Studies on Grafting of Styrene onto Cotton*

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Grafting of styrene onto cotton yarn by the ceric ion method under different experimental conditions, such as varying initiator concentration, time, temperature and cotton monomer ratio, was investigated. Maximum grafting occurred in the low initiator concentration range 0.004-0.006 M. At higher initiator concentration, the grafting efficiency decreased and the amount of homopolymer increased. The optimum reaction period was found to be 4 hr. The percentage graft, percentage homopolymer and grafting efficiency were higher at 90°C than at 65°C. At higher monomer to cotton ratios, the percentage graft as well as percentage homopolymer were higher. Addition of a small amount of acrylonitrile (AN) to the reaction mixture increased the percentage graft and grafting efficiency markedly and also decreased the percentage homopolymer.

Grafting provides a means of modifying cotton without destroying its desirable characteristics. Vinyl monomers can be grafted onto cellulosic substrates by various methods. Excellent reviews on this subject are available1 - 4. The ceric ion initiation method has been used extensively in recent years for graft copolymerization of vinyl monomers onto cellulose5 - 15 on account of its high grafting efficiency compared to other redox systems5,12. However, most of the grafting studies have been carried out with acrylic type monomers or with monomers such as vinyl chloride which are soluble in water to some extent. Relatively little work has been reported on ceric ion grafting of styrene which is only sparingly soluble in water. Detailed information on the effects of various experimental conditions on grafting of styrene onto cotton by the ceric ion method is reported in this paper.

Richards6 showed that covalent attachment of polymer to cellulose existed in the cellulose acrylonitrile (AN) graft copolymer prepared using ceric ammonium sulphate as initiator. However, he failed to obtain grafting with styrene and vinyl acetate. Guzman7 investigated ceric ion initiated grafting of AN, acrylamide (AMD), acrylic anhydride (AA), methyl acrylate (MA), methyl methacrylate (MMA), styrene, vinyl acetate (VA) and isoprene. Very little grafting was obtained with styrene, MMA, VA and isoprene. Ide8 studied the grafting of styrene on viscose rayon fibres by the ceric ion method. He found that the yield of the graft copolymer increased with the initiator concentration and that styrene was the least reactive among the five monomers used, viz. MA, MMA, AN, VA and styrene.

Hebeish and Mehta15 investigated the relative grafting efficiencies of AN, MA, MMA and styrene at 20°, 40° and 60°C. They found that styrene was the least reactive and that no grafting occurred with styrene except at 60°C. The highest level of graft obtained was 4%. Huang and Chandramouli13 obtained higher grafting by pretreating wood pulp with water. They observed that the optimum range of initiator concentration for acrylic monomers was 0.003-0.006 M and for styrene 0.001-0.0018 M, and that the percentage graft increased with temperature.

The mechanism of initiation by ceric ion has been discussed in detail by several workers2,5,10 - 12,16. The mechanism has been reported to be a free radical process which involves the formation of a ceric-cellulose complex, and subsequent disproportionation of the complex, resulting in the formation of free radicals on the cellulose molecule. Graft polymerization reaction with vinyl monomers is then initiated at these radical sites. Arthur et al.11 also found that the ceric-cellulose complex or chelate formation was temperature dependent.

Materials and Methods
Cotton in the form of low-twist 30s yarn, made into 120 yard skein, dewaxed and kier boiled, was used. Styrene and acrylonitrile monomers were freed from inhibitors by washing with 8% solution of sodium hydroxide. Alkali was removed by repeated washing with distilled water. Monomer was then dried over anhydrous calcium chloride overnight, distilled under vacuum and stored in a refrigerator. All the other chemicals used were of analytical reagent grade.

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Results and Discussion

No appreciable grafting of styrene onto cotton was found when graft copolymerization was carried out in air at room temperature. This may be due to oxygen of the air which is reported to inhibit polymerization\(^\text{18}\). Hence, all grafting reactions were conducted under nitrogen at 65° and 90°C.

**Effect of initiator concentration on percentage graft**—Data on ceric ion concentration versus percentage graft are shown in Fig. 1. At 65°C, the percentage graft increased with initiator concentration up to 0.004 \(M\), remained almost constant up to 0.006 \(M\) and then decreased with further increase in initiator concentration. The decrease in percentage graft beyond a certain concentration can be explained by the fact that the oxidative termination rates begin to increase with increase in initiator concentrations\(^\text{13}\). A similar trend was observed at 90°C, but the percentage graft values were higher. The highest graft obtained at 65°C was 4.60%, while it was 15.12% at 90°C. This can be attributed to the temperature dependence\(^\text{11}\) of ceric-cellulose complex formation. In other words, this finding supports the postulate of ceric-cellulose complex formation suggested by the previous investigators\(^\text{5,10}\).

When grafting was carried out in the presence of a small amount (0.2 ml) of AN, the percentage graft increased considerably at 65°C as well as at 90°C. This increase may be due to the synergistic effect\(^\text{19}\). Acrylonitrile seems to favour the grafting reaction by suppressing the homopolymerization of styrene. However, the exact role of acrylonitrile in the present system remains to be determined. Rapson and Kvasnicka\(^\text{20}\) also reported a marked increase in radiation grafting of styrene onto viscose rayon when

![Fig. 1—Effect of initiator concentration on percentage graft](attachment:image.png)
carried out with the addition of AN. In the presence of AN as well the percentage graft increased with initiator concentration showing the earlier trend. However, the highest percentage graft (54.15) at 90°C was obtained at the initiator concentration of 0.006 M.

Initiator concentration and homopolymer—A small amount (0.56-4.26%) of homopolymer was also formed during grafting. The formation of homopolymer has been reported by other workers also. The amount of homopolymer formed increased with increase in initiator concentration at both the temperatures (Fig. 2). But the percentage of homopolymer formed was higher at 90°C than at 65°C. Homopolymer formation decreased considerably when grafting was carried out in the presence of a few drops of AN at both the temperatures. Korshak et al. have reported that the addition of a small amount of styrene markedly reduces the yield of the homopolymer in grafting of AN onto rayon cord.

Initiator concentration and grafting efficiency—The effect of initiator concentration on the grafting efficiency is shown in Fig. 3. At 65°C, the grafting efficiency increased with initiator concentration up to 0.004 M and gradually decreased with further increase in initiator concentration. At 90°C, it increased with initiator concentration up to 0.002 M, remained almost constant up to 0.004 M and decreased gradually thereafter. The grafting efficiency was higher at 90°C (90.1%) than at 65°C (80.2%). It showed a similar trend when grafting was carried out in the presence of AN. But the grafting efficiencies were much higher, i.e. 91.9% and 96.3% at 65°C and 90°C respectively. These data indicate that improvement in grafting efficiency can be achieved by the addition of a small amount of AN to the system. Hebeish and Mehta also observed that AN appeared to increase the efficiency of grafting MA and MMA to cellulose.

Reaction period and percentage graft—It is seen from Fig. 4 that at 65°C the percentage graft increased with increase in reaction period up to 4 hr and remained constant thereafter, while at 90°C, the percentage graft increased with reaction period up to 3 hr and remained constant thereafter. The grafting obtained was 4.5 and 14.9% at 65°C and 90°C respectively. A similar trend was obtained when grafting was carried out in the presence of AN, but the percentage graft was almost double at both the temperatures. These results indicate that the grafting reaction needs about 4 hr for completion at 65°C and slightly lesser time at 90°C.

Reaction time and homopolymer—It is seen from Fig. 5 that the amount of homopolymer increased with increase in reaction period up to 4 hr and remained constant thereafter at both the temperatures. But the amount of homopolymer was higher at 90°C (1.64%) than at 65°C (1.11%). Grafting in the presence of AN resulted in decreased amount of homopolymer, although the trend remained the same. The highest
Table I—Effect of Cotton-Monomer Ratio on Grafting of Styrene onto Cotton

[Reaction period, 4 hr; temperature, 90°C; initiator concentration, 0.004 M; pH, 1.5]

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cotton-monomer ratio</th>
<th>Weight of cotton g</th>
<th>Weight of styrene g</th>
<th>Weight of grafting homopolymer g</th>
<th>Graft %</th>
<th>Grafting efficiency %</th>
<th>Total conversion %</th>
<th>Homo-polymer %</th>
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</thead>
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<td>3.7868</td>
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<td>0.5644</td>
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<td>15.00</td>
<td>90.14</td>
<td>16.64</td>
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<td>0.1348</td>
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<td>90.29</td>
<td>18.32</td>
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<td>1.99</td>
</tr>
</tbody>
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References

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