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Control of cellulose-supported hydrogel microstructures by three-dimensional graft polymerization of glycol methacrylates

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Abstract

This article describes a method for controlled surface coating of cellulose fibers with micro-size hydrogel particles. The addition of ethyleneglycol dimethacrylate (EDMA) to the diethylene glycol methacrylate (DEGMA) monomer mixture used for grafting resulted in a dramatic enhancement of the grafting amount onto ozone-activated fibers and subsequent formation of particles on the fiber surfaces, as observed with AFM and SEM. The enhancement of the amount of grafting was explained by an initiation of the pendent double bonds and autoacceleration of graft polymerization as indicated by differential scanning calorimetry (DSC). Such 3-dimensional growth had a maximum at 4% of crosslinker and was significantly reduced when longer crosslinkers were used. This was explained by a cyclization reaction of the pendant double bonds. The surface structures were controlled by selecting the graft polymerization time.

Keywords: Cellulose-supported hydrogel; Microstructures; Graft polymerization

1. Introduction

The nature of polymer surfaces is of great importance because it is the surface that first comes into contact with the environment and therefore determines all kinds of interactions such as wettability, adhesion and biological response [1–2]. During the last decades, a wide range of techniques have been developed for changing the properties of polymer surfaces. Recent developments in the RF plasma technique, preparation of self-assembled monolayers and surface grafting have made it possible to accurately control the polymer surface chemistry [3–6]. Surface modification of polymers has recently turned in the direction of new areas involving the control of not only the surface chemistry but also the morphology in order to affect specific interactions. It has, for example, been found that spatial features on a surface influence cell functionality and phenotype [7]. Such surfaces may also be important in directing blood interactions, tissue reaction and healing [8,9]. While many techniques used for modifying polymer surface chemistry are known, the field of controlling surface morphology is still incompletely explored. Ratner and collaborators have shown that surface textures can be formed during radiation-induced grafting onto polyethylene [10]. Other methods so far applied for such purposes are photo-lithography, plasma reaction with masking and mechanically inducing surface features with scanning probe microscopies [11–16].

The graft polymerization technique has been widely used for the surface modification of polymers. With this technique, both thin and thick grafted layers with controlled surface chemistry can be obtained. In our laboratory we have recently studied ozone-induced graft polymerization of various hydrogel forming acrylates onto both synthetic and natural fibers [17–21]. We observed that, during graft polymerization of 2-hydroxyethyl methacrylate (HEMA) onto cellulose fibers, the grafting yield and surface coverage were significantly increased by adding a bifunctional monomer, ethylene glycol dimethacrylate (EDMA), to the monomer mixture used for grafting. In addition to a fine coating of the cellulose fibrils, the formation of bumps of the grafted polymer, which later developed into spheres, was seen when the grafting amount was increased. The effect of bifunctional crosslinking agents on radical polymerization systems has been discussed in the literature. Kopecek et al. reported in a series of articles the first extensive investigation of solution polymerization of ethylene glycol monomethacrylates with small amounts of dimethacrylate crosslinkers [22–25]. They showed that the double bond conversion at a given time increased as the

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concentration of the crosslinking agent was increased. They also found evidence of reduced reactivity of the pendent double bonds and concluded that di- and tri(ethylene glycol) dimethacrylates have a greater propensity to form cycles than mono(ethylene glycol) dimethacrylates. Several authors have determined polymerization rate profiles of methacrylates by means of differential scanning calorimetry (DSC). Peppas and collaborators determine the time period before the onset of autoacceleration depending on various reaction parameters [26]. They showed that the time increased and the maximum reaction rate decreased as the solvent concentration or the pendent chain length was increased or the crosslinking agent concentration was decreased. Other authors have also shown that dilution affected the onset of the autoacceleration [27]. Furthermore, it has been reported that autoacceleration occurs at different conversions for different monomers [28].

The aim of this study has been to prepare controlled surface structures by performing an ozone-induced graft polymerization of various acrylate monomers onto cellulose fibers. Special attention was paid to elucidate the relationship between graft reaction parameters, grafting yield and the development of various surface morphologies. The monomethacrylate used for grafting was diethylene glycol methacrylate (DEGMA), and the bifunctional crosslinking agents were mono-, di-, tri- and tetra(ethylene glycol) dimethacrylates. DSC measurements were performed to obtain reaction rate profiles of various monomer mixtures. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize the fiber surfaces before and after grafting.

2. Experimental

2.1. Materials

The cellulose fibers used were a standard sulfate fluff pulp (single fibers), EC 0.1, made from selected wood of softwood, manufactured by STORA Cell (Sweden). The mono functional monomer used in the study was diethyleneglycol methacrylate (DEGMA), and the bifunctional monomers used were mono-, di-, tri- and tetra(ethylene glycol) dimethacrylate. Mono (ethyleneglycol) dimethacrylate (EDMA) purchased from Fluka Chem. AG. (Switzerland) was vacuum-distilled prior to use, whereas the rest of the monomers were supplied by the Institute of Macromolecular Chemistry in Prague.

2.2. Ozone treatment and graft polymerization

Prior to the ozone treatment, the cellulose fibers were stored for a week in an environment with 100% humidity. The treatment of the cellulose fibers was then carried out in a gas phase reactor at 32°C. The equipment used for generating ozone was an NG10 from Ozone Systems Company, which produced an oxygen/ozone flow of 0.250 m^3/h from pure oxygen gas. The ozone concentration was 25 g/m^3. Before reaching the reactor, the gas current was preheated and humidified. A saturated gas mixture at a temperature of 32°C was then blown into the reactor, where the fibers were kept in end-open glass tubes. Immediately after ozone treatment, the substrates were placed in the monomer solution.

The solution was prepared by diluting 2.0 g of monomer in equal amounts (10 cm^3) of methanol and deionized water. The water contained 50 mg of dissolved Fe(II) ammonium sulfate hexahydrate salt (Mohr's salt), which forms a redox initiator. The pH of the solution was set to 3. The grafting process was performed in a nitrogen atmosphere, in sealed glass ampoules. During the graft polymerization, the ampoules were shaken in a water bath at 50°C. The polymerization was interrupted by opening the ampoules and immersing the substrates in water. The grafted substrates were extracted in water overnight to remove monomer residuals. After the extraction, the water was vacuum filtrated from the fibers, which were then vacuum dried at 50°C for 15 h before they were weighed. The extent of grafting was expressed as the percentage increase in weight according to:

$$\text{grafting amount (\%)} = 100(w_2 - w_1)/w_1$$

where w_1 and w_2 represent the weight of the dry substrates before and after grafting, respectively.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to study polymerization profiles of the monomers at 70°C. The equipment used was a Perkin Elmer DSC-7. The temperature was increased to 70°C, and the measurements were then performed isothermally.

2.4. Characterization

The surface morphology of the fibers was examined using the Dimension 3000 Large Sample AFM with type G scanner. A standard silicon tip was used for the analysis, which was performed in air. Scanning electron microscopy (SEM) was used to study the substrates before and after grafting. The surfaces were coated with gold before the analysis, which was performed with a Zeiss DSM 940A operated at 10 kV.

Table 1
The effect of ethyleneglycol dimethacrylate (EDMA) concentration in a DEGMA monomer mixture on the grafting amount (%). Mean value of three measurements

Weight% EDMA	0	2	4	6	8	10	12
Grafting amount (%)	20	70	940[a]	460	190	150	180

[a] Large scatter of the results.

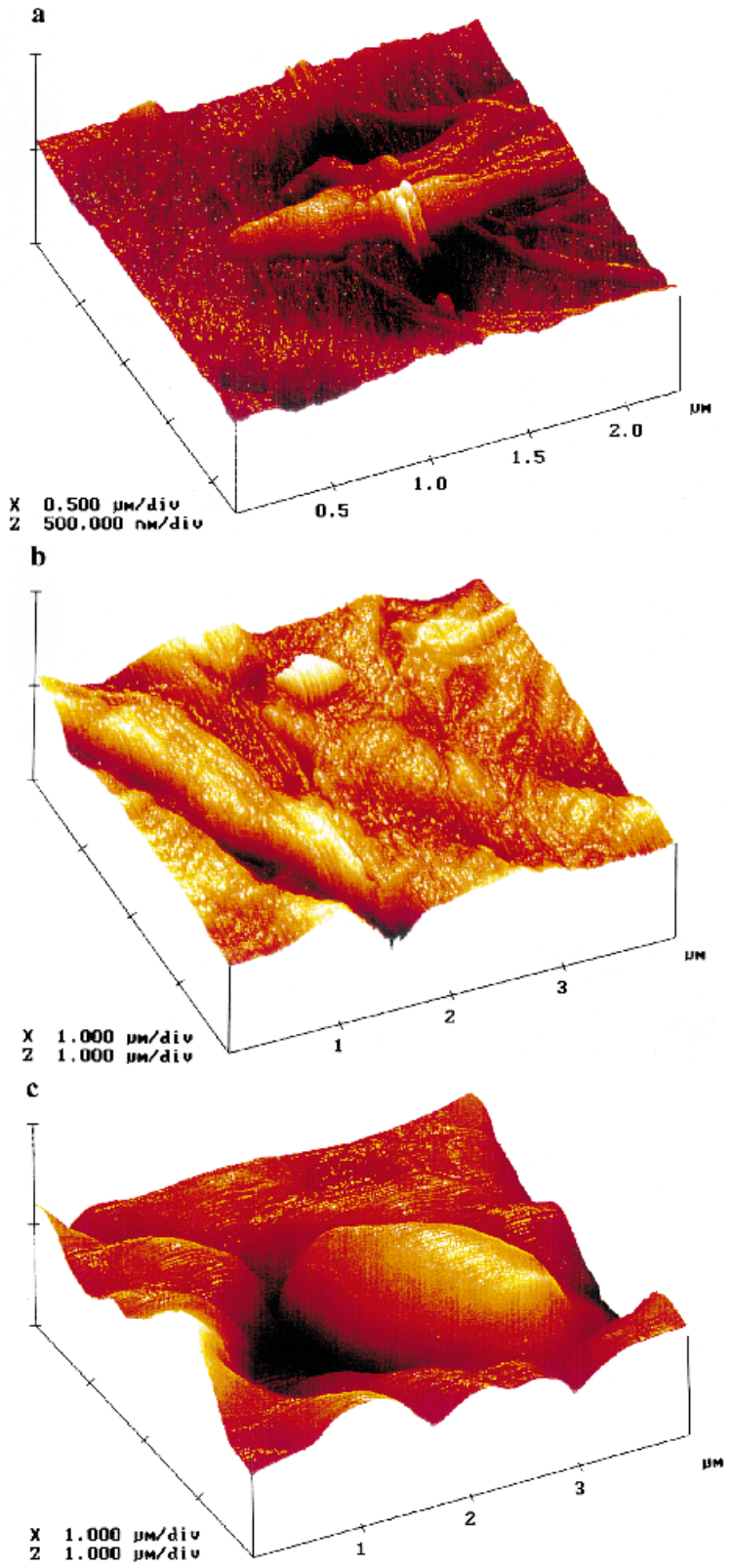

Fig. 1. AFM images of cellulose fiber: (a) untreated fiber; (b) cellulose fiber with a grafting amount of 70% (DEGMA/EDMA); (c) cellulose fiber with a grafting amount of 760% (DEGMA/EDMA).

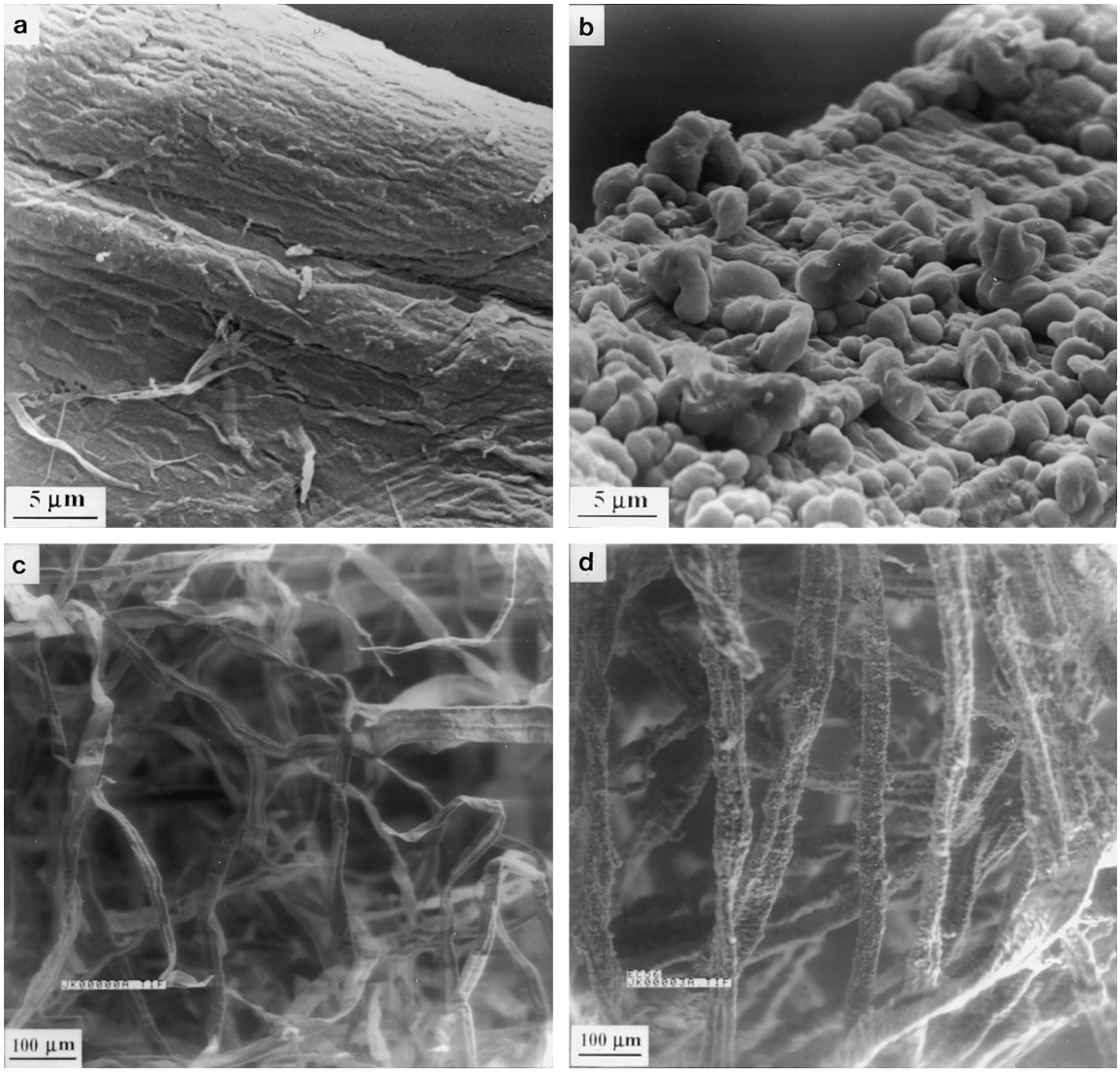

Fig. 2. High magnification pictures of: (a) untreated cellulose fiber; and (b) fiber with several hundred percent grafting. Fiber networks of: (c) untreated cellulose fibers; and (d) cellulose fibers with a grafting amount of 760%.

3. Results

3.1. Enhancement of grafting

When ozone-activated cellulose fibers were placed in a monomer mixture composed of diethyleneglycol methacrylate (DEGMA) monomers, water and methanol (50 vol.% of each solvent), a typical grafting amount of about 20% was obtained. We have recently shown that it was possible to increase the grafting yield by adding bifunctional crosslinking agents to monomer mixtures of HEMA and acrylic acid [19,20]. Various amounts of a bifunctional monomer, ethyleneglycol dimethacrylate (EDMA), was therefore added to the DEGMA monomer mixture used for grafting. Table 1 summarizes the grafting amount (%) obtained at various concentrations of ethyleneglycol dimethacrylate (EDMA) in the DEGMA monomer mixture. It can be observed that the amount of grafting moderately increases when the monomer mixture used for grafting contains a small amount of EDMA (2%). At 4% EDMA content, the yield increases dramatically. The grafting amount decreases when the concentration of bifunctional monomer is further increased. The grafting amount can thus be regulated by changing the composition of the monomer mixture used for grafting.

3.2. Surface morphology

The appearance of the fiber surfaces as a function of grafting amount was determined by using atomic force microscopy (AFM). Untreated and grafted cellulose fibers were investigated with the Tapping Mode technique. Fig. 1(a) shows an AFM image of an untreated fiber. The surface is composed of parallel characteristic fibrils. A fiber with a grafting amount of 70% can be seen in Fig. 1(b). The fibillar structure is less apparent for this fiber, and only hints of an ordered array of microfibrils can be observed. A

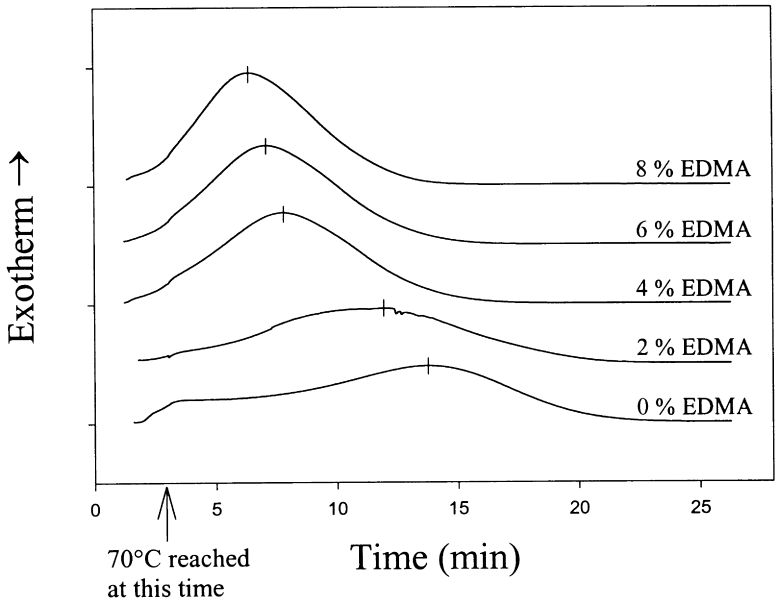

Fig. 3. Polymerization exothermals measured with DSC. DEGMA with various EDMA contents. AIBN, 0.5 wt.%, was used as initiator.

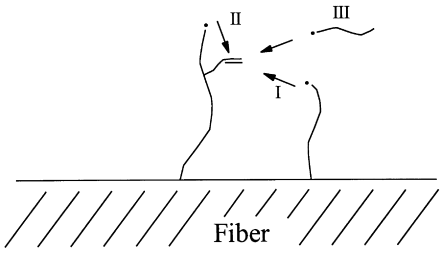

Fig. 4. Proposed model for graft polymerization in the presence of a bifunctional monomer.

grafting yield of this magnitude seems to smooth out the fiber surface by the formation of a thin layer of grafted polymer. We have observed similar behavior during graft polymerization of other monomers onto cellulose fibers. Fig. 1(c) shows the surface of a fiber with 760% grafted polymer. The roughness of this fiber surface is obvious. Bumps that attain a size of a couple of micrometers have been developed on the surface as a result of the graft polymerization.

The surface morphology of the cellulose fibers was also investigated with scanning electron microscopy (SEM). Fig. 2(a) and (b) shows a high magnification of an untreated fiber and a fiber with several hundred percent grafted DEGMA. The SEM micrographs are consistent with the AFM images. The grafted surface has a pronounced roughness that consists of bumps, compared to the untreated surface which is rather smooth. A low magnification was also used in order give a good overview of the fiber networks (Fig. 2(c) and (d)). It can be seen that the appearance of the grafted fibers is completely different from that of the untreated. Bumps of grafted DEGMA are distributed along the fibers, and it can also be observed that the bump-like morphology is the same on all grafted fibers in the network.

3.3. Polymerization profiles

DSC measurements were performed in order to examine the graft polymerization behavior of DEGMA when various amounts of EDMA were added. Isothermal radical chain polymerization at 70°C was performed with DEGMA containing various amounts of bifunctional crosslinker and with DEGMA without crosslinker. AIBN, 0.5 wt.%, was used as the initiator. The maximum reaction rate from such DSC experiments is received from the peak of the heat flow curve. A rapid increase from a moderate reaction rate to a maximum indicates that autoacceleration (gel effect) occurs during the polymerization. In Fig. 3, the heat flow from five monomer mixtures at 70°C is plotted as a function of time. The data have been normalized according to sample weight, and the time at which 70°C was reached is marked with an arrow. An obvious difference in the reaction rate profiles can be observed depending on the composition of the monomer mixture. It can be seen that DEGMA without crosslinker has the lowest reaction rate. This sample also requires the longest time to reach the peak of the exotherm. A slight difference in the reaction rate can be observed when the monomer mixture contains 2% EDMA instead of 0%, and the time required to reach the peak of the exotherm also decreases in this case. As the concentration of bifunctional monomer is increased from 2 to 4%, the maximum reaction rate increases sharply, and the time required to reach the peak furthermore distinctly decreases. At a higher concentration of EDMA, 6 and 8%, the changes in the reaction rate profile are small. The

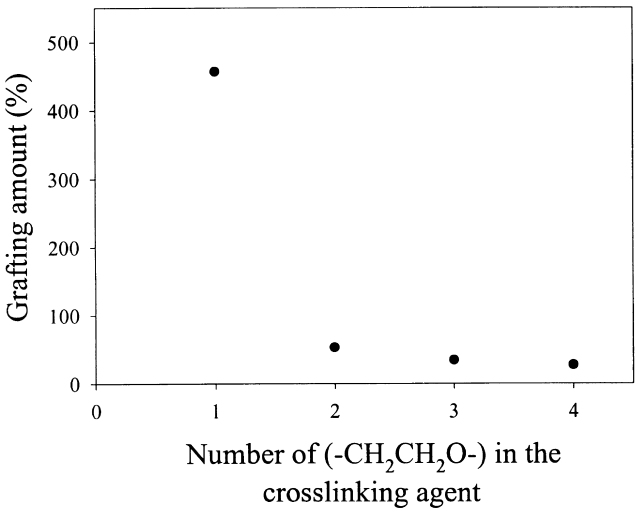

Fig. 5. The effect of crosslinking agent structure on the grafting amount.

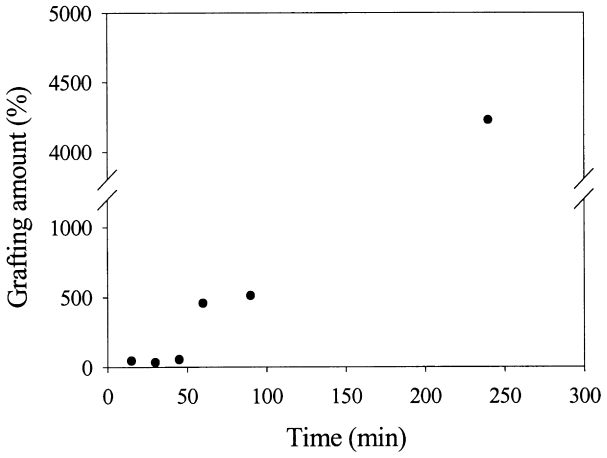

Fig. 6. Grafting amount as a function of grafting time. Cellulose fibers grafted in a DEGMA monomer mixture containing 6 wt.% EDMA crosslinker.

reaction rate slightly increases, however, whereas the time to reach the maximum reaction rate continues to decrease.

The DSC measurements show that the maximum reaction rate is much higher in monomer mixtures with an EDMA content of 4% and more, in comparison with lower EDMA content. As regards the results obtained during our grafting experiments, we have seen that the grafting amount at this EDMA concentration also starts to increase dramatically. One difference, however, between the DSC and the grafting experiments is the initiation step. During radical chain polymerization, initiation takes place in the bulk where reactive species from decomposed initiators are available. Autoacceleration arises during radical chain polymerization when the rate of the diffusion-controlled termination is reduced owing to increased viscosity and chain entanglements, which leads to a decreased mobility and increased concentration of growing chain radicals. The mobility can also be decreased as a consequence of crosslinking between the polymer chains. Although propagation also is hindered the effect is much smaller than the decrease of termination. This results in an increased polymerization rate.

Graft polymerization is initiated by radicals on the substrate formed during decomposition of hydroperoxides that were formed during the ozone treatment. In addition to the formation of radicals on the substrate, free hydroxyl radicals in the solution are formed during hydroperoxide decomposition. Fe^{2+} salt is added to the monomer mixture used for grafting in order to convert the hydroxyl radicals to hydroxyl ions and thereby suppress homopolymerization. If some hydroxyl radicals are not converted and instead start polymerization or if a termination of grafted polymers occurs by chain transfer to a monomer, growing polymers will then be present in the solution. Fig. 4 shows a proposed model for graft polymerization in the presence of both mono- and bifunctional monomers. One of the growing polymers schematically shown contains a bifunctional monomer. The pendent double bond has three possibilities for reaction (I–III): I. crosslinking reaction with an adjacent growing grafted chain; II. cyclization reaction; and III. reaction with a radical in the bulk, either an initiation reaction by a hydroxyl radical or a propagation reaction with a growing polymer chain. The fourth alternative (IV) is for the double bond to remain unreacted. For alternatives I, II and IV, the grafting yield is unchanged, while alternative III results in an increased amount of growing polymer chains connected to the substrate and thus an increased grafting yield.

A higher concentration of bifunctional monomers will subsequently result in an increased amount of pendent unreacted double bonds available for initiation. If these double bonds react according to alternative III, the number of growing polymer chains that may also contain double bonds will further increase. This process can cause increased branching and crosslinking, which in turn will influence the mobility of the growing polymer radicals. Thus, simultaneously as the grafting amount drastically increases, a situation very similar to the gel effect can arise. This is also in accordance with what we have observed for our graft polymerizations. It has furthermore been shown in the literature that an increased amount of Mohr's salt, in a similar system that we have, decreases the grafting yield [29]. The probability of growing polymers in the bulk would thereby decrease, which supports the suggestion that alternative III in our model affects the amount of grafting.

3.4. The effect of crosslinker structure on the grafting amount

A study to investigate the effect of the mobility of the pendent double bonds on the grafting amount was performed by increasing the length between the double bonds in the crosslinking agent. Mono-, di-, tri- and tetra(ethylene glycol) dimethacrylate were used for the experiments and all monomer mixtures contained

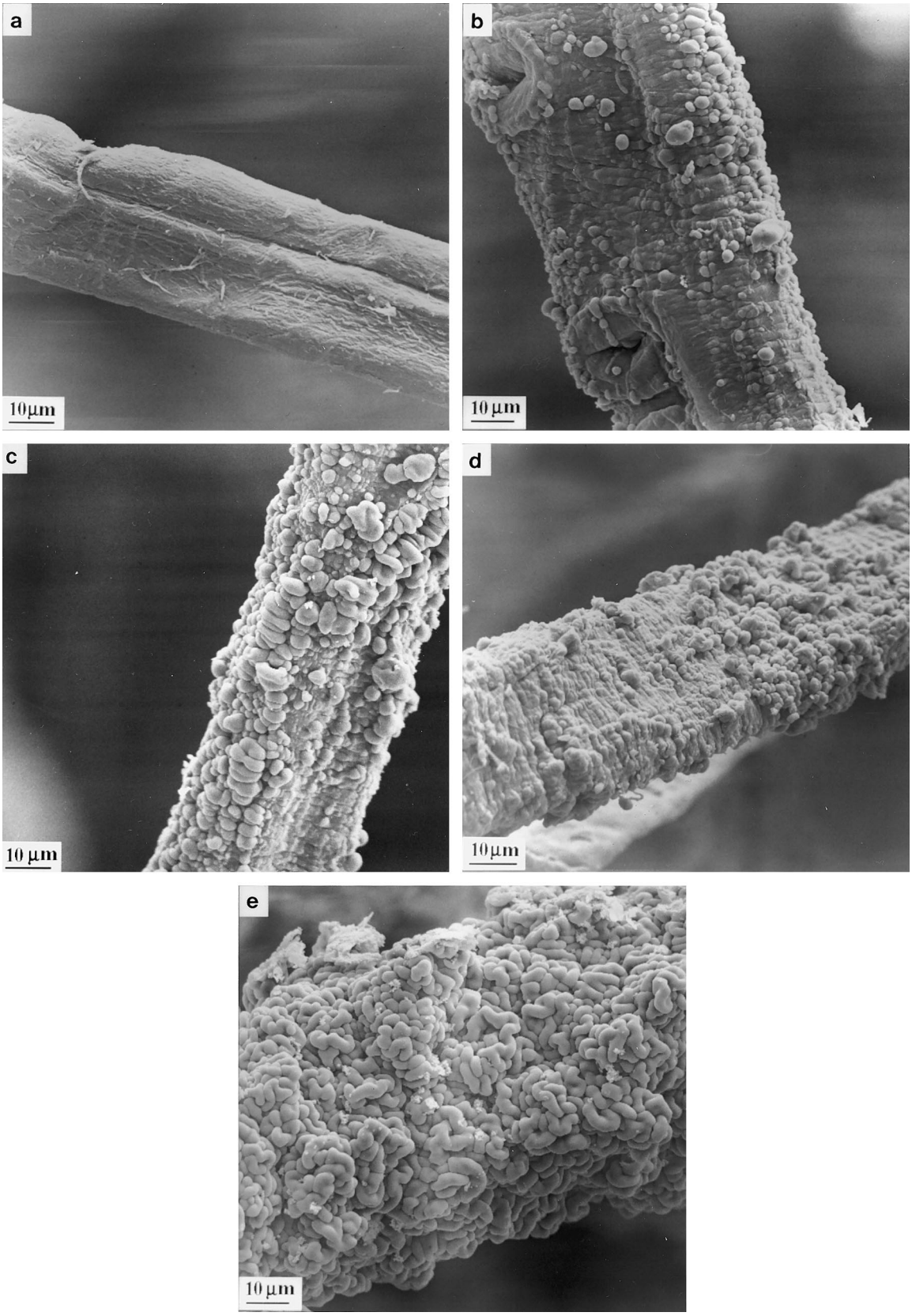

Fig. 7. SEM micrographs of untreated and grafted cellulose fibers: (a) untreated fiber; (b) fiber with a grafting amount of about 100%; (c) fiber with a grafting amount of about three hundred percent; (d) fiber with a grafting amount of several hundred percent; and (e) fiber with a grafting amount of a few thousand percent.

5.3 mol% of the relevant crosslinking agent. The effect of the chain length of the bifunctional monomer on the grafting yield can be observed in Fig. 5.

A grafting amount of 460% was obtained for fibers that were grafted in a monomer mixture mono(ethylene glycol) dimethacrylate. It can be observed that the enhancement of the yield is reduced as the number of ethylene glycol units in the bifunctional crosslinking agent increases. An addition of di(ethylene glycol) dimethacrylates results in a slightly higher grafting amount (50%) is compared with a monomer mixture without crosslinker (20%). The addition of tri- and tetra(ethylene glycol) dimethacrylates does not particularly affect the grafting yield. The choice of bifunctional crosslinking agent thus appears to be a way to influence the amount of grafting.

Kopecek and collaborators reported an increased propensity for cyclization of di- and tri(ethylene glycol) dimethacrylates during radical chain polymerization [22–25]. By applying their findings to our grafting system, the connection between the increased number of ethylene glycol units in the bifunctional monomer and decreased grafting amount can be explained by an increased propensity for reaction II in our model shown in Fig. 4.

3.5. Control of grafting amount

As described above, it was possible to control the grafting yield by varying the amount and the structure of the bifunctional crosslinking agent. Grafting time is another parameter that is often used to change the grafting yield. We investigated the effect of grafting time on the graft polymerization in a DEGMA mixture containing 6% EDMA. Fig. 6 shows the mean values of three measurements at each time.

It can be observed that the grafting amount is almost constant, about 50%, during the first 45 min. A pronounced increase, up to 500%, is however obtained when the grafting time is extended to 60 and 90 min. At further extension of the grafting time, the graft polymerization proceeds and, after 240 min, the amount of grafting is more than 4000%. Samples with different grafting amounts were collected, and their surface morphologies were investigated by SEM. A series of SEM micrographs showing fibers with various grafting yields can be observed in Fig. 7. The apperance of the untreated fiber in Fig. 7(a) is characteristic for untreated cellulose fibers. A fiber with a low grafting amount, about 100%, can be seen in Fig. 7(b). In the micrographs, it can be observed that the morphology of the surface starts to change. As the grafting yield increases small bumps start to appear on the surface, as shown in Fig. 7(c). When the yield is increased to several hundred percent, shown in Fig. 7(d), a new surface structure is fully developed. Globules of grafted DEGMA have formed along the fiber as a consequence of the grafting process. Fig. 7(e) shows a fiber with a grafting amount of a couple of thousand percent. A thick layer with a bump-like surface morphology developed on this fiber.

4. Conclusions

An addition of EDMA to the DEGMA monomer mixture used for grafting resulted in a dramatic enhancement of the grafting amount onto ozone activated fibers and subsequent formation of particles on the fiber surfaces. AFM measurements showed that the particles attained the size of a couple of micrometers and, by using SEM, it was seen that the particles were evenly distributed along the cellulose fibers. The enhancement of the amount of grafting was explained by an initiation of the pendent double bonds originating from the bifunctional crosslinking agent. The graft enhancement effect was significantly reduced when longer crosslinkers were used. This was explained by an increased propensity for a cyclization reaction of the pendant double bonds. The surface microstructures could be controlled by selecting the graft polymerization time.

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