

Preirradiation Grafting Polymerization of DMAEMA onto Cotton Cellulose Fabrics

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ABSTRACT: The grafting yield of *N,N'*-dimethylaminoethyl methacrylate (DMAEMA) on cotton cellulose fabric increased with grafting time, absorbed dose, and concentration of the monomer in the aqueous solution, but decreased with grafting temperature. The dose rate had a small effect on the grafting yield. The optimal grafting yields of DMAEMA on cotton cellulose were rather low, approximately 50% compared with *N*-isopropylacrylamide (NIPAAm), although both monomers could be synthesized to be thermally reversible hydrogels. The relationship between the grafting yield and the grafting temperature indicated that the trapped radicals located in the interphases between crystalline and amorphous regions of irradiated samples were the main active species inducing the grafting reaction. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3578–3581, 2001

Key words: cotton cellulose; DMAEMA; preirradiation grafting polymerization

INTRODUCTION

Some investigations on preirradiation grafting of *N*-isopropylacrylamide (NIPAAm) in aqueous solutions or mixed solutions of water and alcohol on cotton cellulose were performed in the authors' lab.^{1,2} Because of the special structure of NIPAAm and the environmental stimuli responses of polyNIPAAm^{3,4} in these systems, some new phenomena, such as the abnormal temperature effect and the decrease of crystallinity of grafted samples, appeared. To study these phenomena, *N,N'*-dimethylaminoethyl methacrylate (DMAEMA), which has similar structure and functional property^{5–13} as NIPAAm, was used.

In this work, the main conditions of preirradiation grafting of DMAEMA onto cotton cellulose fabric were investigated. The temperature effect

on the grafting reaction indicated that the results were similar to that of acrylamide as monomer rather than that of NIPAAm, which meant that in the grafting system of DMAEMA and cotton cellulose, the grafting reaction was induced only by trapped radicals, whereas the peroxides produced in irradiated samples were not.

EXPERIMENTAL

Materials

The ordinary purchased cotton cloth was extracted with ethanol in the Soxhlet apparatus for 5 h and boiled in a solution of 1% NaOH for 3 h. Then it was washed with distilled water to neutralize it. The cleaned cotton was dried in a vacuum oven and stored in a desiccator for further use. The solutions for the grafting reactions were prepared by dissolving the monomer in tridistilled water. The monomer DMAEMA (Acros, USA) was purified by distillation under reduced

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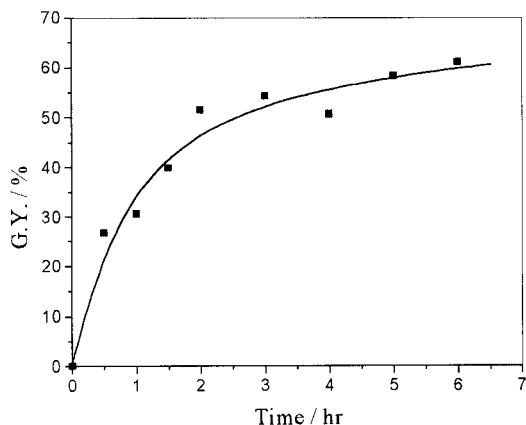


Figure 1 Effect of reaction time on grafting yield. Dose: 16.13 kGy; monomer concentration: 20%; grafting temperature: 21°C.

pressure. Other reagents were used without purification.

METHODS

The treated cotton was cut into pieces of about 0.1 g and weighed. The samples were irradiated in the air to a certain dose by ^{60}Co - γ source. The irradiated samples were immediately immersed in a solution of monomer DMAEMA that was already deoxygenated by N_2 for about half an hour. At a certain temperature in the water bath, the reaction lasted for a certain time with N_2 aerated in. After grafting, the cotton pieces were extracted with ethanol in the Soxhlet extractor for about 12 h to remove the homopolymer of the monomer. Then they were dried in the vacuum oven and weighed again. The grafting yield (G.Y.%) was finally calculated according to the following formula:

$$\text{G.Y.}\% = \frac{W - W_0}{W_0} \times 100\%$$

where W_0 is the original weight of the ungrafted cotton fabric, and W is the weight of the grafted sample.

RESULTS AND DISCUSSION

Main Conditions of Grafting

Effect of Reaction Time on the Grafting Yield

The measurement of kinetic grafting reaction showed that the grafting yield increased with the

reaction time. As shown in Figure 1, when the time was < 2 h, the grafting yield increased drastically, and after 2, h the grafting yield increased gradually. Along with the procedure of grafting reaction, the concentrations of both the monomer and the free radicals produced in the irradiated sample decreased gradually, so that the reaction rate slowed down gradually. The reaction was equilibrated about after 4 h.

Effect of Dose Rate on the Grafting Yield

It can be seen in Figure 2 that the change of dose rate (within 300 Gy/min) had little influence on the grafting yield. The result complied with the accepted theory of preirradiation grafting. Under a certain overall dose, the dose rate did not affect the amount of the radical sites where the consequent grafting copolymerization happened in the cotton cellulose fabric. The dose rate in most of this work was 268.9 Gy/min.

Effect of Dose on the Grafting Yield

As in typical preirradiation grafting procedures, the grafting yield increased rapidly at an initial stage (Fig. 3). After the overall dose reached about 15 kGy, the curve leveled off and the grafting yield increased a little. Higher overall dose produced more free radicals in the sample, which initiated more grafting copolymerization. On the other hand, more free radicals led to more chances of their termination. When the two effects counteracted, the grafting reaction reached its platform. Therefore, in the following experiments, the overall dose chosen was 16.13 kGy.

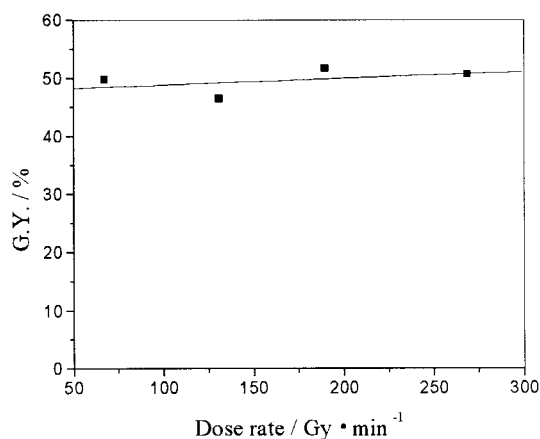


Figure 2 Effect of dose rate on grafting yield. Dose: 16.13 kGy; reaction time: 4 h; monomer concentration: 20%; grafting temperature: 21°C.

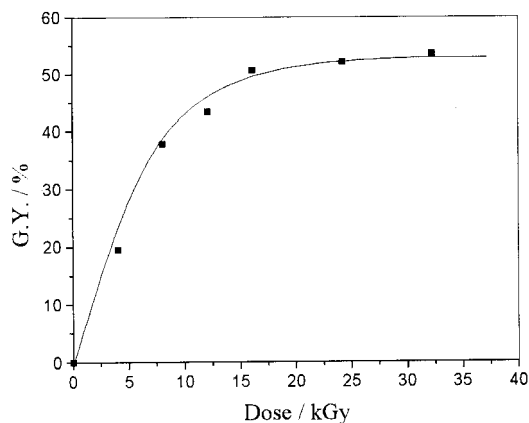


Figure 3 Effect of dose on grafting yield. Reaction time: 4 h; monomer concentration: 20%; grafting temperature: 21°C.

Effect of Monomer Concentration on the Grafting Yield

The grafting yield obviously increased with the increasing concentration of DMAEMA until 30% (v/v) of DMAEMA. When the concentration was higher than 30% (v/v), the increase of the grafting yield tended to stop (Fig. 4). It can be concluded that the grafting reaction in this heterogeneous system was controlled by the diffusive rate of the monomer. The main concentrations used in this work were 20%.

Compared with the grafting yield of NIPAAm,^{1,2} another monomer used to produce sensitive polymer on cotton cellulose, the grafting yield of DMAEMA, was relatively low. This might be attributed to the relative sizes of their molecules. The

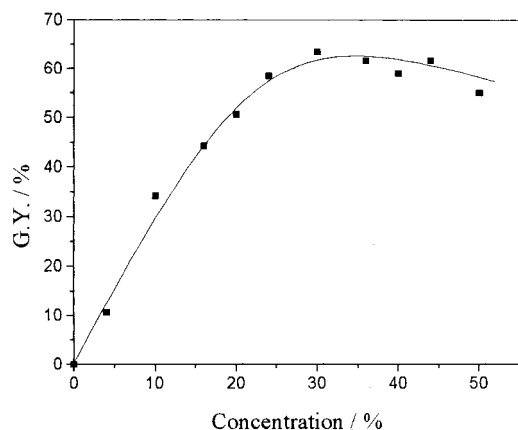


Figure 4 Effect of monomer concentration on grafting yield. Dose: 16.13 kGy; reaction time: 4 h; grafting temperature: 21°C.

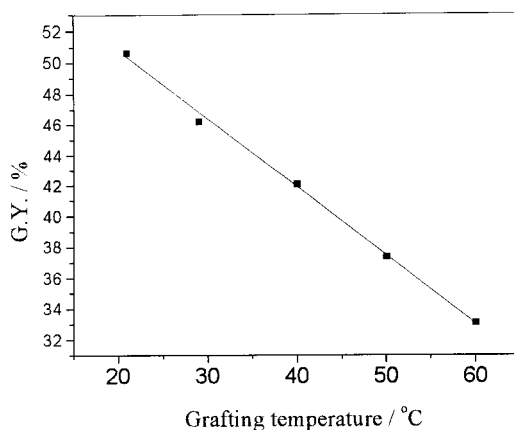


Figure 5 Effect of grafting temperature on grafting yield. Dose: 16.13 kGy; reaction time: 4 h; monomer concentration: 20%.

DMAEMA molecule was larger than NIPAAm, and the grafted chains of polyDMAEMA during the chain propagation were larger than those of polyNIPAAm. Larger chains caused more impediment for continuing chain propagation. Therefore, the overall grafting yield of the larger monomer was relatively lower.

Effect of Grafting Temperature on the Grafting Yield

As the grafting temperature increased, the grafting yield dropped almost linearly (Fig. 5). This was also the normal situation in preirradiation grafting. When the grafting temperature increased, the rates of monomer diffusion and chain propagation both increased. However, the chance

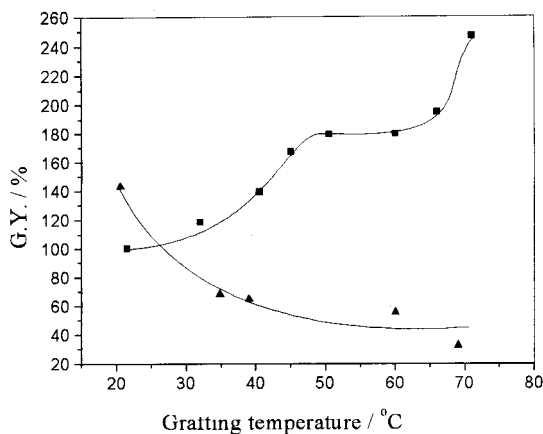


Figure 6 Effect of grafting temperature on grafting yields of NIPAAm (■) and AAm (●).¹ Dose: 32 kGy; reaction time: 4 h; monomer concentration: 6%.

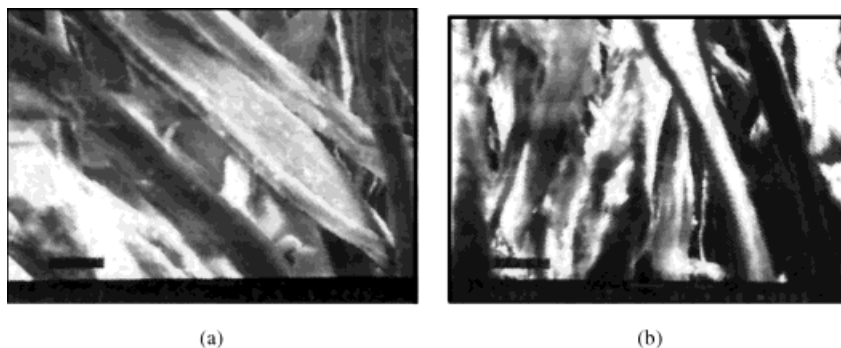


Figure 7 SEM photos of ungrafted and grafted samples. (a) Ungrafted sample; (b) grafted samples with a grafting yield of 64%.

of the free radicals' simultaneous termination increased. The overall tendency of the grafting yield according to the temperature increase was the cooperative effect of the above aspects, which is why the main reactions of this work were performed under 21°C.

From Figure 6 we see that, in aqueous solutions, the changing tendency of grafting of DMAEMA was similar to that of AAm but was opposite to that of NIPAAm.¹ It is concluded that the grafting copolymerization of DMAEMA or AAm was initiated by the trapped radicals, whereas the grafting copolymerization of NIPAAm was initiated partly by peroxide hydrogen.

Property Measurement of Grafted Samples

Result of X-ray Diffraction Measurement

The X-ray diffraction measurement analyzed the crystallinity change of samples. The crystallinity of the grafted sample with a grafting yield of about 65% was 63%, whereas that of the ungrafted sample was 67%. Because the grafting yield was not high enough, the crystallinity was not distinctly changed, which was consistent with the result of the grafting copolymerization of NIPAAm onto cotton cellulose fabrics.²

Result of Scanning Electron Microscope (SEM)

SEM measuring was tried to explore the surface properties of samples. Because of the coarse na-

ture of the cotton fabric surface, the result of SEM did not apparently display the grafting features much. However, some change by grafting could be seen from the photos (Fig. 7).

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