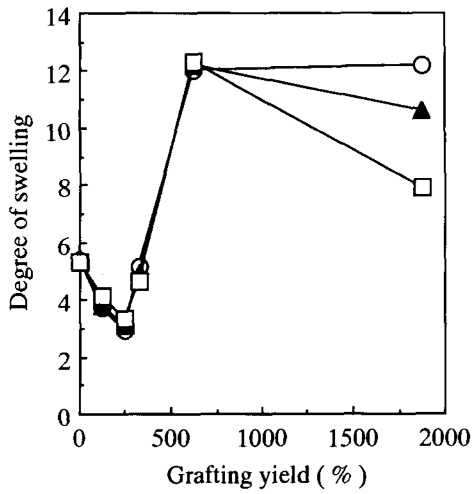

Fig. 6. Influence of grafting yield on the degree of swelling in DMF at 20°C. ○, The first swelling procedure; ▲, the second swelling procedure after reprecipitation with methanol; □, the third swelling procedure after reprecipitation with methanol.

Table 1. The swelling behaviour of graft copolymer with grafting yield of 620% in organic solvents

Solvent	Degree of swelling
Methyl ethyl ketone	4·7
Chloroform	5·1
Acetone	5·7
Toluene	6·7
N,*N*-DMF	12·0

The structure changes of chitin after grafting were examined with IR and DSC. In Fig. 7, IR absorption spectra before and after grafting are shown. The absorptions at 1657, 1555 and 1311 cm^{-1} in the spectrum of chitin are due to the amide groups in chitin, which can be assigned as the amide I, II, and III bands, respectively. The absorption of CH$_2$ wagging is also contained in the band at 1311 cm^{-1} (Pearson *et al.*, 1960). Examining the IR spectrum carefully, it can be

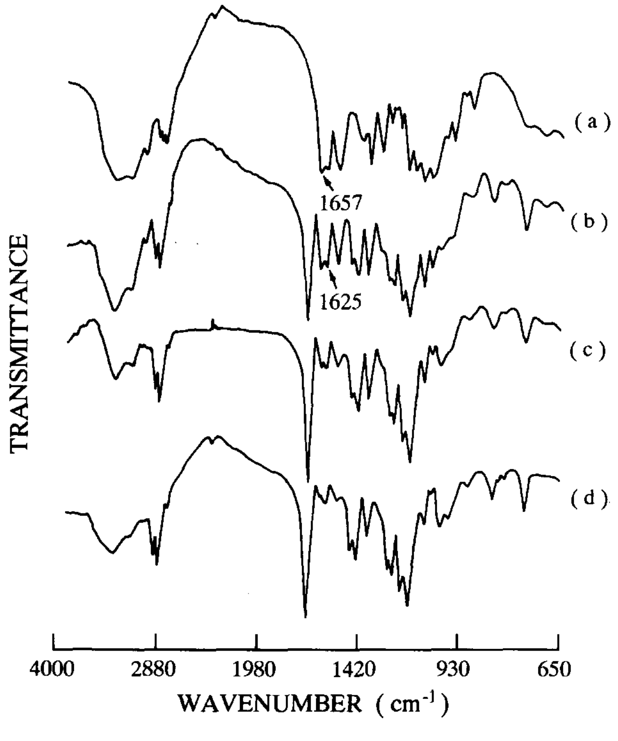

Fig. 7. FTIR spectra of (a) chitin and grafted chitin derivatives with grafting yield of (b) 254%, (c) 806%, and (d) 1876%.

found that the amide I band is further separated to two absorptions at 1657 and 1625 cm^{-1} (Darmon & Rudall, 1950). It was caused by the fact that there are two kinds of amide groups in the chitin crystal, one accepts only the N—H group to form intermolecular hydrogen bond which corresponds to the absorption at 1657 cm^{-1}, and the other acts as acceptors for both CH_2OH group (intramolecular hydrogen bond) and N—H group (intermolecular hydrogen bond) which correspond to the absorption at 1625 cm^{-1} (Minke & Blackwell, 1978).

As can be seen in Fig. 7, after grafting, the absorption band of carbonyl group due to PMMA grafted chains on chitin is observed at 1730 cm^{-1}. The absorption intensity at 1311 cm^{-1} owing to the absorption of amide III and CH_2 groups decreases markedly with increase in the grafting yields. The relative absorption intensities of the absorptions at 1657 and 1625 cm^{-1} are influenced by the grafting yield. The absorption at 1625 cm^{-1} increases relatively with an increase in the grafting yield. The result indicates that more intramolecular hydrogen bonds are formed after grafting between amide group and hydroxyl group. Taking the fact that the O6′ oxygen atom can form only one hydrogen bond into the consideration, the intramolecular hydrogen bond formation within the chitin chain must result in the breaking of the intermolecular hydrogen bonds between chitin chains. This may be caused by the grafting of PMMA on the chitin chain, with the result that grafted chitin swells in organic solvents.

It is also found that the grafted chitin derivatives showed different thermal behaviours from the ungrafted chitin. The DSC profiles of chitin before and after grafting are shown in Fig. 8. The DSC curve of chitin represents a decomposition endothermic peak at 150°C, of which enthalpy change is 122 J/G. After grafting, this decomposition peak tends to shift to a higher temperature (180°C for (b), 225°C for (c)), and become sharper than chitin. The curves of both (b) and (c) display a glass transition for amorphous state about 130°C, and their enthalpy changes of the degradation are 14 and 9 J/G, respectively. Similar trends were described for the case of cellulose-MMA graft copolymers initiated by Ce(IV) salt (Guthrie & Tune, 1991).

This research shows that the ceric-salt-initiated graft copolymerisation is a useful method to improve the solubility and other physical properties of chitin. The gel-like mass of grafted chitin derivative is expected to be employed in the various fields such as the biomedical field.

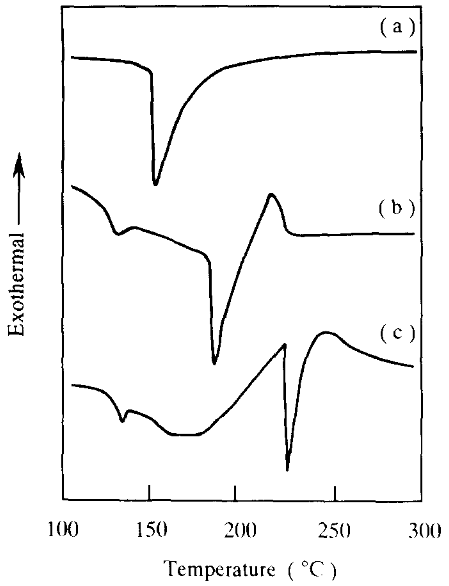

Fig. 8. DSC thermograms of (a) chitin and grafted chitin derivatives with grafting yield of (b) 254%, and (c) 1876%.

REFERENCES

Austin, P.R. (1977). Chitin solution. US Patent 4 059 457.

Chinai, S.N., Matlack, J.D., Resnick, A.L. & Samuels, R.J. (1955). *J. Polym. Sci.*, **XVII**, 391-401.

Darmon, S.E. & Rudall, K.M. (1950). *Discussions Faraday Soc.*, **9**, 251-60.

Guthrie, J.T. & Tune, P.D. (1991). *J. Polym. Sci.*, **A29**, 1301-12.

Hackman, R.H. (1954). *Aus. J. Biol. Sci.*, **7**, 168-78.

Ide, F. & Takayama, Y. (1961). *Kogyo Kagaku Zasshi.*, **64**, 213-18.

Kojima, K., Yoshikuni, M. & Suzuki, T. (1979). *J. Appl. Polym. Sci.*, **24**, 1587-93.

Kurita, K., Kawata, M., Koyama, Y. & Nishimura, S. (1991). *J. Appl. Polym. Sci.*, **42**, 2885-91.

Mansour, O. & Nagaty, A. (1979). *J. Appl. Polym. Sci.*, **23**, 2425-34.

Mcdowall, D.J., Gupta, B.S. & Stannett, V.T. (1984). *Prog. Polym. Sci.*, **10**, 1-50.

Minke, R. & Blackwell, J. (1978). *J. Mol. Biol.*, **120**, 167-81.

Pearson, F.G., Marchessault, R.H. & Liang, C.Y. (1960). *J. Polym. Sci.*, **43**, 101-16.

Prudden, J.F., Migel, P., Hanson, P., Friedrich, L. & Balassa, L. (1970). *Am. J. Surg.*, **119**, 560-4.

Sannan, T., Kurita, K. & Iwakura, Y. (1975). *Makromol. Chem.*, **176**, 1191-5.

Shigeno, Y., Kondo, K. & Takemoto, K. (1982). *J. Macromol. Sci.-Chem.*, **A17**, 571-83.

Takahashi, A., Sugaharu, Y. & Hirano, Y. (1989). *J. Polym. Sci.*, **A27**, 3817-28.