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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Okieimen, F. E. and Tame, A.(1996) 'Graft Copolymerizations of Modified Cellulose. Grafting Acrylamide onto Carboxymethyl Cellulose', Journal of Macromolecular Science, Part A, 33: 1, 49 – 56

To link to this Article: DOI: 10.1080/10601329608020356

URL: <http://dx.doi.org/10.1080/10601329608020356>

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GRAFT COPOLYMERIZATIONS OF MODIFIED CELLULOSE. GRAFTING ACRYLAMIDE ONTO CARBOXYMETHYL CELLULOSE

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INTRODUCTION

The use of ceric ions to initiate graft polymer formation on cellulosic materials has been reported by several workers (1-5). These studies show that the desired modifications in the properties of cellulose resulting from graft copolymerization are only moderate. This is due largely to the infrequent interpositioning of the polymer grafts on the backbone polymer arising from inefficient initiation of grafting. In order to enhance the graftability of cellulosic materials, many workers have reported on methods of modification on cellulose prior to grafting (6-7). In our previous study (8) we reported that the extent of graft polymer formation on holocellulose modified by the incorporation of allyl chloride moieties (D.S=1.5) was greatly enhanced and this was considered to result from the participation of the allylic moieties in graft polymer formation. However the graft copolymerization procedure was heterogeneous process in which the distribution of reacting species between the cellulose-aqueous phase interface and the continuous phase was a limiting factor in graft polymer formation. It was thought that a chemical modification process which does not markedly reduce the degree of polymerization of cellulose, which incorporates into the cellulose backbone groups which could be reactive to graft polymer formation, and which renders cellulose more swellable or soluble in water would enhance its grafting. It was considered that cellulosic materials containing carboxy methyl groups presents such a material.

MATERIALS AND METHODS

Analar grade acrylamide and ceric ammonium sulphate (GPR) obtained from BDH Ltd were used without further purification. Holocellulose from a tropical soft wood *Triplochiton scleroxylon* (Obeche) was obtained and bleached as described previously (5). The preparation of sodium carboxy methyl cellulose (CMC) was carried out using the method described by Paddison and Sommers (9). The method involved steeping the bleached holocellulose in 50%(w/v) sodium hydroxide solution for 1 hour at 29°C followed by the use of chloroacetic acid as the etherifying agent in the presence of isopropanol and benzene. The degree of substitution (modification) of the holocellulose was determined by the titrimetric method described by Pacault and Boutterny (10). Graft copolymerization of acrylamide on the modified and unmodified cellulosic material was carried out using various concentrations of the initiator and monomer. The Polymerization procedure was based on the method reported by Lepoutre and Hui (11). The polymerization was allowed to proceed for hour, and the reaction was stopped by the addition of 2ml of 1%(w/v) quinol solution to the reaction mixture. The mixture was poured into an equal volume of ethanol, filtered and the residue was air-dried and weighed. The ungrafted polyacrylamide was extracted with water at room temperature. The grafted cellulosic material was then air-dried and reweighed. The percentage weight increase (in terms of the weight of the cellulosic substrate) is reported as graft level. The grafted polymer chain were isolated from the cellulosic substrate by treatment with 66%(w/v) sulphuric acid (12). The isolated polyacrylamide was purified by solution in water and precipitation with ethanol. The molecular weight of the grafted polymer was determined from viscosity measurements in water at 25°C using the relationship.

$$\log [\eta] = \log 6.31 \cdot 10^{-5} + 0.80 \log M_v \quad (1)$$

The number of grafted polymer chains, N_g , is given as the ratio of the weight of grafted polymer to the average molecular weight of graft polymer chains and is reported as the frequency of grafting, F_g , per anhydroglucose repeat units of the cellulosic material.

RESULTS AND DISCUSSION

The dependence on initiator concentration of the weight of grafted polyacrylamide on the unmodified and modified cellulosic materials are shown in Fig 1. The results

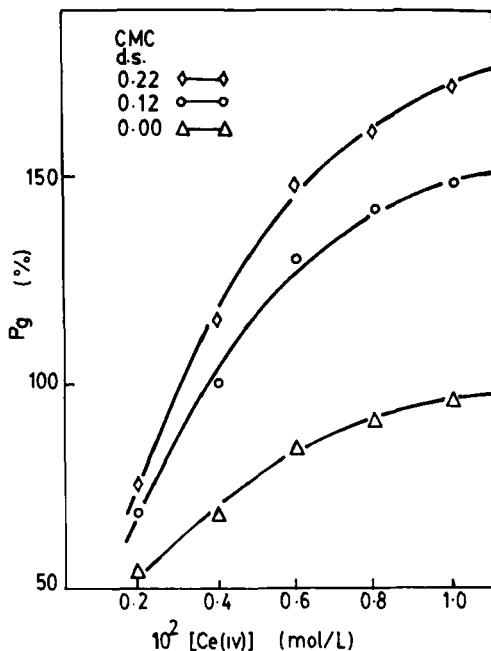
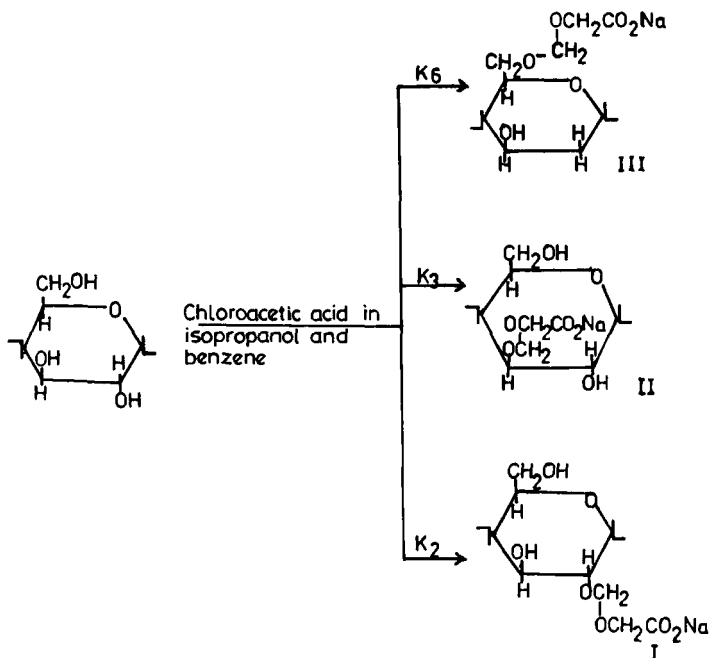


Fig. 1: Graft Copolymerization of Acrylamide on Carboxy methyl cellulose at 29°C. Variations of graft levels with ceric ion concentration.

show that chemical modification of the cellulosic substrate is accompanied by marked increase (of up to 70%) in graft levels. Chemical modification of the cellulosic substrate leads to the incorporation of carboxymethyl moieties on the cellulosic material.

The arrangement of the substituents on the cellulose derivative is determined by the relative rate constants of the reaction of the three hydroxyl groups in the glucose residue. It has been shown from ^{13}C -n.m.r studies that the distribution of carboxymethyl moieties on cellulose follows the order I > III > II(13). The mechanism by which ceric ion initiates graft polymerization is generally believed to involve the secondary hydroxyl groups on the glucose residue leading to the cleavage of the C-C bond. Substitution reaction of the secondary hydroxyl groups will preclude such interactions and would lead to reduced graftability of cellulose. The interaction of ceric ion



with the carboxy methylated cellulose could produce two reactive sites on the substrate; one resulting from the cleavage of C - C bond (possible only with III) and the other resulting from hydrogen atom abstraction from the carboxymethyl moiety. The extents of modification of the cellulosic material used in this study are low (not more than one carboxymethyl group per five anhydroglucose unit) and it is unlikely, considering the chemical environment of any radical formed on the carboxymethyl group, that the latter would produce the observed marked increase in graft levels. However, carboxymethylation generally results in enhanced degree of swelling (solubility) of cellulosic material in water. This enhanced swelling more than the participation of the incorporated carboxy methyl moieties in the initiation of graft polymer formation may explain the observed marked increase in graft levels of carboxy methylated cellulose.

Figure 2 shows the dependence on monomer concentration of the levels of grafting polyacrylamide on the modified and unmodified cellulosic materials.

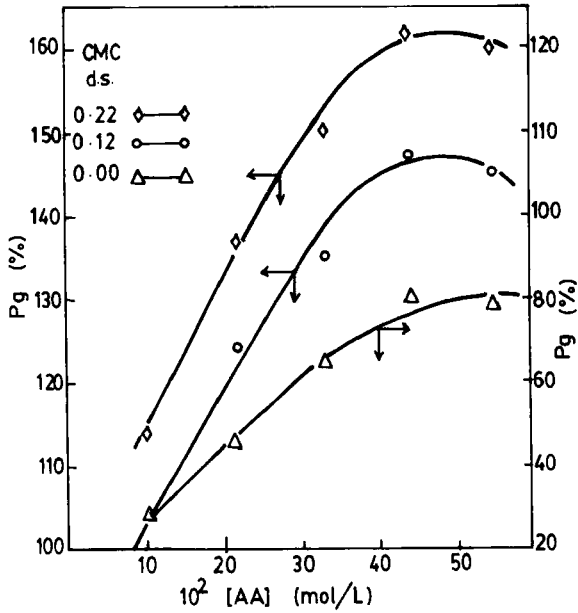


Fig. 2: Graft Copolymerization of Acrylamide on Carboxy methyl cellulose at 29°C. Variations of graft levels with acrylamide concentration

The results show that levels of grafting on the modified cellulosic material are markedly higher than on the unmodified polymeric substrate. This could be explained in terms of the enhanced swelling of the cellulosic material in the dispersion medium brought about by carboxy methylation. It can be seen that the initial increase in graft level with increase in acrylamide concentration levels off at higher monomer concentrations. This behaviour has been explained in terms of a mechanism of graft copolymer formation which involves the formation of monomer-solvent-initiator complex (14,15)

The variation of the molecular weights of polyacrylamide grafts with ceric ion initiator is shown in Fig. 3. The molecular weights of the grafted polymer chains shows the expected dependence on ceric ion initiator and suggest that termination of graft copolymerization proceeds by the interaction of ceric ion with growing graft polymer chains (16) It can be seen that although the molecular weights of the grafted polymer chains are about the

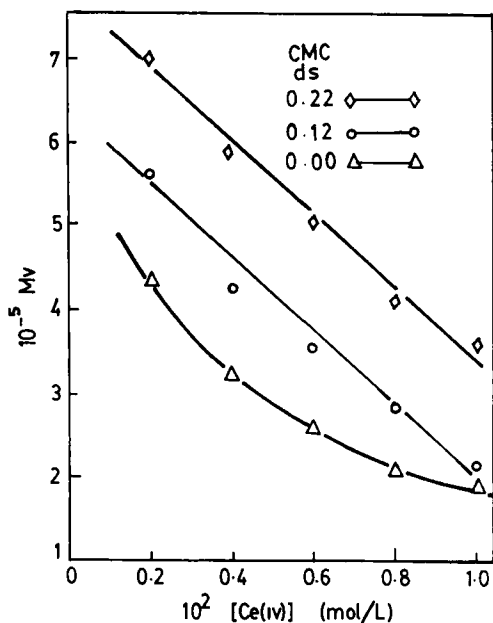


Fig. 3: Graft Copolymerization of Acrylamide on Carboxy methyl cellulose at 29°C. Variation of molecular weight of graft polymer with ceric ion concentration.

same order of magnitude, the molecular weights of the polymer chains grafted onto the modified cellulosic materials are higher than on the unmodified materials.

Figure 4 shows the variation of the number of grafted polyacrylamide with ceric ion concentration. The results show that the frequency of grafting polyacrylamide of cellulosic is relatively high. It can be seen that an increase in the degree of modification of cellulose (by more than 90%) is not accompanied by a corresponding increase in the number of grafted polymer chain; in fact the frequency of grafting onto CMC with a degree of substitution of 0.22 is lower than obtained for the unmodified material. If initiation of graft polymer formation on cellulose occurred by hydrogen abstraction from carbon atoms carrying hydroxy groups, carboxy methylation would accentuate the initiation process leading to enhanced frequency of grafting. The result

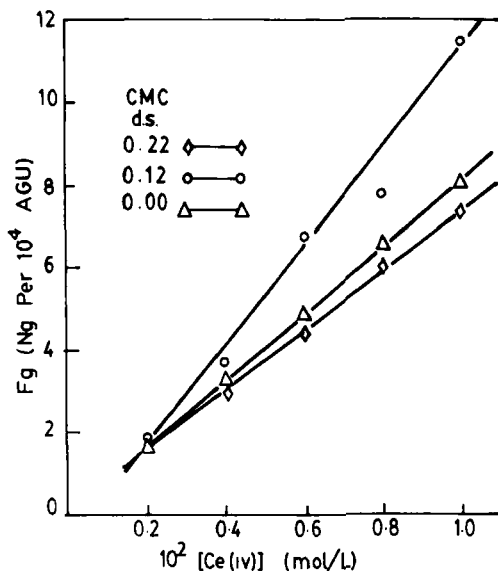


Fig. 4: Graft Copolymerization of Acrylamide on Carboxy methyl cellulose at 29°C. Variation of frequency of grafting with ceric ion concentration.

from this study suggest that hydrogen abstraction reactions may not be an important route to the formation of graft polymer chains and that the carboxy methyl groups of the modified cellulose do not take part in graft polymer formation. The observed reduction in the frequency of grafting on CMC with increase in the degree of carboxy methylation is as would be expected considering that carboxymethylation reduces the sites available for the initiation of graft copolymerization.

The results from this study show that in the carboxymethylation of cellulose, increased in the degree of modification is not accompanied with a concomitant increase in the number of grafted polymer chains. It would therefore seem that rendering cellulose soluble in water via chemical modification (which does not reduce the average molecular weight of cellulose) may not provide a viable route for enhancing the graftability of cellulose.

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