Homogeneous graft copolymerization of acrylamide onto ethylcellulose

E. A. Abdel-Razik

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Homogeneous graft copolymerization of acrylamide onto ethylcellulose using radical initiators such as ammonium persulphate, potassium persulphate and benzoyl peroxide was carried out in a dimethyl-sulphoxide/toluene solvent system. The weight conversion, grafting percentage, grafting efficiency and amide index change were determined as functions of the polymerization temperature and of the concentrations of monomer, ethylcellulose and initiator. The amide index change at the absorption peak of the amide group at $1685 \, cm^{-1}$ in films of the graft copolymers correlates with the grafting efficiency. The grafting efficiency and the amide index change depend greatly on the type of initiator and on the concentration of ethylcellulose. A Trommsdorf effect (accelerated grafting) has been observed in certain systems at moderate temperatures and/or lower concentrations of ethylcellulose. Benzoyl peroxide was found to be unsuitable as an initiator, because it increases the degradation of ethylcellulose chains.

(Keywords: graft copolymers; acrylamide; ethylcellulose; initiation)

INTRODUCTION

Graft copolymerization of vinyl monomers onto cellulose is usually carried out in a heterogeneous solvent system[1-4], and is considered an efficient method for improving its properties. It is considered that graft copolymerization in such a heterogeneous system proceeds only partly and is markedly affected by the fine structure of the cellulose material used. If grafting is carried out in a homogeneous system in which cellulose material dissolves molecularly, most of the complexities mentioned may be overcome[5].

The present paper reports a quantitative study of the graft copolymerization of acrylamide onto ethylcellulose. This was done to modify its properties. Some variables were examined, including the type of initiator and the dependence on the concentrations of initiator, monomer and ethylcellulose. Moreover, the effect of temperature on the polymerization process is considered, as is the mechanism of formation of grafted chains.

EXPERIMENTAL

Ethylcellulose (BDH) with degree of substitution between 2.42 and 2.53 and a viscosity of $\sim 14 \, cP$ $(1.4 \times 10^{-2} \, Pa \, s)$ at 5% w/w in 80/20 toluene/ethanol at 25°C was chosen as the derivative of cellulose. Ammonium persulphate (BDH), potassium persulphate (BDH) and benzoyl peroxide (BDH) were chosen as initiators and used without further purification. Acrylamide (Prolabo) (m.p. 84–85°C) was used without further purification. Solvents such as dimethylsulphoxide (DMSO) and toluene were of pure grade. The polymerization was carried out in a DMSO/toluene $(25/25 \, cm^3)$ solvent system. The loading of ethylcellulose was maintained at 1 g in the mentioned volume of solvents. To 0.5 g acrylamide was added the above-mentioned loading of ethylcellulose and the concentration of reactants changed accordingly. The polymerization process was finally terminated by adding hydroquinone. The polymerization mixture was then poured into boiling distilled water with vigorous stirring. This was seen to be sufficient to dissolve the poly-(acrylamide) homopolymer. The efficiency of extraction was checked by thin-layer chromatography to ensure complete separation of the homopolymer formed during the graft polymerization. The graft products were characterized by the following parameters:

$$\text{Weight conversion percentage} \; (WC\%) = \frac{A}{B} \times 100$$

$$\text{Grafting efficiency percentage} \; (GE\%) = \frac{A-B}{C} \times 100$$

$$\text{Grafting percentage} \; (GP\%) = \frac{A-B}{B} \times 100$$

where A, B and C are the weights of the graft product, ethylcellulose and monomer, respectively.

The composition of the graft copolymer was examined by i.r. spectroscopy (Perkin–Elmer 1430). The graft copolymer films were prepared from concentrated solutions of copolymer in ether (0.02 g in 1 cm^3 ether) cast on sodium chloride plates. Quantitative i.r. analysis was used by applying the internal standard method to compensate for the differences in the thickness of polymer films[6]. The poly(acrylamide) that grafted onto ethylcellulose can be detected by the appearance of a new absorption peak at $1685 \, cm^{-1}$, which is related to the amide group. Similarly, the absorption value of the unchanged peak at $875 \, cm^{-1}$ was taken as a reference peak. Accordingly, the amide index change is calculated as follows:

$$I_{amide} = \frac{A_{amide, 1685}}{A_{ref., 875}}$$

where $A_{amide, 1685}$ and $A_{ref., 875}$ are the absorptions of amide group and reference peak, respectively, at 1685 and $875 \, cm^{-1}$.

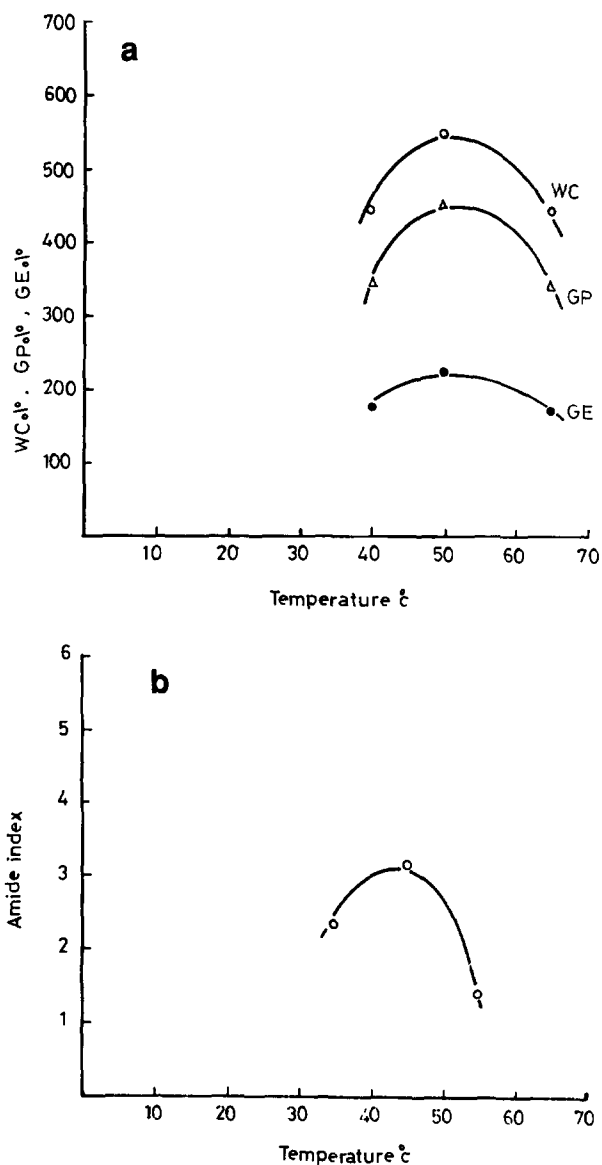a maximum around 50°C and this is similar to the results obtained for the grafting efficiency values (*Figure 1a*). The trend in the grafting percentage follows the change in the molecular weight of grafted poly(acrylamide); the values of grafting percentage go through a maximum at 50°C (*Figure 1a*). This may relate to the Trommsdorf effect that is responsible for a rapid consumption of monomer[8,9].

Figure 1 Temperature dependence of grafting polymerization of AM onto EC with APS in DMSO/toluene (50/50 cm³) solvent system: (a) WC%, GP% and GE%; (b) amide index of graft copolymer (grafting time, 3 h; EC, 2 g/100 cm³; APS, 0.4 g/100 cm³)

A modified Ostwald viscometer was used for viscosity measurement at 30°C.

RESULTS AND DISCUSSION

Initiation with ammonium persulphate (APS)

The initiation of polymerization of vinyl monomers involves the formation of a cellulose radical. However, it was proposed that the sites for attachment of grafted polymers are not necessarily the sites of cellulosic radicals[7].

A chemical redox initiator such as ammonium persulphate (APS) is used for the graft polymerization of acrylamide (AM) onto ethylcellulose (EC). *Figure 1a* shows the effect of polymerization temperature on the grafting parameters. The data of weight conversion and grafting percentage show maxima around 50°C, showing that there is an optimum temperature. At the same time, the amide index change (*Figure 1b*) reveals that the true poly(acrylamide) grafted onto ethylcellulose also shows
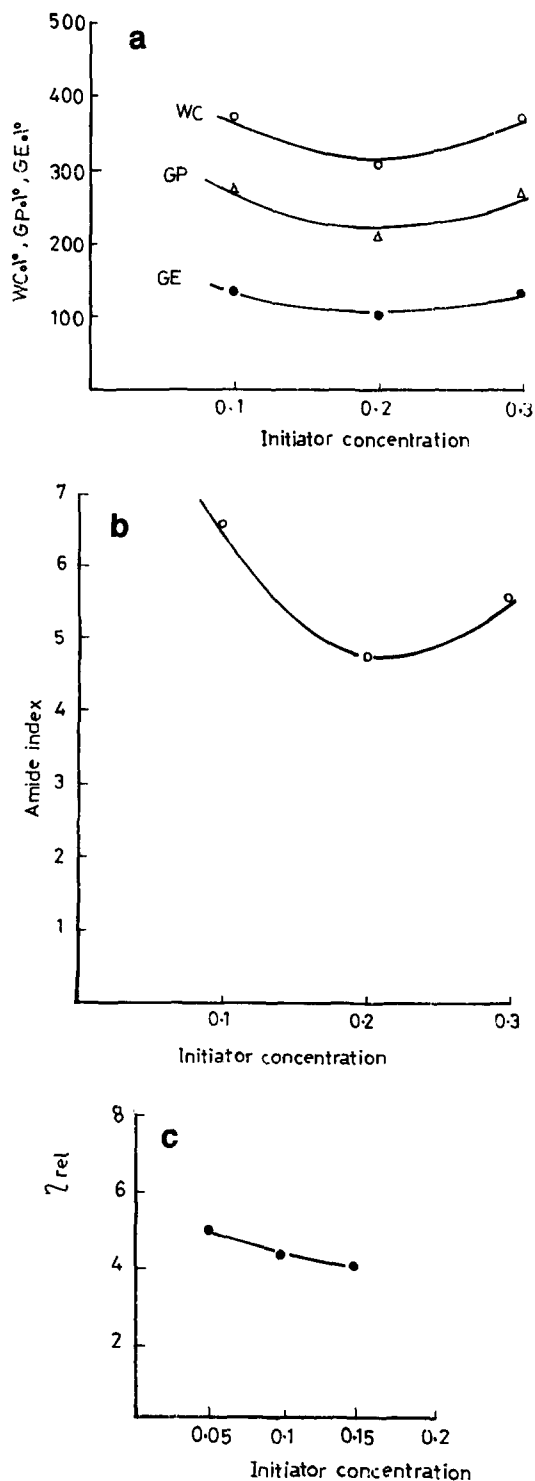
Figure 2 Effects of initiator concentration on the grafting of AM onto EC with APS in DMSO/toluene (50/50 cm³) solvent system: (a) WC%, GP% and GE%; (b) amide index of graft copolymer (grafting time, 3 h; EC, 2 g/100 cm³; AM, 4 g/100 cm³; temp., 50°C). (c) Influence of APS concentration on viscosity of EC (2 g/100 cm³ in toluene solution at 50°C)
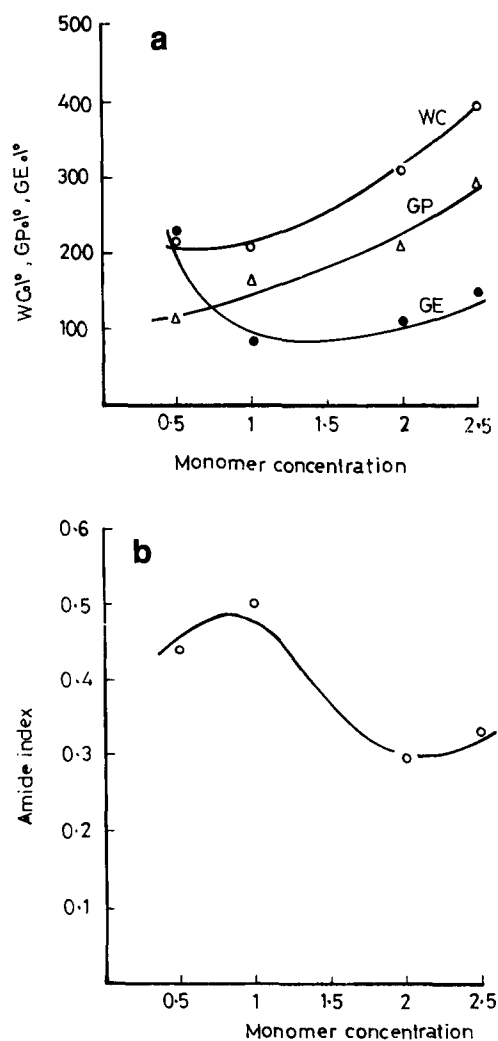
Figure 3 Effects of monomer concentration on the grafting of AM onto EC with APS in DMSO/toluene (50/50 cm³) solvent system: (a) WC%, GP% and GE%; (b) amide index of graft copolymer (grafting time, 3 h; EC, 2 g/100 cm³; APS, 0.4 g/100 cm³; temp., 50°C)

Macrocellulosic radicals initiated by chemical redox systems are temperature-sensitive and short-lived[10,11], as established by the temperature dependence of the graft polymerization of AM onto EC (*Figure 1a*).

The chemical modification of cellulose or cellulose derivatives increases their reactivity towards selected oxidizing and reducing agents. These, on reaction, yield macrocellulosic radicals[12,13]. Accordingly, the effect of APS concentration on the graft polymerization of AM onto EC was investigated (*Figure 2a*). The data of the three grafting parameters decreased on increasing the APS concentration. Hence, the amide index also decreased on increasing the initiator concentration, as shown in *Figure 2b*. This can be explained in that further increase in initiator concentration would lead to the termination of primary radicals. The consequences of the increase in initiator concentration probably cause the slight decrease in viscosity of ethylcellulose in toluene solution using APS as initiator and the optimum at 50°C as shown in *Figure 2c*. APS is therefore considered a suitable initiator for grafting AM onto EC because no degradation occurred.

An increase in monomer concentration would be expected to increase the molecular weight of graft polymer[14]. Therefore, the effect of concentration of AM

was investigated, as shown in *Figure 3a*. It was found that the weight conversion and grafting percentage values increased on increasing the monomer concentration. The increase in AM concentration facilitates the consumption of primary radicals and thus reduces the formation of ethylcellulose macroradicals. This in turn decreases the grafting efficiency. *Figure 3b* shows that the amide index change values decreased on increasing the monomer concentration. This is in accordance with the results obtained in the case of grafting efficiency (*Figure 3a*).

It has been reported that the grafting efficiency increases with increasing polymer concentration[14]. Thus, the effect of ethylcellulose concentration was studied (*Figure 4a*). The three grafting parameters show maxima around a concentration of ~1%. This means that an optimum condition is obtained at this concentration. The amide index change increased on increasing the EC concentration (*Figure 4b*). These results are similar to those shown in *Figure 4a*. Furthermore, the grafting percentage has a maximum around ~1% concentration and shows a Trommsdorf effect. The advantages of observing such an effect are valuable both from the fundamental mechanistic aspect of the process and also for commercial exploitation of the grafting reaction[8,9]. It should be noted that a relatively low temperature (50°C) is required to give significant copolymerization, as illustrated in *Figure 4a*.
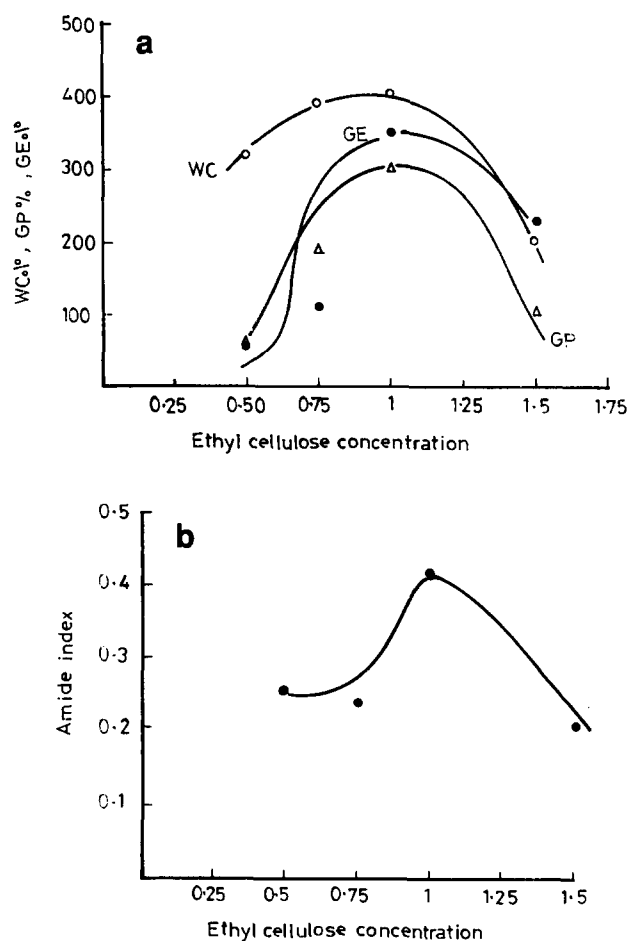

Figure 4 Influence of EC concentration on the grafting of AM onto EC with APS in DMSO/toluene (50/50 cm³) solvent system: (a) WC%, GP% and GE%; (b) amide index of graft copolymer (grafting time, 3 h; AM, 4 g/100 cm³; APS, 0.4 g/100 cm³; temp., 50°C)
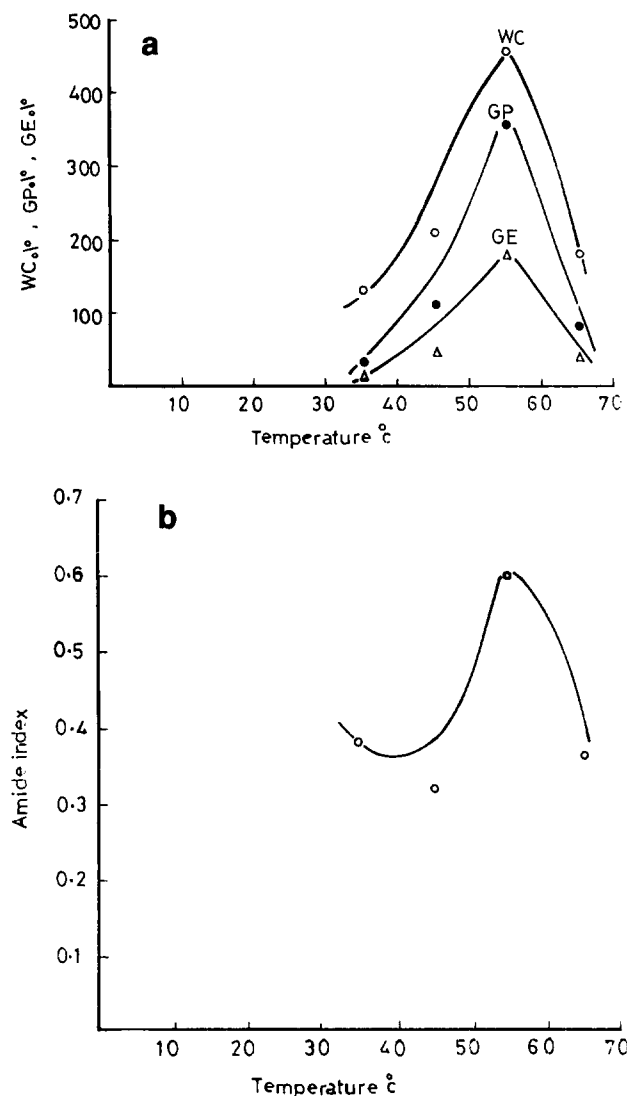
Figure 5 Effects of polymerization temperature on the grafting of AM onto EC with KPS in DMSO/toluene ($50/50\,\text{cm}^3$) solvent system: (a) $WC\%$, $GP\%$ and $GE\%$; (b) amide index of graft copolymer (grafting time, 3 h; AM, $4\,\text{g}/100\,\text{cm}^3$; KPS, $0.4\,\text{g}/100\,\text{cm}^3$)

Initiation with potassium persulphate (KPS)

In another example of initiation by a chemical redox process, potassium persulphate (KPS) was used as initiator for graft polymerization of AM onto EC. The objective was to see how the initiator structure affects the grafting parameters.

The effects of polymerization temperature on the grafting process were investigated. The results are shown in *Figure 5a*. The grafting parameters show maxima at around 55°C, indicating that an optimum temperature exists. These results are similar to those shown in *Figure 1a*, for a different initiator system. Also, the amide index change results (*Figure 5b*) show a maximum around 55°C. Hence, the grafting percentage increases remarkably and shows a Trommsdorf effect. This 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.

It was thought to be necessary to examine the effect of the concentration of KPS on the grafting process of AM onto EC (*Figure 6a*). The weight conversion

gradually increases as the concentration of initiator increases. Meanwhile the grafting percentage and grafting efficiency values are slightly increased. However, the amide index change decreases on increasing the initiator concentration (*Figure 6b*). It is clear that the degradation of ethylcellulose chains is a feature. It is stated in the literature that macrocellulosic free radicals may be formed through dehydrogenation, depolymerization or oxidation of cellulose[13]. Increase in monomer concentration causes an increase in the molecular weight of graft polymer[12]. Thus, the effect of AM concentration on grafting onto ethylcellulose was studied. The results obtained are shown in *Figure 7a*, indicating that the weight conversion, grafting percentage and grafting efficiency values increased with increasing AM concentration. At the same time, the amide index change also increases with increase in the AM concentration (*Figure 7b*). Thus, in the presence of KPS, the consumption of
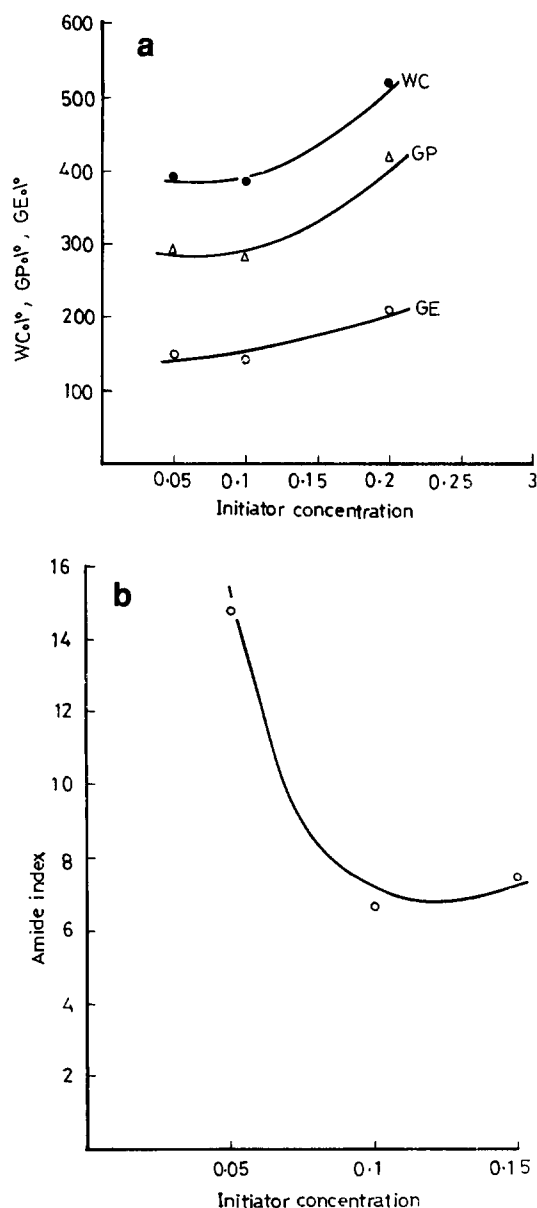

Figure 6 Effects of initiator concentration on the grafting of AM onto EC with KPS in DMSO/toluene ($50/50\,\text{cm}^3$) solvent system: (a) $WC\%$, $GP\%$ and $GE\%$; (b) amide index of graft copolymer (grafting time, 3 h; EC, $2\,\text{g}/100\,\text{cm}^3$; AM, $4\,\text{g}/100\,\text{cm}^3$; KPS, $0.4\,\text{g}/100\,\text{cm}^3$; temp., 50°C)
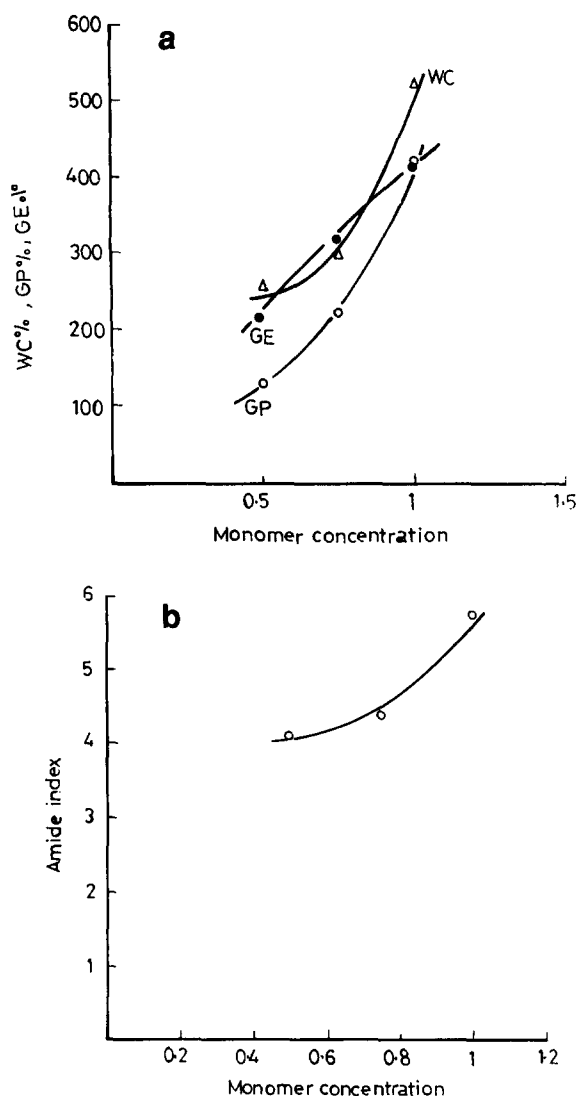
Figure 7 Effects of AM concentration on the grafting of AM onto EC with KPS in DMSO/toluene (50/50 cm^3) solvent system: (a) WC%, GP% and GE%; (b) amide index of graft copolymer (grafting time, 3 h; EC, 2 g/100 cm^3; KPS, 0.4 g/100 cm^3; temp., 50°C)

primary radicals does not result in reduction of the formation of ethylcellulose macroradicals. This increases the values of grafting efficiency in a wide range between 130 and 400% (*Figure 7a*). However APS, as shown before (*Figure 3a*) under the same conditions, gives results that differ greatly. This may be due to the difference in decomposition rate of APS and KPS initiators[15].

The sites for the attachment of grafted polymers are usually considered to be the site of the macrocellulosic radicals.

The reaction mechanism of the graft polymerization of acrylamide onto ethylcellulose is proposed to be of the form shown in *Figure 8*, where the following symbols apply: Enol, enolization; In, initiator; AM, acrylamide monomer. This mechanism shows that cellulose and radicals of growing chains exhibit different properties with respect to addition to the involvement in redox interactions.

The mixed solvent of DMSO/toluene is considered to be a neutral medium; acrylamide is more stable towards hydrolysis and is considered to be reactive with the hydroxyl groups of ethylcellulose. This is due to the special behaviour of AM when copolymerized in different

solvents. The effect could arise from a displacement of the equilibria:
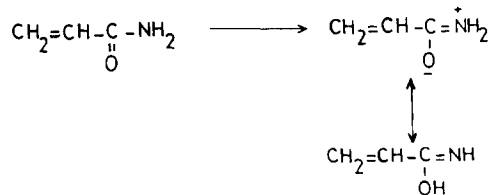
As the ethylcellulose concentration increases, the weight conversion, grafting percentage and grafting efficiency increase to an upper limit (*Figure 9a*). This means that when the ethylcellulose concentration increases, the formation of ethylcellulose macroradicals is made easier because of an increase in the relative ratio of ethylcellulose to primary radicals, leading to an increase in grafting efficiency. Hence, the amide index change increases by increasing the ethylcellulose concentration until no further change in its value (*Figure 9b*) occurs. This confirms the results shown in *Figure 9a*. Comparison of *Figure 9a* with *Figure 4a*, showing the effect of polymer parameters for EC–AM–APS in DMSO/toluene solvent system, shows a Trommsdorf effect around the concentration ~ 1 g EC. On the other hand, the EC–AM–KPS system, in the same solvents used in the above experiment, did not show the Trommsdorf effect (*Figure 9a*). This Trommsdorf effect or gel effect functions as the viscosity of the medium increases or precipitation of the polymer occurs[8]. Therefore, it is established that the structure of the initiator is an important factor in the grafting process.

One explanation of grafting onto cellulose and some derivatives is that grafting results from the termination of the growing chain at sites on cellulose rather than from the initiation of radical sites on cellulose[16,17].

Initiation with benzoyl peroxide (BPO)

The effect of BPO as initiator for graft polymerization of AM onto EC was studied. The results are shown in *Figure 10*. It was found that the values of the three grafting parameters are slightly changed. This means that BPO is not a suitable initiator for the grafting of AM onto EC. Further confirmation is needed to assess the
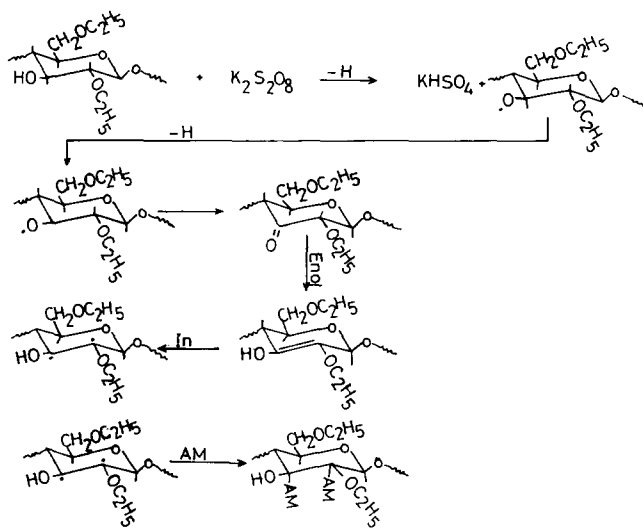

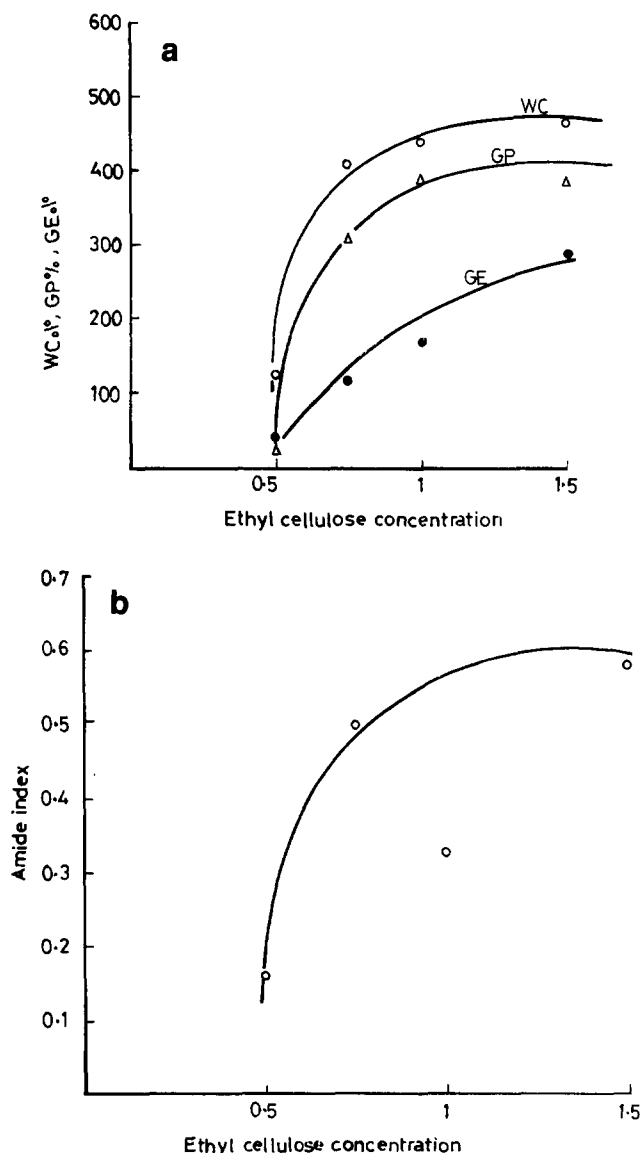**Figure 8** Mechanism of graft copolymerization of AM onto EC

Figure 10 Influence of initiator concentration on the grafting of AM onto EC with BPO in DMSO/toluene $(50/50\,cm^3)$ solvent system: $WC\%$, $GP\%$ and $GE\%$ (grafting time, 3 h; EC, $2\,g/100\,cm^3$; AM, $4\,g/100\,cm^3$; temp., 50°C)
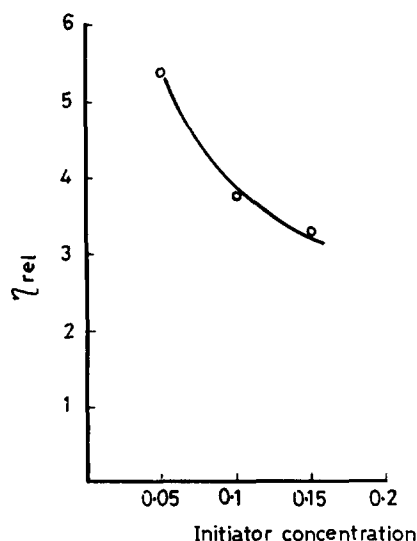
Figure 11 Dependence of BPO concentration on viscosity of EC $(2\,g/100\,cm^3)$ in toluene at 50°C

Figure 9 Influence of EC concentration on the grafting of AM onto EC with KPS in DMSO/toluene $(50/50\,cm^3)$ solvent system: (a) $WC\%$, $GP\%$ and $GE\%$; (b) amide index of graft copolymer (grafting time, 3 h; AM, $4\,g/100\,cm^3$; KPS, $0.4\,g/100\,cm^3$; temp., 50°C)

suitability of BPO as a grafting initiator for the AM–EC system. Accordingly, toluene solutions of ethylcellulose in different concentrations containing BPO were kept at 50°C for 3 h with shaking and then poured with stirring into distilled water, filtered and then dried. The viscosity of the precipitated ethylcellulose in toluene solution was measured at 30°C. The results obtained are shown in *Figure 11*. These indicate that the viscosity decreases sharply at first and then only slightly at higher initiator concentrations. This means that the degradation of ethylcellulose chains may occur, and this respectively decreases the values of grafting efficiency as shown in *Figure 10*. Thus BPO is an unsuitable initiator for the AM–EC system.

REFERENCES

1 Immergut, E. M., Mark, H. F. and Gaylord, N. G. 'Encyclopedia of Polymer Science and Technology', Interscience, New York, 1965, Vol. 3, p. 242
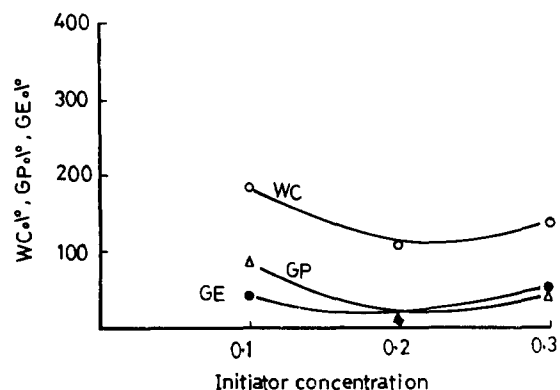
2 Stannet, V. T., Hopfenberg, H. B., Bikales, N. B. and Segal, L. 'Cellulose and Cellulose Derivatives', Wiley, New York, 1971, Vol. V, Part V, p. 907

3 Kurliankina, V. I., Molotkov, V. A., Klenin, S. I. and Liubina, S. Ya. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 3369

4 Leptoure, P. and Hui, S. H. *J. Appl. Polym. Sci.* 1975, **19**, 1257

5 Mansour, O. Y. and Nagaty, A. *J. Appl. Polym. Sci.* 1979, **23**, 2425

6 Carlesson, D. J. and Wiles, D. M. *Macromolecules* 1971, **4**, 147

7 Gaylord, N. *J. Polym. Sci. (C)* 1972, **37**, 153

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

9 Dilli, S. and Garnett, J. L. *J. Appl. Polym. Sci.* 1967, **11**, 839

10 Arthur, J. C., Jr, Baugh, P. J. and Hinojosa, O. *J. Appl. Polym. Sci.* 1966, **10**, 1591

11 Arthur, J. C. Jr, Hinojosa, O. and Bains, M. S. *J. Appl. Polym. Sci.* 1968, **13**, 1411

12 Faessinger, R. W. and Conte, J. S. Belgian Patent 646284, 1964

13 Faessinger, R. W. and Conte, J. S. US Patent 3330787, 3359224, 1967

14 Hornof, V., Kokta, B. V. and Valade, J. L. *J. Appl. Polym. Sci.* 1975, **19**, 545

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

16 Gaylord, N. Abstracts of Papers, 161st ACS Meeting, Los Angeles, April 1971

17 Kokta, B. V. and Valade, J. L. *Tappi* 1973, **55**(3), 366