GRAFT COPOLYMERIZATION ONTO CHITOSAN–I. GRAFTING OF ETHYLMETHACRYLATE USING CERIC AMMONIUM NITRATE AS AN INITIATOR

Mohammad M. Fares *

Department of Applied chemistry, Jordan University of Science & Technology, P.O. box: 3030, 22110, Irbid, Jordan

Bashar Al-Ta'ani

Faculty of Pharmacy, Jordan University of Science & Technology, P.O. box: 3030, 22110, Irbid, Jordan

Received 16-09-2002

Abstract

Grafting of ethylmethacrylate (EMA) onto chitosan in aqueous medium initiated by ceric ammonium nitrate (CAN) under N_2 atmosphere has been studied. The effect of monomer concentration, initiator concentration, polymerization temperature, polymerization time and material to liquor ratio have been studied in terms of %GE and %Add-on. The optimum conditions obtained for the grafting of EMA on 1.0 g chitosan were: [CAN] = 0.0018 mol/L, [EMA]= 0.025 mol/L, Temperature= 30 °C, Time=180 min, and material to liquor ratio = 1:7. The graft copolymer was characterized by FTIR, x-ray diffraction (XRD) for the crystallinity of the copolymer and TGA for thermal stability of the copolymer.

Introduction

Chitosan is a modified carbohydrate polymer derived from the chitin component of the shells of crustacean, such as crab, shrimp and cuttlefish, which is prepared by acetylation of chitin and form a natural cationic polymer. The outstanding chemical, biological and pharmaceutical applications of chitosan have attracted attention to the potential utility of chitosan-grafted polymers in different areas such as drug delivery systems,[1,2] hydrogel formation,[3] and ion exchangers.[4] A variety of chitosan grafted with vinyl monomers such as acrylic acid and methacrylic acid have been synthesized in the literature.[5-8] Chemical modification of chitosan via grafting of vinyl monomers is gaining much interest not only because they are low in cost, but mainly because the polysaccharide portion of the product is biodegradable and it looses its integrity through time. Vinyl graft copolymerization onto chitosan can be initiated by various means such as epychlorohydrine,[9] ceric ammonium nitrate (CAN),[10] n-butyl lithium (BuLi),[11] and through complexed sodium aliginate.[12] Grafting using CAN has been thoroughly investigated[10,13,14] due to simple mechanism of single electron transfer, low activation energy and formation of free radicals on the reducing agent itself (chitosan in this case).

These features of ceric ion initiation lead to high grafting efficiency at room temperature and result in the formation of a pure graft copolymer.[15] The present work aims at optimizing the conditions for graft copolymerization of ethylmethacrylate (EMA) onto chitosan with respect to concentration of the monomer and initiator, polymerization temperature and time, and material to liquor ratio.

Results and discussion

Grafting Evidence

Gravimetric Estimation: The grafting polymerization process was followed gravimetrically. The increase of the weight of the grafted chitosan over the weight of chitosan indicated the grafting of EMA on chitosan.

FTIR spectroscopy: The FTIR spectra of the pure chitosan, Chitosan-g-EMA copolymer and poly(ethylmethacrylate) (PEMA) are shown in Figure 1. It can be seen that a characteristic transmittance peak at 1735 cm^{-1} is observed in the grafted chitosan spectrum, and not in pure chitosan. This peak is the carbonyl group stretching of the ester group providing evidence of grafting of EMA onto chitosan. This characteristic peak is clearly seen in PEMA.

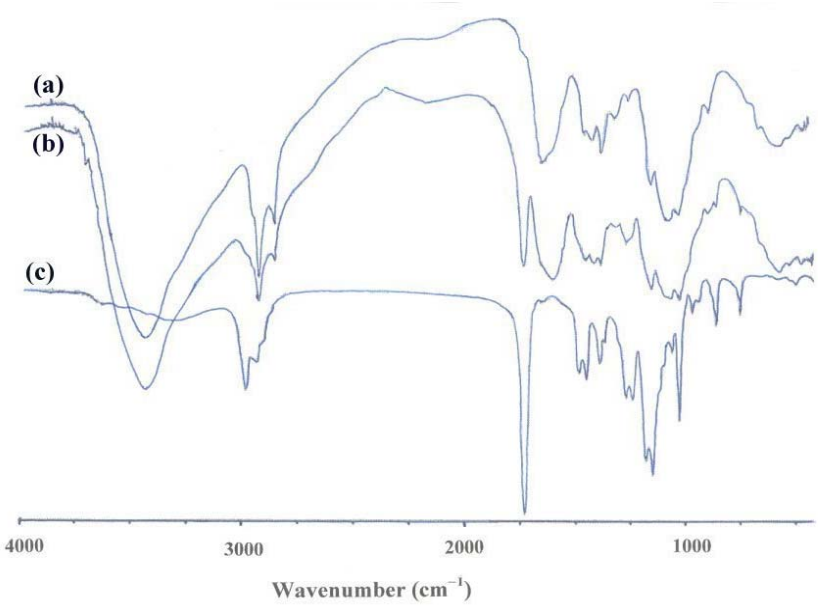

Figure 1. FTIR spectra of (a) Pure Chitosan, (b) Chitosan-g-EMA copolymer (%Add-on=45.6), (c) pure PEMA.

Acid hydrolysis: Chitosan on acid hydrolysis is converted into 2-amino glucose (chitosan monomer units), which is soluble in water and does not precipitate with methanol. In order to see the effect on acid on grafted chitosan, 0.3 g of the copolymer was subjected to acid hydrolysis by refluxing it with 100 mL of 0.5 M HCl for two hours. The solution after cooling is poured in a large amount of methanol, and the precipitate collected by filtration is expected to be PEMA chains that were grafted to chitosan. The IR spectrum of the precipitate showed typical spectrum of poly(EMA) (Fig. 1-c) with a characteristic transmittance peak at 1735 cm^{-1} providing evidence of grafting process.

Effect of monomer concentration

The monomer concentration effect on grafting and on average molecular weight (M_v) of homopolymer after acid hydrolysis is illustrated in Table 1.

Table 1. Effect of monomer concentration on grafting of EMA onto chitosan and on average molecular weight (M_v) of homopolymer after acid hydrolysis (reaction conditions: Chitosan =1.0 g, [CAN] = 0.0018 mol/L, Temp.= 30 °C, Time = 120 min in 100 mL solution).

[EMA] (mol/L)	%GE	%Add-on	$M_v \times 10^{-5}$
0.025	70.2	16.7	1.17
0.050	54.4	23.7	1.39
0.100	46.5	34.6	1.52
0.200	36.8	45.6	1.79
0.400	11.0	33.3	1.92

It can be seen that as the monomer concentration increases the %GE decreases, which is mainly due to the formation of homopolymers.[19] These homopolymers successfully hinder the rate of penetration of monomer molecules to chitosan macroradicals, resulting with formation of relatively low molecular weight chains of PEMA and decrease in %GE. As the monomer concentration increases, the rate of homopolymerization increases also, and then termination of some macroradicals by chain transfer[20] is highly expected. The unterminated macroradicals then interact with monomers to form relatively high molecular weight chains as seen in the average molecular weight of PEMA chains in Table 1, which indeed causes steadily increase in

%Add-on. At [EMA] = 0.400 mol/L, the %Add-on decreased to 33.3%, which is attributed to large increase of homopolymer resulting in decrease of solubility of the copolymer that is reflected on the %Add-on value.

Effect of Initiator concentration

The initiator concentration effect on the grafting of EMA on chitosan and on average molecular weight (M_v) of homopolymer after acid hydrolysis is illustrated in Table 2.

Table 2. Effect of initiator concentration on grafting of EMA onto chitosan and on average molecular weight (M_v) of homopolymer after acid hydrolysis (reaction conditions: Chitosan =1.0 g, [EMA] = 0.025 mol/L, Temp. = 30 °C, Time = 120 min in 100 mL solution).

[CAN] (mol/L)	%GE	%Add-on	$M_v \times 10^{-5}$
0.00018	0.0	0.0	0.00
0.00090	26.0	6.9	0.62
0.00180	70.2	16.7	1.17
0.00360	61.0	14.8	0.81
0.00540	26.3	7.0	0.25
0.00730	14.0	3.8	0.07

Initially both %GE and %Add-on increases with increasing [CAN]. This is expected to be due to increasing number of macroradicals on chitosan, which is then reflected on the increasing average molecular weight of PEMA chains grafted onto chitosan. Then at [CAN]= 0.0036 mol/L and above both %GE and %Add-on starts declining. This can be attributed to the formation of homopolymers and termination of growing grafted chains by excess primary radicals generated.[21] Thus the M_v of PEMA chains grafted onto chitosan will form low molecular weight chains as seen in Table 2.

Effect of reaction temperature

It can be noted that %GE and %Add-on reach its maximum value at 30 °C and then decrease steadily as temperature increases up to 55 °C with lowest %GE and %Add-on. This can be due to increase in chain transfer reactions with higher activation energy, which in most cases contribute nothing to the grafting.[22] It is likely that at higher temperatures there is an increase in rate of oxidation of some saccharaides.[23]

Table 3 shows the effect of temperature on grafting parameters.

Table 3. Effect of reaction temperature on grafting of EMA onto chitosan (reaction conditions: Chitosan = 1.0 g, [EMA] = 0.025 mol/L, [CAN] = 0.0018 mol/L, Time = 120 min in 100 mL solution).

Temperature (°C)	%GE	%Add-on
30	70.2	16.7
35	56.1	13.8
40	45.6	11.5
45	28.1	7.4
50	24.6	6.5
55	17.5	4.7

Effect of polymerization Time

Table 4 illustrates the effect of polymerization time from 60 min up to 180 min.

Table 4. Effect of reaction temperature on grafting of EMA onto chitosan (reaction conditions: Chitosan = 1.0 g, [EMA] = 0.025 mol/L, [CAN] = 0.0018 mol/L, Temp. = 30 °C in 100 mL solution).

Time (min)	%GE	%Add-on
60	52.6	13.0
90	59.6	14.5
120	70.2	16.7
150	71.9	17.0
180	72.2	17.1

It appears that grafting is increasing rapidly in between the intervals of 60 min to 120 min, then it decrease and finally stays approximately constant at 150 min. The rapid increase of grafting below 120 min is due to an increase in rate of initiation and propagation, and the constancy of grafting at about 150 min is a clear remark on the depletion of monomer from the solution. Thus it is concluded that 150 min is an optimum polymerization time for grafting of EMA onto chitosan.

Effect of material to liquor ratio.

Table 5 shows the effect of material to liquor ratio from 1 : 14 to 1 : 4.

Table 5. Effect of material to liquor ratio on grafting of EMA onto chitosan (reaction conditions: Chitosan =1.0 g, [EMA] = 0.025 mol/L, [CAN] = 0.0018 mol/L, Temp. = 30 °C, Time = 120 min in 100 mL solution).

Material to liquor ratio	Liquor (mL)	%GE	%Add-on
1 : 14	200	17.5	4.7
1 : 11	150	52.6	13.0
1 : 7	100	70.2	16.7
1 : 5	75	31.6	8.2
1 : 4	50	17.5	4.7

The material to liquor ratio were changed by reducing the volume of solvent in the reaction mixture. It can be seen that %GE and %Add-on increases as the material to liquor ratio increases. This is due to increase in probability of collisions between chitosan macroradicals and monomer molecules, then at material to liquor ratio of 1: 5 grafting is reduced due to restricted movement of monomer molecules leading to lower %GE and %Add-on values. Thus it is concluded that the best material to liquor ratio is 1:7.

Characterization of Grafted Chitosan

X-ray diffraction (XRD)

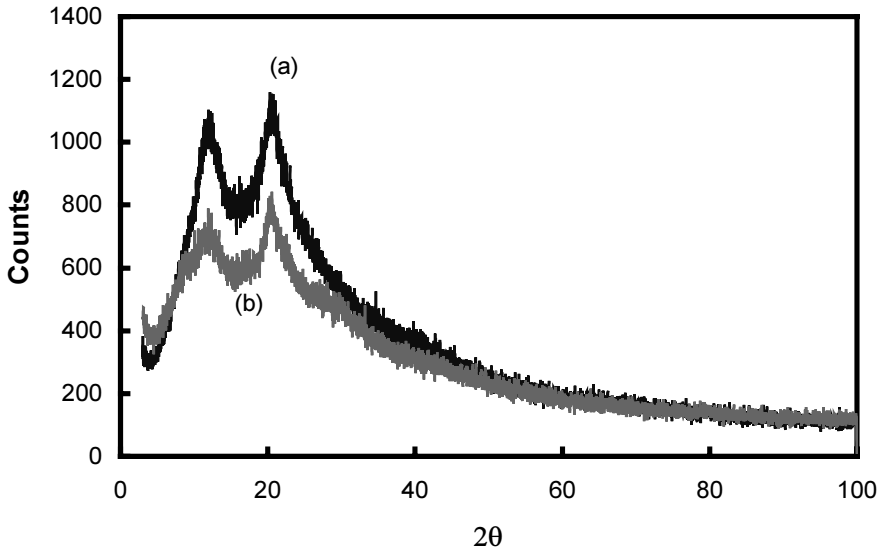

Figure 2. X-ray diffraction pattern for (a) Pure Chitosan, (b) Chitosan-g-EMA copolymer (%Add-on= 45.6).

Figure 2 shows the X-ray diffraction pattern of pure chitosan and grafted chitosan.

Chitosan like cellulose is a partially crystalline natural polymer, crystallinity is mainly formed due to the accumulation of linear chains in the structure. The low counts of chitosan (only up to 1200) indicates that it has low crystallinity. Upon grafting of EMA onto chitosan, the count rate of chitosan has been further reduced to about 800, which gives an indication of destruction of some crystalline chains, and the involvement of the crystalline region in grafting together with the amorphous Region.[24]

Thermogravimetric Analysis (TGA)

Figure 3 shows the thermogram and its derivatogram of pure chitosan (a), pure PEMA (b), and Chitosan-g-EMA copolymer (c) respectively. It can be clearly noticed that both chitosan and PEMA decomposes above 200 °C, and as a result of that grafted chitosan decomposes at similar temperature range.

Table 6 illustrates the thermal decomposition data of chitosan, PEMA and Chitosan-g-EMA copolymer respectively.

Table 6. The thermal decomposition data of Chitosan, PEMA and Chitosan-g-EMA copolymer.

Substance	Number of stages	Temperature range (°C)	T_{max} (°C)	Weight loss (%)
Chitosan	1	23-200	--	9.80
	2	200-365	305	50.8
	3	365-500	--	22.0
PEMA	1	200-365	315	89.5
	2	365-500	378	4.80
Chitosan-g-EMA (%GE=70.2)	1	200-290	274	35.0
	2	290-500	316	65.0

Pure chitosan shows three decomposition stages with the major weight loss of 50.8% takes place in the range of 200-365 °C at T_{max}= 305 °C derived from derivatogram, whereas PEMA shows two stages of decomposition with a major weight loss of 89.5% in the range of 200-365 °C at T_{max}= 315 °C. The grafted chitosan contains two well-identified stages; the first is the range of 200-290 °C at T_{max}= 274 °C, and the second is at the range of 290-500 °C at T_{max}= 316 °C. The second peak is clearly due to

PEMA chains grafted to chitosan, whereas the first peak refers to chitosan in the copolymer. The T_{max} of chitosan have appeared to be at 305 °C in the pure form, and at 274 °C in the grafted form. This difference in degradation temperature confirms that

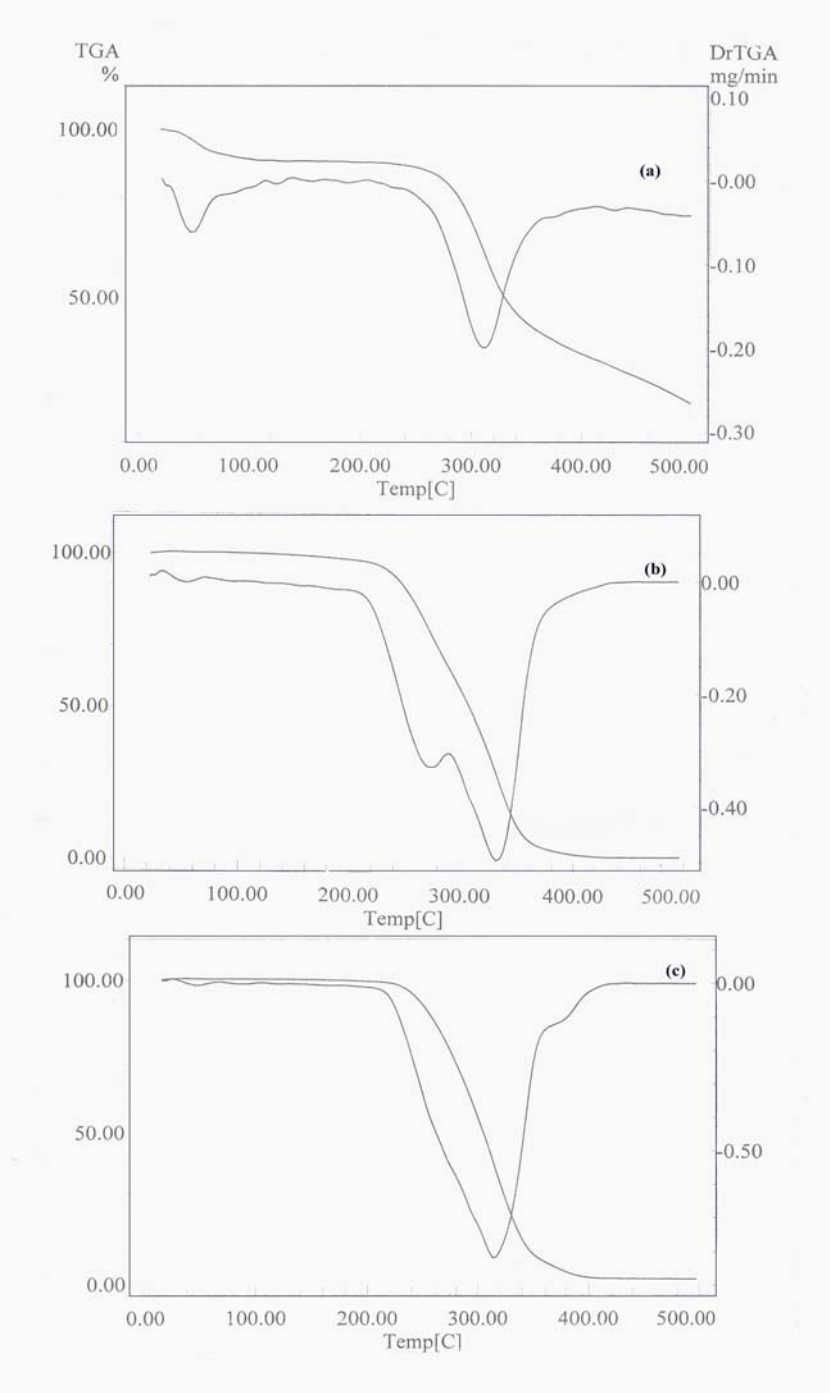

Figure 3. TGA and DrTGA profiles of (a) Pure chitosan, (b) Chitosan-g-EMA (%GE=70.2), (c) pure PEMA.

upon grafting of EMA onto chitosan, some chemical changes in the structure of chitosan take place. The destruction of the some crystalline chitosan chains upon grafting can lead to thermally less stable chitosan which in turn leads to the degradation of chitosan on lower temperatures.[24] Thus, the grafting of chitosan with EMA alters the thermal behavior of chitosan, which could be seen from T_{max} for both chitosan and grafted chitosan. The %weight loss of chitosan fraction in the copolymer is 35%, whereas the %weight loss of PEMA fraction is 65%, which indicates that the ratio of chitosan to PEMA is 1:2 in the backbone of the copolymer.

Conclusions

Ceric ammonium nitrate can successfully initiate graft copolymerization of EMA into chitosan at room temperature. The maximum %GE and %Add-on are 70.2% and 45.6% respectively. The optimum conditions for grafting EMA onto chitosan are; [EMA] = 0.025 mol/L, [CAN] = 0.0018 mol/L, reaction temperature = 30 °C, reaction time = 150 min and material to liquor ratio of 1:7. The grafting of EMA onto chitosan causes a decrease of the crystallinity in chitosan chains, also it alters the thermal stability of chitosan and makes it thermally less stable.

Experimental

Materials

Chitosan (degree of deacetylation > 90%) was purchased from Broker (Hamburg, Germany) and used without further purification, ethylmethacrylate (EMA) monomer (>99%, Fluka) was purified from inhibitor by vacuum distillation at 30 °C and kept at 0 °C until used, ceric ammonium nitrate (CAN) (>98%, Fluka) was used as obtained. All reagents used were of analytical grade.

Copolymerization Process

A mixture of 1 g of dried chitosan and 75 mL distilled water was stirred magnetically under N_2 atmosphere, and then was treated with a predetermined amount of CAN in 25 mL of 5% acetic acid solution for 15 min to facilitate free radical formation on chitosan.[15] This treatment was followed with dropwise addition of EMA monomer and the polymerization proceeded at 30 °C for 120 min unless stated elsewhere. After

120 min is over, the solution is allowed to cool and the graft copolymer was precipitated with 5% sodium hydroxide solution. The precipitate was washed several times with warm distilled water and warm 5% acetic acid solution to remove excess alkali, excess chitosan and homopolymer. Trace amounts of excess homopolymer can be removed by warm 5% acetic acid solution and can be checked by precipitation with methanol, which was followed by FTIR spectra. This process is repeated until no precipitation of homopolymer was observed; then the copolymer precipitate was dried to constant weight. The percentage grafting efficiency (%GE)[16] and add-on (%Add-on)[17] can be calculated from the relations

$$\%GE = 100(W_2 - W_1)/W_3 \quad (1)$$

$$\%Add\text{-}on = 100(W_2 - W_1)/W_2 \quad (2)$$

Where W_1, W_2 and W_3 are the weights of chitosan, graft copolymer and the monomer respectively. Poly(Ethylmethacrylate) (PEMA) was synthesized by bulk polymerization of distilled monomer using benzoyl peroxide as an initiator at 60 °C for 180 min. The viscosity average molecular weight (M_v) of PEMA chains was determined from the relation [18] : $[\eta] = 2.60 \times 10^{-3} M_v^{0.66}$, using 0.5 g/dL in ethyl acetate solvent at 30 °C.

FTIR analysis

A Nicolet (avator-360, USA) FTIR spectrometer in the range of 4000-400 cm^{-1} was used to record the IR spectra for grafted and ungrafted chitosan in the form of KBr pellets.

X-ray diffraction (XRD)

The X-ray diffraction studies were performed using a Philips-Holland diffractometer (model PW 1729) with copper as target material in an X-ray tube under the operational conditions 30 KV, 40 mA and wavelength between 1.54060 and 1.54438 Å. The samples were scanned between 3° and 100°.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using Shimadzu TGA-50 (Japan) under N_2 atmosphere at a heating rate of 10 °C/min.

Acknowledgements

The author wish to acknowledge Jordan University of Science & Technology (JUST) for their research grant 209/99 and for providing necessary facilities, also the author thanks Shugairat Shadi and Muneeb Bilal for helping performing experiments.

References

1. V. R. Patel, and M. M. Amiji, *Pharmaceutical Research* **1996**, *13*, 588–593.
2. T. Takahashi, K. Takayama, Y. Machida, and T. Nagai, *Int. J. Pharmaceutics* **1990**, *61*, 35–39.
3. D. K. Kweon, and D. W. Kang, *J. Appl. Polym. Sci.* **1999**, *74*, 458–463.
4. R. Schmuhl, H. M. Kreig, and K. Keizer, *Water SA* **2001**, *27*, 1–7.
5. K. L. Shanta, U. Bala, and P. Rao, *Eur. Polym. J,* **1995**, *31*, 377–382.
6. K. Kojima, M. Yoshikuni, and T. Suzuki, *J. Appl. Polym. Sci.* **1979**, *24*, 1587–1590.
7. Y. Shigeno, K. Kondo, and K. Takemoto, *J. Macromol. Sci. Chem.* **1982**, *A17*, 571–575.
8. K. Kurita, A. Yoshida, and Y. Koyama, *Macromolecules* **1988**, *21*, 1579–1584.
9. D. W. Kang, H. R. Choi, and D. K. Kweon, *J. Appl. Polym. Sci.* **1999**, *73*, 469–473.
10. W. M. Doane, *Polym. Perpr.* **1987**, *28*, 103–108.
11. D. K. Kweon, *Polymer Bulletin* **1998**, *41*, 645–650.
12. K. Y. Lee, W. H. Park, and W. S. Ha, *J. Appl. Polym. Sci.* **1998**, *63*, 425–429.
13. B. Feng, and S. Wu, *Hebei Gongxueyan Xuebao* **1989**, *18*, 75–82 (in Chinese); *Chem. Abstr.* **1989**, *115*, 9993b.
14. R. Tian, and X. Liu, *Gaofenzi Xuebao* **1992**, *1*, 103–108, (in Chinese); *Chem. Abstr.* **1992**, *120*, 108439h.
15. G. Mino, and S. Kaizerman, *J. Polym. Sci.* **1958**, *31*, 122–127.
16. V. D. Athawale, and V. Lele, *Carbohydrate Polymers* **2000**, *41*, 407–411.
17. V. Pacheco, M. Vazquez-Torros, and J. Canche-Escamilla, *J. Appl. Polym. Sci.* **1993**, *47*, 53–57.
18. J. Brandrup, E. H. Immergut, *Polymer Handbook*, Wiley & sons, pVII-68, **1966**.
19. M. I. Khalil, K. M. Mostafa, and A. Hebeish, *Starch* **1990,** *42*, 107–110.
20. R. B. Seymour, and C. E. Carraher, Polymer Chemistry, An Introduction, Marcel Dekker, 1st edition, Newyork, pp 295–299, **1981**.
21. J. S. Shukla, and G. K. Sharma, *J. Polym. Sci., Part A: polym Chem.* **1987**, *25*, 595–599.
22. B. N. Mishra, R. Dogra, I. Kaur, and D. Sood, *J. Polym. Sci., Part A: polym Chem.* **1980**, *18*, 341–345.
23. D. R. Patil, and G. F. Fanta, *J. Appl. Polym. Sci.* **1993**, *47*, 1765–1771.
24. J. Gao, R. Tian, J. Yu, and M. Duan, *J. Appl. Polym. Sci.* **1994**, *53*, 1091–1095.

Povzetek

V članku je opisan postopek cepljenja etil metakrilata (EMA) na hitosan v vodnem mediju. Kot iniciator smo uporabili cerijev amonijev nitrat (CAN), reakcija pa je potekala v dušikovi atmosferi. Raziskovali smo vpliv koncentracije monomera, iniciatorja, temperature, časa polimerizacije in razmerja trdna snov/raztopina na učinkovitost polimerizacije, ki smo jo opredelili s konverzijo monomera (%GE) in prirastkom mase (%Add-On). Optimalni pogoji za cepljenje EMA na 1 g hitosana so: [CAN] = 0,0018 mol/L, [EMA] = 0,025 mol/L, temperatura 30 °C, čas reakcije 180 min, trdna snov/raztopina = 1:7. Cepljeni kopolimer smo analizirali z infrardečo spektroskopijo (FTIR), rentgensko difrakcijo (XRD) in termično gravimetrično analizo (TGA).