

### ***Ceric Ion Induced Redox Polymerization of Acrylonitrile in Presence of Cellulose\****

Use of ceric salts (ceric ammonium nitrate and sulfate) for grafting vinyl monomers on to primary alcohols, amines, thiols, etc. has been reported by Mino et al.<sup>1-3</sup> In the present investigation ceric ammonium nitrate is used to study grafting of acrylonitrile (AN) on to cellulose (cotton fibers).

Grafting was effected by a solution polymerization technique in stoppered 150-ml. Pyrex flasks using 1 g. cotton fibers. The reaction was carried out at  $40 \pm 0.2^\circ\text{C}$ . over periods ranging from 5 to 60 min. The grafted samples were washed well and then extracted overnight with cold dimethyl formamide (DMF) for removing the superfluous polyacrylonitrile (PAN).

In general the rate and yields of grafting are very high as compared to those obtained with a persulfate-thiosulfate redox system reported earlier.<sup>4</sup>

The grafting reaction starts instantaneously, since no induction period could be observed.

Separate studies on silica spheres substituted for the cotton fibers indicate that the high rate of grafting is not merely due to the large surface area of cellulose available for reaction, but is mainly due to the reducing action of cellulose.

The effect of monomer and initiator concentrations respectively on the yield of grafting has also been studied.

Mino et al.<sup>2</sup> have shown that during oxidation of alcohols, such as pinacol with ceric salts, the ceric ions are responsible for generation as well as termination of free radical sites.

It may thus be assumed that during the grafting of PAN to cellulose, too, the ceric ions would be consumed in a similar manner, i.e., for initiation and termination of free radical sites. It is observed that the  $[\text{Ce}^{\text{IV}}]$  consumption during the grafting reaction is more than that during oxidation of cellulose alone. It is, therefore, postulated that this difference is due to the formation of some ungrafted PAN within the cellulose fibers.

Number average molecular weights ( $M_n$ ) of the grafted PAN chains, obtained by using the equation of Marchessault et al.<sup>5</sup> range between 140,000-290,000.

Osmometric data on the values of  $M_n$  are awaited for substantiating the theoretical values mentioned above.

These together with other data on the oxidation of cellulose with ceric ions will be published shortly.

The authors thank the Director and members of the Council of Administration of ATIRA for permission to publish this work.

#### **References**

1. Mino, G., and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
2. Mino, G., S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
3. Mino, G., S. Kaizerman, and E. Rasmussen, *J. Polymer Sci.*, **39**, 523 (1959).
4. Kulkarni, A. Y., A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polymer Sci.*, **7**, 1581 (1963).
5. Katai, A. A., V. K. Kulshrestha, and R. H. Marchessault, *J. Polymer Sci.*, **C2**, 403 (1963).

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Received April 12, 1965

\* This work forms part of the Ph.D. thesis of A. Y. Kulkarni.