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Graft Copolymerization of Acrylonitrile on Bleached Holocellulose

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NOTE

GRAFT COPOLYMERIZATION OF ACRYLONITRILE ON BLEACHED HOLOCELLULOSE

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INTRODUCTION

The mechanism by which ceric ions interact with cellulosic materials in the presence of vinyl monomers to initiate graft copolymer formation is generally believed to involve propagation by radicals generated on the cellulosic substrate [1-5]. However, the relatively high levels of homopolymerization and low efficiencies of grafting associated with graft copolymerization suggest that loci of initiation other than radicals formed on the cellulosic materials may be important in graft copolymerization [6].

EXPERIMENTAL

Acrylonitrile monomer from BDH Ltd. was purified as described previously [7, 8]. Ceric ammonium nitrate was used without further purification. Bleached holocellulose from a tropical hardwood, *Gosweilerodenron balsamiferum*, was prepared as described previously [9, 10].

Graft copolymerization of acrylonitrile on the bleached holocellulose was carried out by using various amounts of the monomer and ceric ions and a constant amount of holocellulosic substrate (1.0 g) dispersed in 100 mL of distilled water 29°C. The polymerization procedure was based on the method described by Lepoutre and Hui [11]. Polymerization was allowed to proceed for 90 min, and the reaction was stopped by the addition of 1 mL of 1% (w/v)

quinol solution to the reaction mixture. The mixture was filtered, and the residue was air dried and weighed.

The ungrafted polyacrylonitrile homopolymer was Soxhlet extracted with dimethylformamide. The grafted holocellulosic fibers were then air dried and reweighed. The measured weight increase (in terms of the cellulosic substrate) multiplied by 100 was reported as the percent graft level (P_g). The grafted copolymer chains were isolated from the holocellulosic substrate by the method described by Ogiwara et al. [12]. The isolated polyacrylonitrile copolymer and the extracted homopolymer were purified by solution in dimethylformamide and precipitation in ethanol. The molecular weights of the samples were obtained from viscosity measurements on dilute solution of the polymer samples in dimethylformamide at 30°C and the relationship

$$\log_{10} [\eta] = \log_{10} 2.09 \times 10^{-4} + 0.75 \log_{10} \bar{M}_v. \quad (1)$$

RESULTS AND DISCUSSION

The P_g values for polyacrylonitrile (Fig. 1) are generally lower than those reported for poly(methyl methacrylate) [9]. The increase in P_g accompanying the increase in ceric ion concentration reached its maximum at 10.0 mmol Ce(IV)/g cellulose. The ceric ion concentration at which maximum grafting was obtained for acrylonitrile graft copolymerization is relatively higher than the 7.5 mmol Ce(IV)/g cellulose reported for methyl methacrylate [9]. The ceric ion concentration at which maximum grafting is attained has been shown to correspond to the reduction equivalent of the cellulosic substrate and can be correlated with the total carbonyl content of cellulose [12]. The different initial ceric ion concentration that gives maximum grafting for the two monomers suggests that functional groups other than carbonyl groups may be important in graft copolymer formation [10]. Figure 1 shows that an increase in acrylonitrile concentration from 45.6 to 76.0 mmol/g cellulose gave only a 5% increase in P_g . This may be because the extent of grafting, irrespective of the mechanism, would be markedly influenced by the amount of the monomer at the grafting loci (cellulose-water interface) [13].

Gaylord and Anand [6] in their study of the graft copolymerization of methacrylonitrile on cellulose suggested that 1) graft copolymer formation resulted from an interaction between cellulose-water-monomer-ceric ion complex and uncomplexed monomer, 2) the extent of graft copolymer formation depends on the monomer complexed, and 3) that the more polar the monomer, the smaller P_g . In a polymerizing system containing fixed amounts of

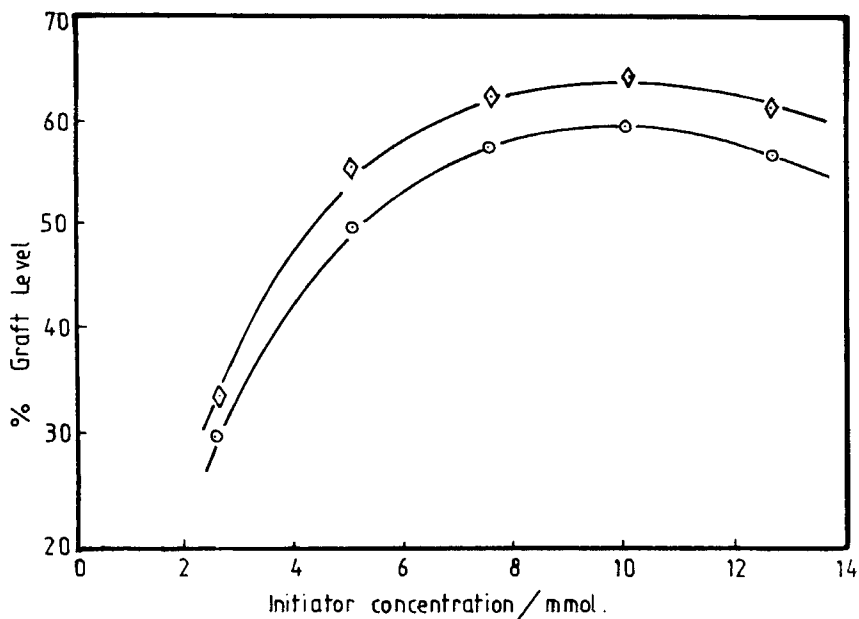


FIG. 1. Grafting acrylonitrile. Monomer concentration: (\diamond) 76.0 mmol and (\circ) 45.6 mmol. Temperature: 29°C.

initiator, cellulose, and water, there would be an optimum amount of the monomer that can be complexed, and an increase beyond this may not cause a marked increase in grafting. It would therefore seem from the results in Fig. 2 that the grafting of polyacrylonitrile may not go solely via propagation by radicals formed on the cellulosic backbone.

The molecular weights of the grafted polyacrylonitrile chains (Table 1) are lower than those reported for poly(methyl methacrylate) [9]. The molecular weights of the homopolymer are markedly higher than those reported for the grafted copolymer. These results, together with the observed facile homopolymerization of acrylonitrile in aqueous suspensions initiated by ceric ions, resulting in molecular weights of the order of 10^5 to 10^6 [13], suggest lower concentrations of acrylonitrile at the grafting loci than in the bulk dispersion phase. The number of grafted polyacrylonitrile chains varied from 6.11 $\mu\text{mol}/100$ g cellulose at 30.4 mmol acrylonitrile/g cellulose to 3.64 $\mu\text{mol}/100$ g cellulose at 106.3 mmol monomer/g. This corresponds to a frequency of grafting [14] of between 2.65×10^6 and 4.33×10^6 repeat units per polyacrylonitrile

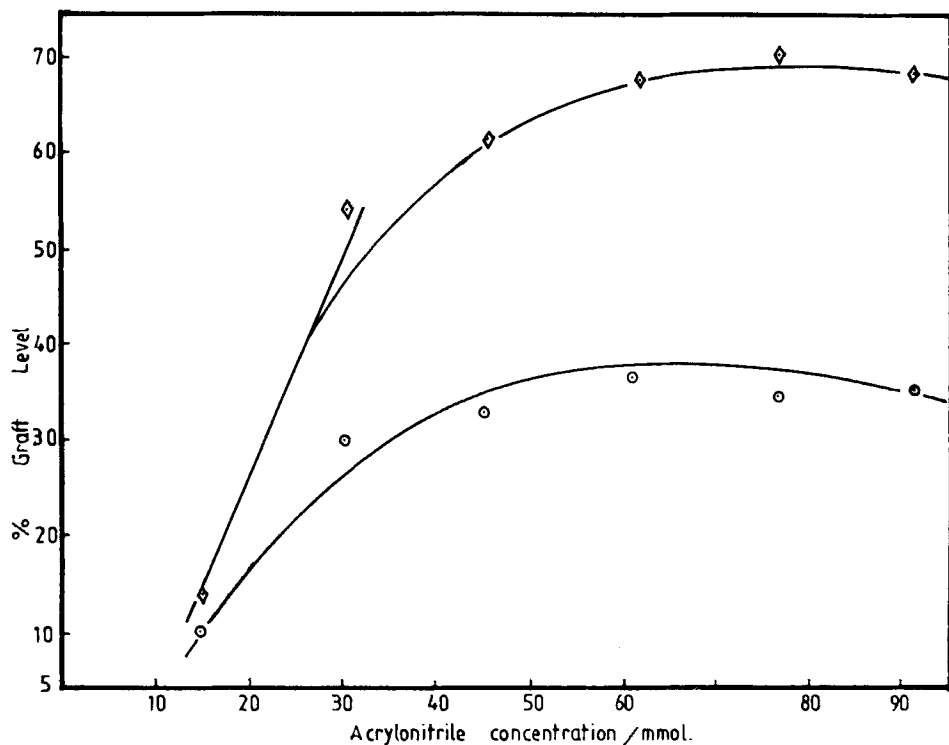


FIG. 2. Graft copolymerization of acrylonitrile. Initiator concentration: (\diamond) 7.5 mmol and (\circ) 5.0 mmol Ce(IV). Temperature: 29°C.

TABLE 1. Molecular Weight of Grafted Polyacrylonitrile Copolymer and Ungrafted Homopolymer

Ceric ion concentration, mmol/g cellulose	Monomer concentration, mmol/g cellulose	Average molecular weight, $\bar{M}_v \times 10^{-3}$	
		Grafted copolymer	Ungrafted homopolymer
5.0	106.3	9.62	401
5.0	76.0	9.83	190
5.0	30.4	4.91	70.3

graft, indicating that there is less than one graft per cellulose chain. Although an exact determination of the frequency of grafting cannot be made without knowing the molecular weight of the cellulose, the observed low frequency of grafting suggests that graft copolymers may actually be block copolymers resulting from reactions of the terminal hemiacetal on the cellulose chain [15].

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