

Infrared Spectroscopy Studies of the Effects of the Catalyst on the Ester Cross-Linking of Cellulose by Poly(carboxylic acids)

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SYNOPSIS

The esterification of cellulose by a poly(carboxylic acid) proceeds in two steps: the formation of a 5-membered cyclic anhydride intermediate by the dehydration of two carboxyls, and the reaction between cellulose and the anhydride intermediate to form an ester. Sodium hypophosphite is the most effective catalyst for the esterification. The effect of sodium hypophosphite on the esterification of cotton cellulose was studied by Fourier transform infrared spectroscopy (FTIR). It was found that sodium hypophosphite accelerates both the formation of the cyclic anhydride intermediate and the reaction between the anhydride intermediate and cellulose. The chief role of sodium hypophosphite is possibly the acceleration of the esterification of cellulose by the anhydride intermediate. © 1993 John Wiley & Sons, Inc.

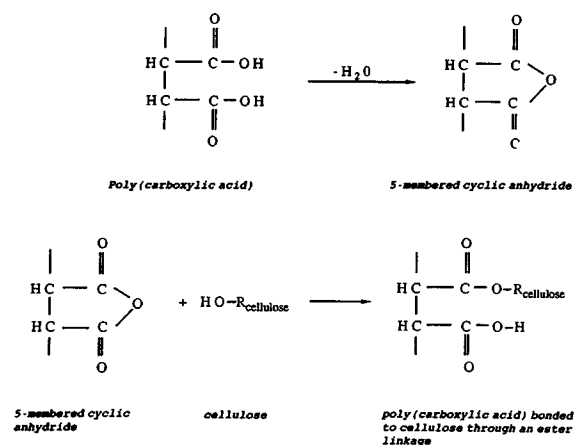
INTRODUCTION

In recent years, research on the cross-linking of cotton cellulose has focused on the use of poly(carboxylic acids) to replace the traditional *N*-methylol reagents such as dimethyloldihydroxyethyleneurea (DMDHEU) because of the increasing concern about the formaldehyde release during the production, storage, and consumer use of DMDHEU-treated cotton fabrics.¹⁻¹² Poly(carboxylic acids) cross-link cellulose molecules through ester linkages,¹³ thus providing excellent wrinkle resistance to the treated cotton fabrics. The catalysts used for the ester cross-linking include sodium hypophosphite and the salts of phosphorous acid such as monobasic sodium phosphate and dibasic sodium phosphate.^{2,3} Sodium hypophosphite is the most effective catalyst.¹⁴

Welch suggested the formation of an acid anhydride as an intermediate for the esterification of cellulose.² In our previous research, we used Fourier

transform infrared spectroscopy (FTIR) to study the possible mechanism of the reaction between a poly(carboxylic acid) and cellulose. We used two stereoisomers of butenedicarboxylic acids, i.e., *cis*-isomer (maleic acid) and *trans*-isomer (fumaric acid), to treat cotton fabric. The infrared spectroscopy data indicated that only the *cis*-isomer was able to form ester linkages with cotton cellulose.¹⁵ We identified a five-membered cyclic anhydride intermediate in the cotton fabric treated with poly(maleic acid) using FTIR spectroscopy.¹⁶ We also found that those poly(carboxylic acids), which form five-membered cyclic anhydride intermediates, cross-link cotton cellulose more effectively than did those poly(carboxylic acids) that form six-membered cyclic anhydride intermediates.¹⁶

Thus, the infrared spectroscopy data indicated that the esterification of cellulose by a poly(carboxylic acid) proceeds in two steps: the formation of a 5-membered cyclic anhydride intermediate by the dehydration of two carboxyl groups, and the reaction between cellulose and the anhydride intermediate to form an ester. The esterification of cotton cellulose by a poly(carboxylic acid) is shown as follows:



It is important to understand the effects of the catalysts on this two-step reaction. Knowledge about the effects of catalysts is essential for finding new and more effective catalysts. In this research, we used FTIR to investigate the effects of sodium hypophosphite on the formation of the anhydride intermediate and the reaction between the anhydride intermediate and cellulose.

EXPERIMENTAL

Infrared Spectroscopy Instrumentation

A Nicolet 510 FTIR spectrometer with a Specac "selector" diffuse reflectance accessory was used to collect the infrared spectroscopy data. All the infrared spectra of cotton fabric were collected with the diffuse reflectance accessory and presented at the absorbance mode ($-\log R/R_0$). Resolution for all the infrared spectra was 4 cm^{-1} and there were 100 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. No smoothing function or base-line correction was used.

The carbonyl band intensities in the infrared spectra of the finished cotton fabric presented in Table II was normalized against the 1317 cm^{-1} band, which is associated with the C—H bending mode of the cellulose molecule. Even though the 1370 and 1430 cm^{-1} bands of cellulose are more commonly used as references, the presence of a band in the $1440\text{--}1360 \text{ cm}^{-1}$ region due to the symmetric stretching mode of carboxylate carbonyl prevents the use of these two bands for normalization.

Materials

The cotton fabric used was a desized and bleached print cloth (Testfabrics Style 400). Sodium hypo-

phosphite was supplied by Aldrich. The poly(maleic acid) solution (50% solid in water) was supplied by Ciba-Geigy. The molecular weight of the poly(maleic acid) ranges from 500 to 1000.

Fabric Treatment

The cotton fabric was impregnated with a solution containing 8% poly(maleic acid)/4% NaH_2PO_2 or 8% poly(maleic acid). The impregnated fabric was passed through the squeeze rolls of a Cromtex 3-Roll Laboratory Padder to give a wet pickup of 100–110% based on the original weight of the fabric. The treated fabric was dried at 85°C for 10 min, then cured in an oven at a specified temperature. The cured cotton fabric was analyzed by FTIR immediately after the curing process. The cured fabric was also washed in tap water at room temperature for 5 min to remove the unreacted acid and catalyst, dried at 85°C for 5 min, and then treated in a $0.1M$ NaOH solution for 2 min at room temperature to convert carboxyl in the fabric to carboxylate and, finally, dried at 85°C for 5 min.

RESULTS AND DISCUSSION

A cotton fabric sample was treated with an aqueous solution containing 8% poly(maleic acid) (the cross-linking agent) and 4% sodium hypophosphite (the catalyst) and then dried at 85°C for 10 min. Another cotton fabric sample was treated with 8% poly(maleic acid) using the same method. The diffuse reflectance infrared spectra of the two treated cotton fabric samples are shown in Figure 1. The intense band at 1721 cm^{-1} shown in Figure 1(A) and (B) is due to the stretching mode of the carboxyl carbonyl in the poly(maleic acid) molecules. The bands at 2357 and 816 cm^{-1} in Figure 1(A) are due to the P—H stretching and bending modes, respectively, of hypophosphite (H_2PO_2^-).¹⁷ The frequencies and assignments for the bands of interest in the infrared spectra presented here and later in this paper are listed in Table I.

The two treated cotton fabric samples were cured at 170°C for 2 min. The infrared spectra of the two cured cotton fabric samples show two new bands at 1850 and 1781 cm^{-1} [Fig. 2(A) and (C)]. Our previous research indicated that the two bands at 1850 and 1781 cm^{-1} were due to the asymmetric and symmetric stretching modes, respectively, of the carbonyl of a 5-membered cyclic anhydride, which was formed by the dehydration of two adjacent carboxyl groups in a poly(maleic acid) molecule and was a

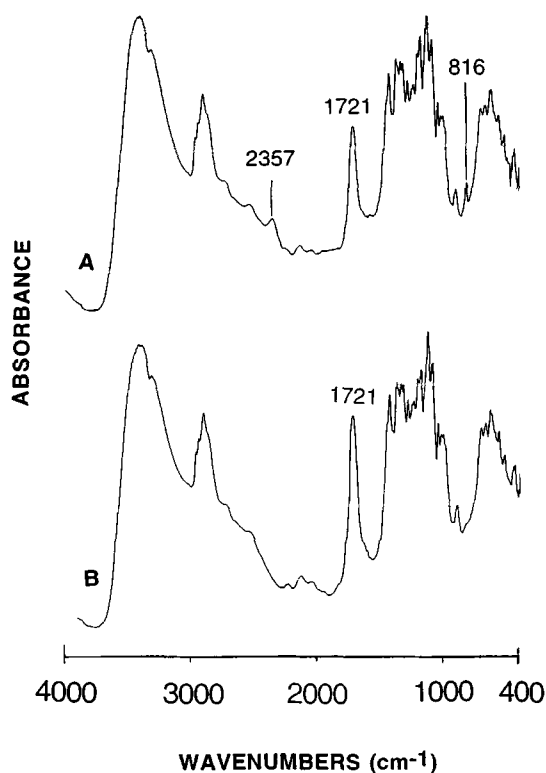


Figure 1 (A) The infrared spectrum of the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 ; (B) the infrared spectrum of the cotton fabric treated with 8% poly(maleic acid).

reactive intermediate for esterification of cellulose.¹⁶ It is observed in Figure 2(C) that a substantial amount of the anhydride intermediate exists in the cotton fabric treated with poly(maleic acid) without the presence of the catalyst. The intensity of the anhydride carbonyl band at 1881 cm^{-1} for the two fabric samples is presented in Table II.

The two treated cotton fabric samples were also cured at 200°C for 2 min and then examined by FTIR. The infrared spectra of the two cotton fabric samples cured at 200°C are shown in Figure 3(A) and (C). A strong band at 1781 cm^{-1} was also

observed in the spectrum of the cotton fabric treated by poly(maleic acid) without the catalyst [Fig. 3(C)].

The cotton fabric samples cured at 170 and 200°C were washed in water to remove the unreacted acid and the catalyst, then treated in a 0.1 M NaOH solution to convert carboxyl to carboxylate. The infrared spectra of the two sets of cotton fabric samples thus treated are presented in Figure 2(B) and (D) and Figure 3(B) and (D), respectively. The ester carbonyl band intensity and the carbonyl band intensity ratio (ester/carboxylate) of the infrared spectra of the two sets of cotton fabric samples are presented in Table II.

Our previous research has shown that the ester carbonyl band in an infrared spectrum of a cured cotton fabric could be separated from the overlapping carboxyl carbonyl band.^{13,18} When a finished cotton fabric was treated with a 0.1 M NaOH solution at room temperature, all the carboxyl in the fabric could be converted to carboxylate.^{13,18} Consequently, the amount of ester in the cotton fabric could be determined quantitatively by measuring the ester carbonyl band intensity. The carbonyl band intensity ratio (ester/carbonyl) was determined by the number of ester groups formed per each acid molecule; therefore, it was an indication of the effectiveness of the poly(carboxylic acid) as a cross-linking agent for cellulose.^{13,18}

The data in Table II demonstrate that the ester carbonyl intensity increases from 0.31 and 0.55 to 0.59 and 0.66, respectively, when sodium hypophosphite was used as a catalyst at the two different curing temperatures. The carbonyl band intensity ratio (ester/carbonyl) also increases significantly in the presence of the catalyst. The acceleration of the esterification of cotton cellulose in the presence of NaH_2PO_2 is obvious.

Table II indicates that at 170°C the anhydride carbonyl band intensity decreased from 0.37 to 0.28, whereas the ester carbonyl band intensity increased

Table I The Frequency and Assignment of the Bands of Interest in the Infrared Spectra (Fig. 1–5)

Band Frequency (cm^{-1})	Band Assignment
1721	Carboxyl carbonyl stretching
1721–1728	Ester carbonyl stretching
1580–1588	Carboxylate carbonyl asymmetric stretching
1777–1781	Anhydride carbonyl symmetric stretching
1848–1850	Anhydride carbonyl asymmetric stretching
2338	P—H stretching
814	P—H bending

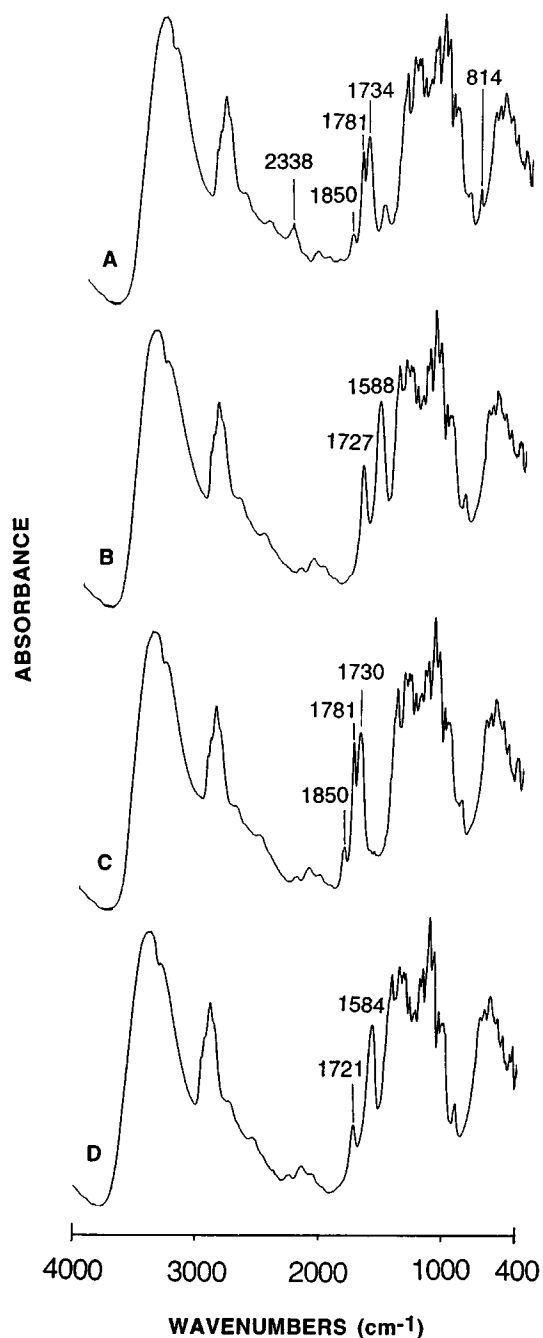


Figure 2 The infrared spectra of (A) the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 and cured at 170°C for 2 min; (B) the cotton fabric in A, treated with 0.1M NaOH; (C) the cotton fabric treated with 8% poly(maleic acid) and cured at 170°C for 2 min; (D) the cotton fabric in C, treated with a 0.1M NaOH.

from 0.31 to 0.59 when NaH_2PO_2 was used as a catalyst. When the fabric was cured at 200°C , the anhydride carbonyl band intensity decreased from 0.40 to 0.15, whereas the ester carbonyl band intensity increased from 0.55 to 0.63 when the catalyst was

used. This is because the reaction between the anhydride intermediate and cellulose was accelerated in the presence of the catalyst. As a result of the acceleration of the reaction, the amount of ester was increased whereas the amount of the remaining an-

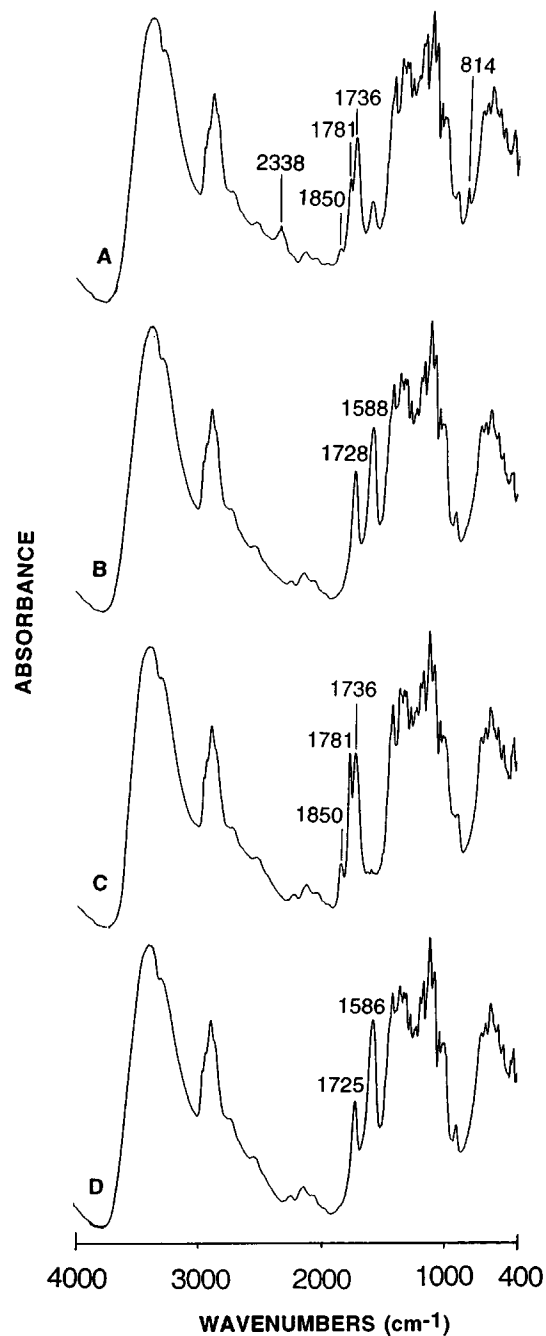


Figure 3 The infrared spectra of (A) the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 and cured at 200°C for 2 min; (B) the cotton fabric in A, treated with 0.1M NaOH; (C) the cotton fabric treated with 8% poly(maleic acid) and cured at 200°C for 2 min; (D) the cotton fabric in C, treated with 0.1M NaOH.

Table II The Anhydride Carbonyl Band (1881 cm^{-1}) Intensity, the Ester Carbonyl Band Intensity, and the Carbonyl Band Intensity Ratio (Ester/Carboxylate) of the Cotton Fabric Treated with 8% Poly(maleic acid) and Cured at Different Temperatures^a

Catalyst	Curing Temperature ($^{\circ}\text{C}$)					
	200	170	140	200	170	140
	$\text{NaH}_2\text{PO}_2^{\text{b}}$			No catalyst		
Anhydride carbonyl band intensity	0.15	0.28	0.27	0.40	0.37	0.30
Ester carbonyl band intensity	0.63	0.59	0.44	0.55	0.31	0.13
Carbonyl band intensity ratio (ester/carboxylate)	0.77	0.66	0.48	0.58	0.39	0.31

^a All the cotton fabric was cured at the specified temperature for 2 min, washed to remove the unreacted acid and catalyst, and then treated with a 0.1M NaOH solution for 2 min prior to analysis.

^b Catalyst.

hydride was reduced. Without the presence of the catalyst, more anhydride intermediate remained intact so that the intensity of the anhydride carbonyl band at 1781 cm^{-1} was increased (Table II). The reduction in the intensity of the anhydride carbonyl band and the increase in the intensity of the ester carbonyl band in the presence of the catalyst is a clear indication that sodium hypophosphite catalyzes the reaction between the anhydride intermediate and cellulose to form an ester.

The two cotton fabric samples treated with 8% poly(maleic acid)/4% NaH_2PO_2 and with 8% poly(maleic acid), respectively, were also cured at 140°C . The spectra of the fabric samples thus treated are presented in Figure 4(A) and (C). The curing temperature used here (140°C) is much lower than the curing temperatures commonly used in textile finishing ($170\text{--}180^{\circ}\text{C}$). It is noted that the anhydride intermediate was formed in a significant quantity at 140°C without the presence of the catalyst [Fig. 4(C)]. However, only a small amount of ester formed, as demonstrated by a weak ester carbonyl band at 1721 cm^{-1} in Figure 4(D). The ester carbonyl intensity increased from 0.13 to 0.44 when sodium hypophosphite was used as a catalyst (Table II). The infrared spectroscopy data presented here again support the hypothesis that the reaction between the anhydride intermediate and cellulose is catalyzed by sodium hypophosphite.

All the anhydride intermediates observed in Figures 2–4 was the anhydride that remained in the cured cotton fabric after the reaction between the anhydride and cellulose had taken place. Therefore, the total amount of anhydride formed as a reactive intermediate was unknown and the effects of the catalyst on the formation of the anhydride intermediate could not be determined based on the data discussed above.

Two cotton fabric samples treated with 8% poly(maleic acid)/4% NaH_2PO_2 and with 8% poly(maleic acid), respectively, were cured at 115°C for 2 min. The infrared spectrum of the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 shows two distinct bands at 1779 and 1848 cm^{-1} due to the 5-membered cyclic anhydride [Fig. 5(A)]. However, little anhydride was formed in the cotton fabric without the presence of the catalyst [Fig. 5(C)]. It is evident in Figure 5 that sodium hypophosphite accelerates the formation of the anhydride intermediate. Thus, the infrared spectroscopy data presented here demonstrated that sodium hypophosphite has catalytic effects on both the formation of the five-membered cyclic anhydride intermediate and the reaction between the anhydride intermediate and cellulose.

Table II shows that the intensity of the anhydride carbonyl band at 1881 cm^{-1} in the cotton fabric treated with poly(maleic acid)/ NaH_2PO_2 was reduced from 0.28 to 0.15, whereas the ester carbonyl band intensity increased from 0.59 to 0.63 when the curing temperature was increased from 170 to 200°C . The infrared spectroscopy data indicate that the reaction between the anhydride and cellulose is likely a reaction slower than the formation of the anhydride intermediate. An increase in the curing temperature resulted in the reduction of the amount of the remaining intermediate (anhydride) and an increase in the amount of the final product (ester) as shown in Table II.

Figure 4 indicates that a substantial amount of the 5-membered cyclic anhydride was formed in the poly(maleic acid)-treated cotton fabric without the presence of the catalyst at 140° , which was much lower than the curing temperatures commonly used in textile finishing. The amount of ester formed in the cotton fabric, however, was very low without the

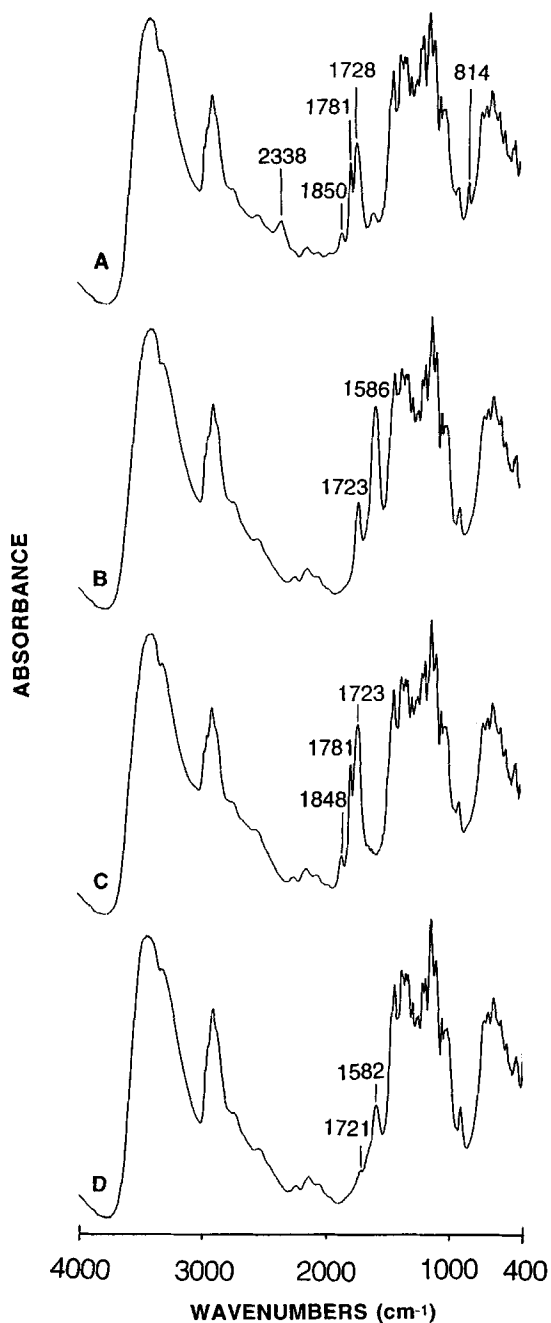


Figure 4 The infrared spectra of (A) the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 and cured at 140°C for 2 min; (B) the cotton fabric in A, treated with a 0.1M NaOH; (C) the cotton fabric treated with 8% poly(maleic acid) and cured at 140°C for 2 min; (D) the cotton fabric in C, treated with a 0.1M NaOH.

presence of the sodium hypophosphite [Fig. 4(D)]. Therefore, the chief role of sodium hypophosphite is possibly the acceleration of the esterification of cellulose by the anhydride intermediate.

CONCLUSIONS

When sodium hypophosphite is used as a catalyst for the esterification of cotton cellulose by a

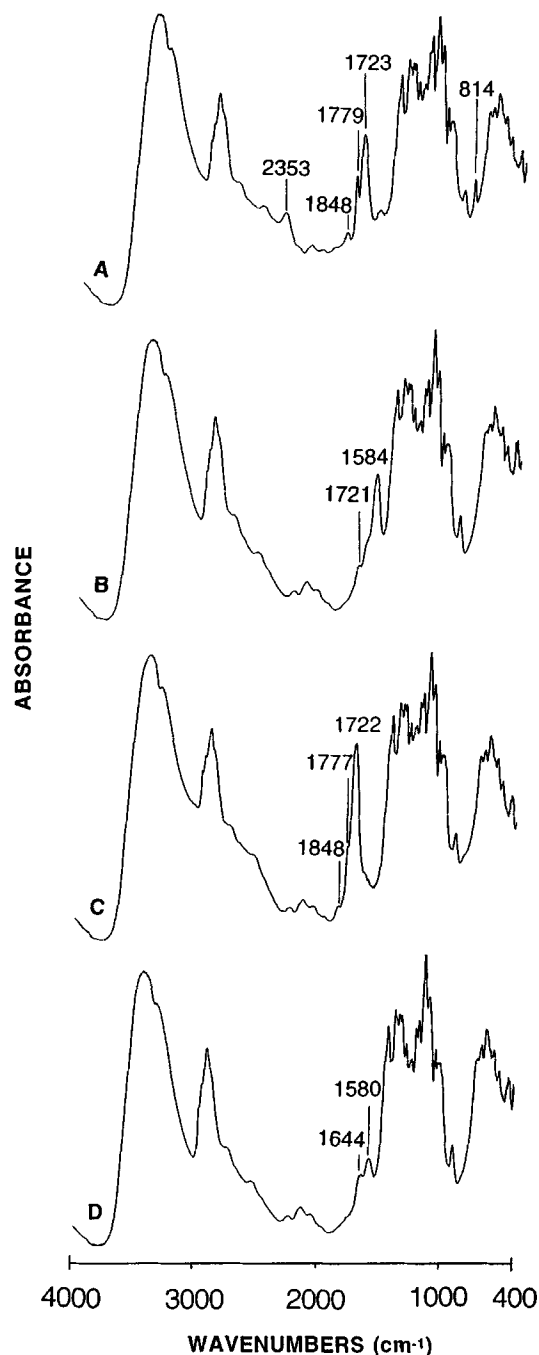


Figure 5 The infrared spectra of (A) the cotton fabric treated with 8% poly(maleic acid)/4% NaH_2PO_2 and cured at 115°C for 2 min; (B) the cotton fabric in A, treated with 0.1M NaOH; (C) the cotton fabric treated with 8% poly(maleic acid) and cured at 115°C for 2 min; (D) the cotton fabric in C, treated with a 0.1M NaOH.

poly(carboxylic acid), it accelerates both the formation of the five-membered cyclic anhydride intermediate and the reaction between the anhydride intermediate and cellulose. As a result, both the amount of the ester formed in the cotton fabric and the effectiveness of poly(maleic acid) as a cross-linking agent are increased. The chief role of sodium hypophosphite is possibly the acceleration of the esterification of cellulose by the anhydride intermediate.

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