ELSEVIER

PII: S0144-8617(96)00085-9

Carbohydrate Polymers **31** (1996) 23–27

0144-8617/96/$15.00 + .00

Aspects of thermal graft copolymerization of methyl methacrylate onto ethyl cellulose in homogeneous media

E.A. Abdel-Razik

Chemistry Department, Faculty of Science, Mansoura University, Egypt

(Received 11 April 1996; revised version received 25 June 1996; accepted 5 July 1996)

Homogeneous graft copolymerization of methyl methacrylate onto ethyl cellulose using radical initiators such as ammonium persulphate, potassium persulphate and benzoyl peroxide was carried out in benzene/dimethylsulphoxide (1/1 v/v) mixed solvent system. The grafting yield was determined as functions of the polymerization temperature and the concentrations of monomer, ethyl cellulose and initiator. Different techniques were used for confirming the presence of polymethyl methacrylate grafted chains such as IR, TLC and NMR. The efficiency of grafting methyl methacrylate onto ethyl cellulose with ammonium persulphate and potassium persulphate was studied in different solvent systems. The power of solvents for increasing the grafting yield was found as follows: chloroform > toluene > benzene. The highest overall rates for copolymerization of methyl methacrylate onto ethyl cellulose using ammonium persulphate and potassium persulphate initiators were determined as 0.2% min^{-1} and 0.08% min^{-1}, respectively. Benzoyl peroxide was found to be an unsuitable initiator for grafting methyl methacrylate onto ethyl cellulose. A Trommsdorf effect was observed in certain systems. The mechanism of grafting reaction of methyl methacrylate onto ethyl cellulose is discussed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Modification of the organochemical properties of cellulose or cellulose derivatives by graft copolymerization with selected monomers impart new chemical properties.

Graft copolymerization of vinyl monomers onto cellulose is usually carried out in a heterogeneous solvent system, so far as the grafting process proceeds only in amorphous regions (Arthur, 1969, 1970, 1971; Bikales & Segal, 1971; Sakurada *et al.*, 1972; Ogiwara *et al.*, 1982). On the other hand in homogeneous graft copolymerization all the cellulosic chains participate in the copolymerization process (Nishioka & Kosai, 1981; Abdel-Razik, 1990). Homogeneous graft copolymerization of methyl methacrylate (MMA) onto cellulose dissolved in a dimethylsulphoxide/paraformaldehyde solvent system was carried out using many radical initiators and higher grafting yields were obtained (Kishoika & Kosai, 1981).

It was reported that acrylamide, 4-vinylpyridine and acrylonitrile were grafted homogeneously onto ethyl cellulose using persulphate initiators and higher grafting yields were also obtained (Abdel-Razik, 1990, 1994, 1995).

In the present study the macromolecular modification of ethyl cellulose by homogeneous graft copolymerization with MMA using the mentioned persulphate initiators has been investigated.

EXPERIMENTAL

Ethyl cellulose (EC; BDH) with a degree of substitution between 2.42–2.53 was chosen as the cellulose derivative. Ammonium persulphate (APS; BDH), potassium persulphate (KPS; BDH) and benzoyl peroxide (BPO; Merck) were selected as initiators and used without further purification. Methyl methacrylate (MMA; BDH) was purified and distilled under reduced pressure. Solvents such as chloroform, toluene, benzene and dimethylsulphoxide (DMSO) were of pure grade. The polymerization process was carried out in benzene/DMSO (10/10 cm^3) solvent system. The polymerization reaction was finally terminated by adding hydroquinone (5%). The polymerization mixture was then poured onto distilled water with vigorous stirring to precipitate the reaction product. The extraction of polymethyl methacrylate homopolymer was carried out by an ethyl alcohol/water (1/1 v/v) solvent system at room temperature. Moreover the efficiency of extraction was checked by thin layer chromatography (TLC) (Abdel-Razik, 1994).

The grafting yield (GY%) was derived from the expression:

$$\mathrm{GY\%} = \frac{D - B}{B} \times 100$$

where D and B are the weights of extract graft product and ethyl cellulose, respectively.

The composition of the graft products were examined by IR spectroscopy (Perkin Elmer 1430). The graft copolymer films were prepared from concentrated solutions of the copolymer in benzene (0.02 g ml^{-1}) casted on sodium chloride plate.

Nuclear magnetic resonance (NMR) spectra of EC and EC-g-PMMA graft copolymers were recorded in deuterated chloroform using a Varian Gemeni 200, 200 MHz instrument.

The overall rate of graft copolymerization was determined from the slope of the linear part of the plot of time vs GY at the initial stages of the reaction (Misra *et al.*, 1978; Eaton *et al.*, 1991; Abdel-Razik, 1994).

RESULTS AND DISCUSSION

The initiation of copolymerization of vinyl monomers onto cellulose materials involves the formation of a cellulose free radicals. That the initiating free radical is generally a macrocellulosic radical. The sites for attachments of grafted polymers are usually considered to be the site of the macro-cellulosic radical (Gaylord, 1972). So it was suggested that grafting onto cellulose is a termination reaction of a growing polymer chain on cellulose (Arthur, 1982).

Uninitiated grafting of MMA onto EC did not succeed. Accordingly, chemical redox initiators such as APS and KPS were used for grafting MMA onto EC. Table 1 shows the effects of polymerization temperature on the grafting process. The values of grafting yield that belong to APS and KPS show the highest values at 67.5% and 13.5%, respectively, that correspond to temperatures at 50°C and 40°C. This finding may be due to the Trommsdorf effect (Dilli & Garnet, 1967; Dilli *et al.*, 1972). This effect is responsible for the production of high molecular weight graft polymers and is further accentuated in grafting because the mobility of the polymer chains is restricted by the cellulose derivative (Abdel-Razik, 1990). The high difference present between the two mentioned GY values may be due to the difference in their decomposition rates in presence of ethyl cellulose macrochains. Furthermore, both APS and KPS are persulphate salts but there exists a difference in degradation. This finding is clearly shown from investigations that were carried out by adding APS and KPS in solution of cellulose and heated at certain lower temperatures (Nishioka *et al.*, 1986). So far the solution viscosity of recovered cellulose decreases remarkably with increasing KPS content while a slight decrease was observed in case of APS. This indicated the degradation of cellulosic chains at higher initiator contents (Nishioka *et al.*, 1986). This can explain the decrease observed when using KPS initiator as shown in Table 1. A similar temperature dependence of graft yield has been found for other grafting systems (Maekawa *et al.*, 1964). Also, these tendencies are consistent with the expectation based on the kinetics of radical polymerization (Ide, 1977).

The increase in initiator concentration probably causes both a decrease in the molecular weight of graft polymer and the graft yield (Ogiwara *et al.*, 1962; Hornof *et al.*, 1975; Abdel-Razik, 1990). The effects of APS and KPS contents on the graft copolymerization of MMA onto EC were investigated (Table 2). Thus, it was found that the GY in the case of APS increased by increasing its concentration. This finding is contrary to KPS which decreases the GY. The decrease observed in GY in the presence of KPS can be explained by the increase in degradation of cellulose chains as well as the decrease in the molecular weight of graft polymethyl methacrylate. Moreover, the further increase in radical content would lead to the termination of primary radicals and this in turn decreases the GY as was found in the case of using KPS.

Table 1. Effect of temperature on the graft copolymerization of MMA onto EC with APS and KPS in benzene/DMSO (50/50) cm^3 solvent system[a]

Temperature	GY% (APS)	GY% (KPS)
30° C	14	5.32
40° C	68.68	14.4
50° C	60	6
60° C	43.02	4
70° C	35.02	5.46

[a]Conditions: grafting time, 3 h; EC, 2 g/100 cm^3; MMA, 3.74 g/100 cm^3, APS and or KPS, 0.2 g/100 cm^3.

Table 2. Effects of initiator concentration on the grafting of MMA onto EC with APS and or KPS in benzene/DMSO (50/50) cm^3 solvent system[a]

Initiator content	GY% (APS)	GY% (KPS)
0.1	4.22	77.1
0.2	14.34	47.6
0.3	10.1	30
0.4	34	19.1
0.5	50	

[a]Conditions: grafting time, 3 h; EC, 2 g/100 cm^3; MMA, 3.74 g/100 cm^3 and temp., 50°C.

Table 3. Effect of monomer concentration on the grafting of MMA onto EC with APS and or KPS in benzene/DMSO (50/50) cm^3 solvent system[a]

Monomer content	GY% (APS)	GY% (KPS)
4	76	19.82
8	147.76	50.92
12	128.74	94.46
16	77.88	142.22

[a]Condition: grafting time, 3 h; EC, 2 g/100 cm^3; APS and or KPS, 0.2 g/100 cm^3 and temp., 50°C.

Table 4. Grafting yield % as a function of EC content on grafting of MMA onto EC with APS and or KPS in benzene/DMSO (50/50) cm^3 solvent system[a]

EC content	GY% (APS)	GY% (KPS)
1	12.12	2.4
2	12	9.2
3	13.16	17.97
4	19.4	5.7
5	18.54	6.1

[a]Conditions: grafting time, 3 h; MMA, 3.74 g/100 cm^3, APS and or KPS, 0.2 g/100 cm^3 and temp., 50°C.

It was accepted that an increase in monomer content would be expected to increase in grafting yield (Ide *et al.*, 1966; Hornof *et al.*, 1975; Abdel-Razik, 1990, 1995). So the effect of MMA content towards the GY was studied as shown in Table 3. Firstly, when using APS, it was found that as the monomer content increases the GY also increases till it reached the highest value at a concentration of MMA at 8 g/100 ml, then a decrease of GY was observed, this may be due to the Trommsdorf effect (Dilli & Garnet, 1967; Dilli *et al.*, 1972). Furthermore, the increase in monomer content facilitates the consumption of primary radicals to reduce the formation of cellulose macroradicals (Nishioka *et al.*, 1986), and this in turn encourages the homopolymerization reaction. On the other hand when using KPS as an initiator, it was found that the increase in monomer content increased the GY and no optimum condition was observed as was found in case of APS. This finding may explain the difference in the decomposition rates of APS and KPS in the presence of EC macrochains and MMA molecules. So far it has been reported that the decomposition rate of persulphate is greatly enhanced by the presence of polyvinyl alcohol (PVA) because of the redox reaction between PVA and persulphate (Ide *et al.*, 1966; Ikada *et al.*, 1974) and that the solution viscosity of PVA decreases remarkably with increasing time in presence of APS initiator (Okamura & Yamashita, 1958). By extrapolation to this the free hydroxyl groups present in the EC structure may enhance to some extent the redox reaction and prevail the tendencies of APS and KPS for increasing or decreasing the redox reaction.

It must be mentioned that the quantity of extracted PMMA homopolymer did not increase more than 7% of the weight of obtained crude graft products that belong to the data in Table 3. This means that APS and KPS are suitable initiators for grafting of MMA onto EC in the benzene/DMSO solvent system and accompanied the least amount of PMMA homopolymers.

It has been reported that GY increases with increasing polymer concentration in certain systems (Srinivasan *et al.*, 1982; Nishioka *et al.*, 1983; Abdel-Razik, 1995). In the case of using KPS it was found that GY increases up to 3 g/100 cm^3 of EC, then decreases more with further increase, whereas, in the case of APS the GY increases with increasing of EC content then levels off (Table 4). So this can be explained by the increase in the relative ratio of EC to persulphate content.

The graft copolymerization of MMA onto EC is shown as a function of time in Fig. 1. The data obtained show an increase in grafting in the two curves of APS and KPS initiators. The highest rates of propagation observed are 0.2% min^{-1} and 0.08% min^{-1} for APS and KPS, respectively. Thus the power of both initiators for increasing the grafting yield was found as follows: APS > KPS

Initiation with benzoyl peroxide (BPO)

In general, it is certain that BPO is a good initiator for bulk polymerization of MMA. Therefore, it was investigated in the graft copolymerization of MMA onto EC (Table 5). The data obtained showed that the change of BPO content has no significant effect on the grafting process. This could be due to the specific reactivity of the monomer-substrate towards the specific initiator

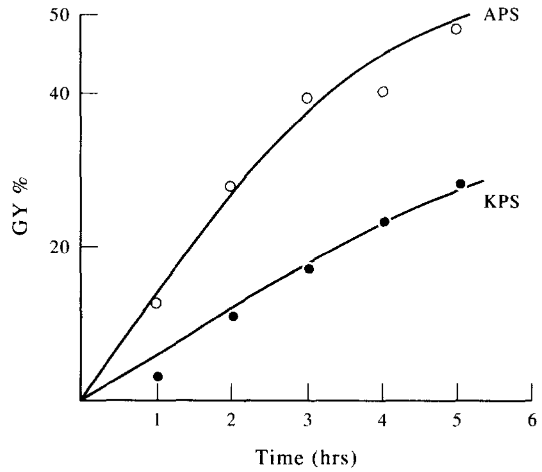

Fig. 1. Time dependence of grafting of MMA onto EC with APS and KPS in benzene/DMSO (50/50) cm^3 solvent system, Conditions: EC, 2 g/100 cm^3; MMA, 3.74 g/100 cm^3; Initiator concn, 0.2/100 cm^3 and temp., 50°C.

Table 5. Effect of benzoyl peroxide content on the graft copolymerization of MMA onto EC in benzene solution[a]

BPO content	GY%
0.08	3.04
0.16	9.64
0.24	7.34
0.32	8.50

[a] Conditions: grafting time, 3 h; temperature, 50°C, EC, 2 g/100 cm^3 and MMA, 3.74/100 cm^3.

Table 6. Effect of the type of solvents on the graft copolymerization of MMA onto EC with APS and or KPS in solvent/DMSO (50/50) cm^3 solvent system[a]

Solvent	Dielectric constant	GY% (APS)	GY% (KPS)
Benzene	2.275	28	6.64
Toluene	2.379	43.56	19.5
Chloroform	4.806	84.50	44

[a] Conditions: grafting time, 3 h; temperature, 50°C, EC, 2 g/

(Ito & Otsu, 1969). So this prevails that BPO is unsuitable initiator for grafting MMA onto EC.

Effects of various solvents

It is reported that the polarization of the carbonyl group of MMA is known to be sensitive to the nature of the solvents used (Srinivasan *et al.*, 1982). Accordingly, the copolymerization of MMA onto EC using APS and KPS as initiators in different solvents such as toluene, benzene and chloroform was investigated (Table 6). The data obtained showed that the GY % was correlated to the dielectric constant of the tested solvents and their order for increasing the grafting yield was found as follows: chloroform > toluene > benzene.

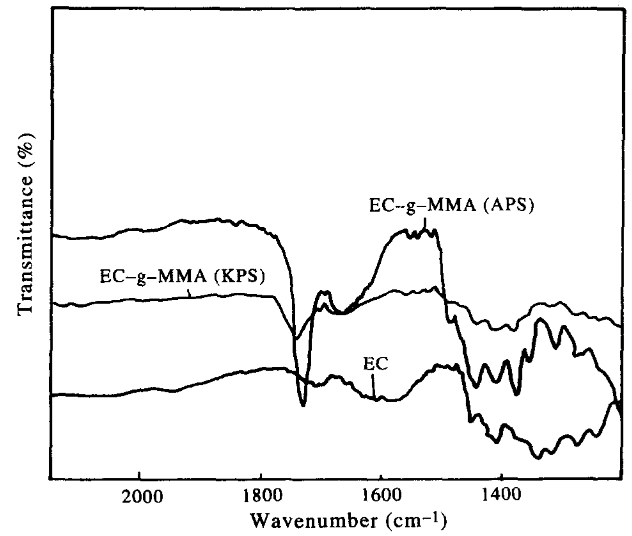

Fig. 2. IR spectra of EC and EC-g-PMMA. Conditions: grafting time, 3 h; EC, 2 g/100 cm^3; MMA, 3.74 g/100 cm^3; Initiator concn, 0.2 g/100 cm^3 and temp., 50°C.

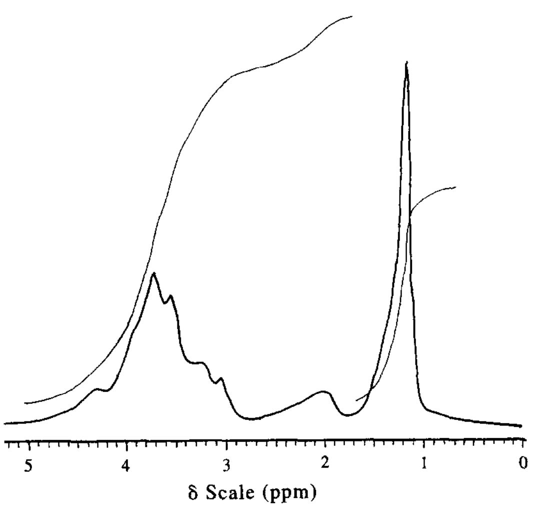

Fig. 3. NMR spectrum of EC in deuterated chloroform.

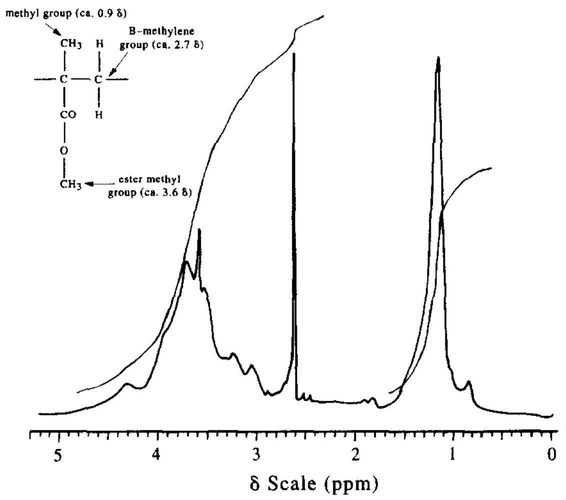

Fig. 4. NMR spectrum of EC-g-PMMA. Conditions: grafting time, 3 h; EC, 2 g/100 cm^3; MMA, 3.74 g/100 cm^3, APS, 0.2 g/100 cm^3 and temp., 50°C.

Evidence of grafting

The infrared spectra of EC and EC-g-PMMA when using APS and KPS are shown in Fig. 2. Strong absorption peaks at 1740 cm^{-1}, indicate the presence of carbonyl groups of grafted chains. The nuclear magnetic resonance (NMR) spectra of EC and EC-g-PMMA graft copolymers are shown in Figs 3 and 4. The graft copolymer spectra shows the presence of -B-methylene group at $\delta = 2.6$, the ester methyl group at $\delta = 3.6$ and a small peak due to α methyl group at $\delta = 0.9$, indicating the presence of polymethyl methacrylate grafted chains.

The mechanism explains the graft copolymerization of MMA onto EC using persulphate initiator and according to the data obtained can be proposed as follows:

THE MECHANISM

Initiation:

$$(NH_4)_2S_2O_8 \rightarrow 2S\dot{O}_4^-$$
$$2S\dot{O}_4^- + Cell - OH \rightarrow 2KHSO_4 + Cell - \dot{O}$$

Propagation

$$Cell - \dot{O} + M \rightarrow Cell - O - \dot{M}$$
$$Cell - O - \dot{M}n + M \rightarrow Cell - O - Mn + 1$$
$$\dot{M}m + M \rightarrow Mm + 1$$

Termination

$$Cell - O - \dot{M}n + S\dot{O}_4^- \rightarrow Cell.O.Mn + S_2^{-2}O_8$$
$$\dot{M}m + S\dot{O}_4^- \rightarrow Mm + S_2O_8^{-2}$$

Here Cell − OH denotes a reactive group in cellulose and M is the monomer.

REFERENCES

Abdel-Razik, E.A. (1990). *Polymer*, **31**, 1739–1744.

Abdel-Razik, E.A, (1994). *Acta Polymer*, **45**, 34–38.

Abdel-Razik, E.A. (1995). *Acta Polymer*, **46**, 134–138.

Arthur, Jr, J.C. (1969). *Advanc. Chem. Ser.*, No. **91**, 574–591.

Arthur, Jr, J.C. (1970). *Graft Polymerization onto Polysaccharides in Advances in Macromolecular Chemistry*, Pasika, W.M. (ed.) Academic Press, London, Vol. 2, p. 1–87.

Arthur, Jr, J.C. (1971). *Advanc. Chem. Ser.*, No. **99**, 321–339.

Arthur, Jr, J.C. (1982). *ACS. Symp. Series*, No. **187**, 21–31.

Bikales, N.M. & Segal, L. (eds) (1971). *Cellulose and Cellulose Derivatives. High Polymers*, Vol. V, Parts IV and V. Wiley Interscience, New York.

Dilli, S. & Garnet, J.L. (1967). *J. Appl. Polym. Sci.*, **11**, 839.

Dilli, S., Garnet, J.L., Martin, E.C. & Phouc, D.H. (1972). *J. Polym. Sci.* (C), **37**, 57.

Eaton, D.F., Horgen, A.G. & Horgen, J.P. (1991). *J. Photochem. Photobiol.*, A: Chem., **58**, 373–391.

Gaylord, N. (1972). *J. Polym. Sci.*, Part C, **37**, 153–172.

Hornof, V., Kokta, B.V. & Valade, J.L. (1975). *J. Appl. Polym. Sci.*, **19**, 545.

Ide, F. (1977). *Graft Jugo to Sono Oyo.* Kobunshi Kanko Kai, Kyoto.

Ide, F., Nakatsuka, K. & Tamura, H. (1966). *Kobunshi kagaku*, **23**, 45.

Ikada, Y., Nishizaki, Y. & Sakurada, I. (1974). *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1829.

Ito, T. & Otsu, T. (1969). *J. Macromol. Sci., Chem.*, A3**(2)**, 197–203.

Maekawa, T., Hayashi, K., Uno, K. & Okamura, S. (1964). *Kobunshi Kagaku*, **21**, 323.

Misra, B.N., Kasal, J.K. & Pande, C.S. (1978). *J. Polym. Sci., Chem. ed*, **16**, 295.

Nishioka, N. & Kosai, K. (1981). *Polym. J.*, **13**, 1125.

Nishioka, N., Minami, K. & Kosai, K. (1983). *Polym. J.*, **15**, 591–596.

Nishioka, N., Matsumoto, Y., Yumen, T., Monamie, K. & Kosai, K. (1986). *Polym. J.*, **18**, 4, 323–330.

Ogiwara, Yo., Ogiwara, Yu. & Kubota, H. (1962). *J. Polym. Sci.*, A-I, **5**, 2791.

Ogiwara, Y., Kubota, H. & Arai, K. (1982). *J. Appl. Polym. Sci.*, **14**, 1049.

Okamura, S. & Yamashita, T. (1958). Kobunshi Kogaku, **15**, 165.

Sakurada, I., Ikada, Y. & Nishizaki, Y. (1972). *J. Polym. Sci.*, C, No. **37**, 265.

Srinivasan, K.S.V., Hon D.N.S. & Sanpappa, M. (1982). *Amer. Chem. Soc.*, **11**, 155–178.