Photoinduced graft copolymerization of ethyl acrylate, methyl methacrylate and methyl acrylate onto ethyl cellulose in homogeneous media

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Abstract

The vinyl monomers ethyl acrylate (EA), methyl methacrylate (MMA) and methyl acrylate (MA) were photografted onto ethyl cellulose (EC) in the presence of azobisisobutyronitrile (AIBN) and benzil (Bz) using UV irradiation in the range 310–460 nm in homogeneous media. Variables affecting the grafting yield (GY (%)), such as the time of UV irradiation and the concentrations of monomer and initiator, were investigated. Different techniques were used, e.g. IR, UV and viscosity measurements. The UV spectra of AIBN and Bz show strong absorption in the near-UV region due to $n-\pi^*$ transitions. The order of the monomers used in terms of increasing GY values and increasing intrinsic viscosities of the graft copolymers and attendant homopolymers was found to be EA > MMA > MA. The order of reactivity of the initiators used in terms of increasing G'/ was found to be AIBN > Bz. The highest rates of propagation of graft copolymerization of the vinyl monomers onto EC in the presence of Bz and tetrahydrofuran (THF) were found to be 0.22% min^{-1}, 0.11% min^{-1} and 0.1% min^{-1} for EA, MMA and MA respectively. The mechanism of grafting in the presence of Bz and THF is discussed. © 1997 Elsevier Science S.A.

Keywords: Ethyl acrylate; Ethyl cellulose; Methyl acrylate; Methyl methacrylate; Photoinduced graft copolymerization

1. Introduction

The grafting of vinyl monomers onto cellulose or cellulose derivatives often changes their chemical and physical properties. Ethyl cellulose (EC) compositions are used in many applications, e.g. paper and textile coating, gel lacquers, etc. The photoinduced graft copolymerization of vinyl monomers onto cellulose and its derivatives has been reported [1–4]. The general features of the photopolymerization reactions associated with grafting have been reviewed [3–5]. Benzil (Bz) has been used as a photosensitizer in the presence and absence of tetrahydrofuran (THF) [6–9]. Strong evidence against the photocleavage of Bz in solution has been obtained from radical scavenger studies [10]. The structure of azobisisobutyronitrile (AIBN) has been studied previously, and the cleavage and production of free radicals have been reported [11,12].

2. Experimental details

EC (BDH) with a degree of substitution in the range 2.42–2.53 was chosen as the derivative of cellulose. AIBN (Merck) and Bz (BDH) were used as initiators. The solvents benzene, acetone, THF and chloroform were of pure grade. Methyl methacrylate (MMA, BDH) and methyl acrylate (MA, BDH) were washed with a solution of sodium carbonate, dried over calcium chloride and distilled under reduced pressure. Ethyl acrylate (EA, BDH) was washed with a solution of sodium hydroxide (5%) and water and dried over calcium chloride and then molecular sieves. Hydroquinone (BDH) was used as inhibitor.

A high-pressure mercury lamp (Hanau, Germany, 500 W) with a filter solution was used to produce the wavelength range 310–460 nm. The filter solution contained 200 g of $CoCl_2 \cdot 6H_2O$ in a mixture of 75% acetone and 25% water containing HCl (1 mol l^{-1}) [13].

Different quantities of EC, EA, MMA, MA and initiator were added to benzene in Pyrex tubes and irradiated with UV light (310–460 nm). The polymerization process was finally terminated by adding hydroquinone solution (5%). The products were filtered and washed with water. The extraction of polyethyl acrylate and polymethyl methacrylate homopolymers was achieved using ethanol–water (50 : 50 v/v), and the extraction of polymethyl acrylate was performed using acetone–water (50 : 50 v/v).

Table 1
Influence of monomer concentration on the photografting of EA, MMA and MA onto EC with AIBN and Bz in benzene and benzene–THF ($90 \, cm^3 : 10 \, cm^3$) respectively (EC, 2.5 g per 100 cm^3; initiator concentration, 0.2 g per 100 cm^3; grafting time, 3 h)

Monomer	Monomer concentration (g l^{-1})	GY (Bz) (%)	GY (AIBN) (%)	Homopolymer (%)
EA	61.4	22.7	34.92	10.5
	122.8	31.5	56.99	21
	184.2	65.87	78.75	22.3
	245.6	110.7	105.75	31
	307	130.8	179.92	42.3
MMA	62	17.1	25.3	5.5
	124.7	22.1	37.2	4.7
	187	37.3	40.45	12.5
	249	59.3	57.36	14.5
	311.2	82.4	40.42	17.3
	374	–	25.57	22
MA	60	7.2	10.21	6
	120	13.32	17.32	7.7
	180	24.45	27.45	7.6
	240	36.64	34.45	12.5
	300	49.79	46.37	14.5
	360	–	38.23	16.8

The graft products were characterized by the following parameters

$$GY \, (\%) = \frac{A - B}{B} \times 100$$

where A and B are the weights of the graft product and EC respectively.

The composition of the graft copolymer was examined by IR spectroscopy using a Perkin–Elmer 1430 spectrophotometer. UV spectroscopy measurements were made using a Perkin–Elmer Lambda 3B spectrometer with a 1 cm cell.

The intrinsic viscosity [η] ($cm^3 \, g^{-1}$) of the graft copolymer was determined in $CHCl_3$ at 30 °C using a modified Ostwald viscometer according to the following relation [14]

$$[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{SP} - \ln(\eta_{rel})}$$

where C is the concentration of the graft copolymer at 0.4 g per 100 cm^3.

The overall rate of graft copolymerization was determined from the slope of a plot of time vs. the grafting percentage at the initial stages of the reaction [15,16].

3. Results and discussion

The selection of Bz and AIBN as photosensitizers was mainly based on the fact that they absorb strongly in the near-UV region. The UV spectra show bands with λ_{max} (log ϵ) at 260 nm (4.3) for AIBN and at 330 nm (3.2) and 252 nm (3.3) for Bz. Therefore the high absorptivity of AIBN and Bz makes them particularly attractive as photosensitizers for photoinduced grafting reactions. AIBN has been examined previously as a photosensitizer in different photoinduced grafting systems in which high grafting yields have been

obtained [17,18]. However, Bz undergoes photoinduced H abstraction. Flash photolysis studies using aromatic ketone-containing photoinitiators, such as Bz, have been interpreted to indicate the CO–CO photocleavage of Bz as the primary step for initiator radical generation [19,20]. It is important to note that the unsensitized photoinduced grafting of EA, MMA and MA onto EC was not successful.

An increase in monomer content leads to an increase in GY (confirmed in different grafting systems [21,22]). Thus the effect of the concentration of MA, MMA and EA was investigated (Table 1). The data obtained show that, with increasing monomer content in the presence of Bz as photosensitizer, GY increases. In addition, the intrinsic viscosity of the grafted copolymers increases with increasing monomer content in the presence of Bz as photosensitizer (Fig. 1). The different GY values may be ascribed to the different monomer reactivities; their order in terms of increasing GY values is found to be EA > MMA > MA. When AIBN is used as pho-
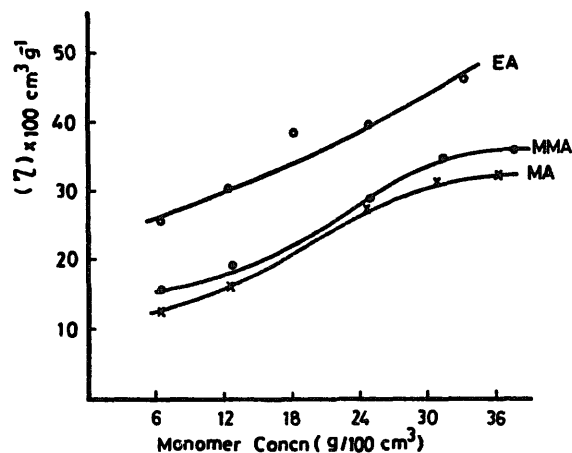

Fig. 1. Influence of the change in monomer content on the intrinsic viscosities [η] of the graft copolymers of EA, MMA and MA with EC. The experimental conditions of grafting are given in Table 1; Bz used as initiator.
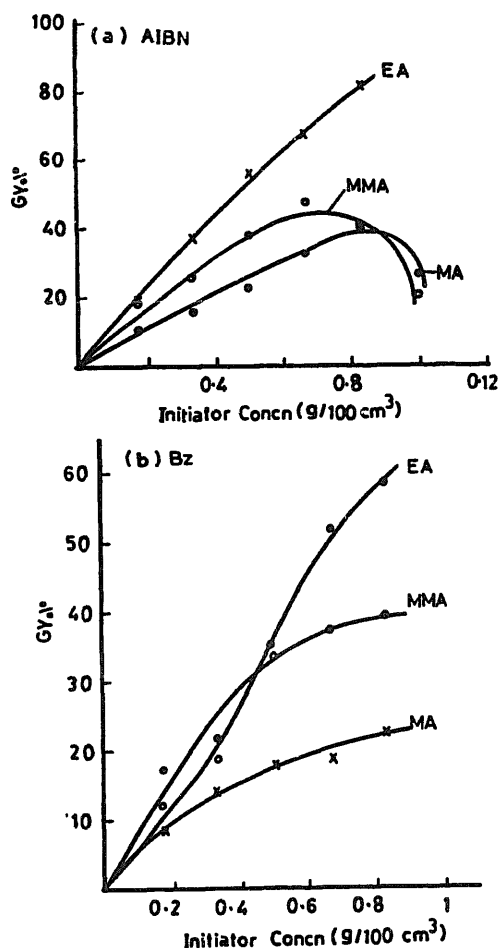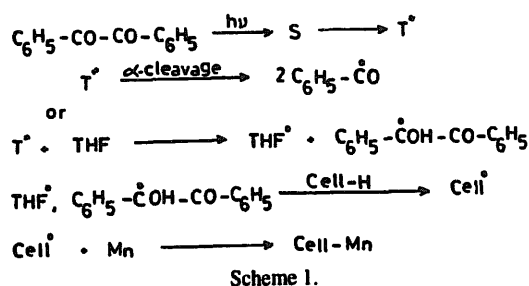
Fig. 2. Effect of Bz and AIBN concentration on the photoinduced grafting of EA, MMA and MA onto EC using AIBN in benzene (a) and Bz in benzene-THF (90 cm^3 : 10 cm^3) (b). Conditions: EC, 2.5 g per 100 cm^3; monomer concentration, 6.2 cm^3 per 100 cm^3; grafting time, 3 h.

Scheme 1.

tent is accompanied by an increase in GY for EA, whereas the curves for MMA and MA decrease or level off at higher contents of AIBN and Bz. An increase in the radical content leads to the termination of growing macrocellulose radicals by primary radicals [23-25]. The increase in the free radical concentration above a certain value may increase the rate of homopolymerization vs. the rate of graft copolymerization and this in turn will lead to a decrease in the GY values.

The action of Bz during the photoinduced grafting of the vinyl monomers onto EC in the presence of THF is explained in Scheme 1, where Cell-H and Mn denote EC and the monomer respectively.

The observed higher activity of AIBN as photoinitiator may be due to its higher absorption in the UV region as well as the lower energy (42 kcal mol^{-1}) required for cleavage and the production of free radicals [26,27]. The mechanism of grafting of vinyl monomers onto EC using AIBN has been reported previously [17,18].

A comparison of the effect of the concentration of AIBN and Bz + THF on the photografting of EA onto EC indicates that their activities are in the order AIBN > Bz + THF (Fig. 3).

Fig. 4 shows the changes in the extent of grafting (GY (%)) with time during the photoinduced grafting of EA, MMA and MA in the presence of Bz as photosensitizer. The
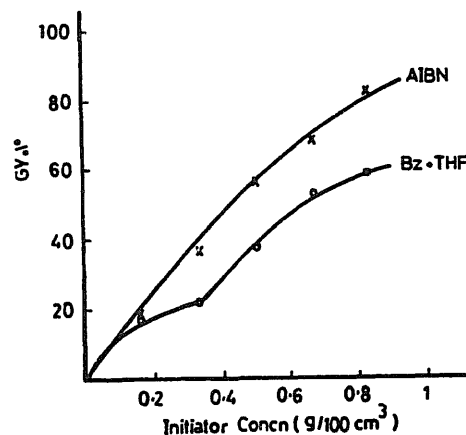

Fig. 3. Effect of AIBN and Bz + THF concentration on the photoinduced grafting of EA onto EC in benzene and benzene-THF (90 cm^3 : 10 cm^3) respectively. Conditions: EC, 2.5 g per 100 cm^3; EA, 6.2 cm^3 per 100 cm^3; grafting time, 3 h.

tosensitizer, the GY values of EA, MMA and MA increase up to an AIBN content of 0.7 g per 100 cm^3 and then decrease again for MMA and MA only. The increase in the amount of attendant homopolymer (homopolymer (%)) formed during the grafting reactions of EA, MMA and MA may explain the decrease in GY observed for MMA and MA at higher contents of AIBN (Table 1). Moreover, the increase in monomer content will facilitate the consumption of primary radicals and thus reduce the formation of EC macroradicals; this explains the levelling off or decrease in the GY values (Table 1).

Fig. 2 illustrates the effect of the initiator content on the photoinduced grafting of EA, MMA and MA onto EC. The data for AIBN and Bz show that an increase in initiator con-
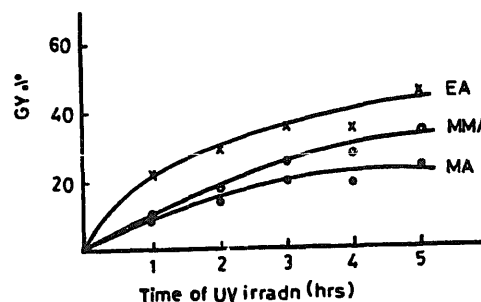

Fig. 4. Dependence of the photoinduced grafting of EA, MMA and MA onto EC in the presence of Bz on the time of UV irradiation in benzene-THF (90 cm^3 : 10 cm^3). Conditions: EC, 2.5 g per 100 cm^3; monomer concentration, 6.2 cm^3 per 100 cm^3; Bz concentration, 0.2 g per 100 cm^3.
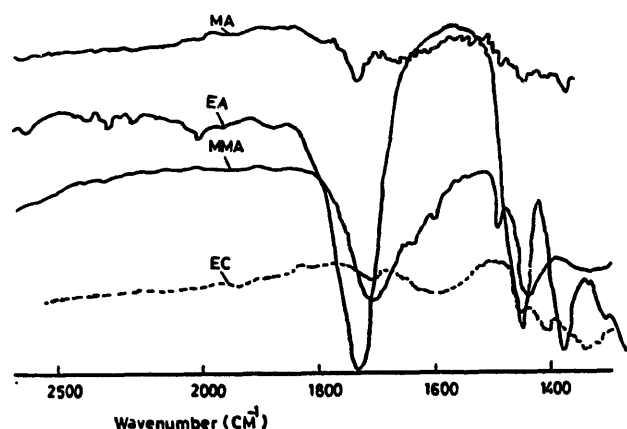
Fig. 5. IR spectra of graft copolymers of EA, MMA and MA on EC in the presence of Bz (experimental conditions are given in Fig. 4; samples at a grafting time of 5 h were examined).

highest rates of propagation (R_p) observed are 0.22% min^{-1}, 0.11% min^{-1} and 0.1% min^{-1} for EA, MMA and MA respectively. This means that the order of reactivity of the acrylic monomers with regard to grafting onto EC is as follows: EA > MMA > MA.

It has been reported that the grafting reactions of cellulose derivatives occur at the substituted side chains, and are enhanced by UV light (above 280 nm) in homogeneous medium [4]. The mechanism of cleavage of EC was examined by electron spin resonance (ESR) spectroscopy

$$Cell - O - CH_2CH_3 \xrightarrow{h\nu} Cell - O^{\bullet} + {}^{\bullet}CH_2CH_3$$
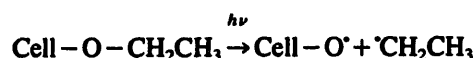
The IR spectra of EC and the graft copolymers are shown in Fig. 5. New peaks appear in the range 1700–1740 cm^{-1} indicating the presence of ester groups of the polymer chains grafted onto the EC backbone.

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