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Graftpolymerization of Methacrylamide onto Silk

by

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絹에 對한 Methacrylamide의 그라프트 重合에 關한 硏究

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요 약

Ceric salt 를 觸媒로 使用하여 여러 가지 反應條件下에서 絹布上에 Methacrylamide 를 grafting 시키고, Schweitzer 試藥에 依한 溶解性및 赤外線吸收 스펙트럼을 比較檢討하여 그라프트重合物의 生成을 確認하였다. 그라프트率은 溫度, 反應時間 및 Monomer 濃度가 增加함에 따라 增加하였으며 그라프트率을 極大化하는 最適의 pH 値가 있음을 알았다. 그라프트率에 關한 理論式을 誘導하고 그 結果를 檢討하였다.

1. INTRODUCTION

It is well known that tetravalent ceric salts form very effective redox system with alcohol, glycol, aldehyde, amine etc., and a number of studies have been made on the mechanism of the reactions.(1)-(5) In the case of alcohols, the mechanism of initiation is

$$[\mathrm{Ce}^{IV}(X)_6]+\mathrm{RCH_2OH} \rightleftharpoons \mathrm{B}_{complex} \longrightarrow \mathrm{Ce}^{III}$$
$$+\mathrm{H}^+ + \dot{\mathrm{C}}\mathrm{HOH}\ (\text{or } \mathrm{CH_2O}\cdot)$$

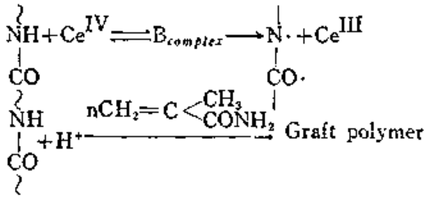
where X is OH^- or NO_3^- or H_2O, $B_{complex}$ is ceric-alcohol complex.

In the reaction above, if reducible high polymer is used in place of alcohols, free radicals formed on it can initiate graft polymerization in the presence of vinyl monomers.

Since G. Mino and S. Kaizerman found that acrylonitrile and acrylamide can be grafted onto polyvinyl alcohol by this mothod, there were many studies on grafting vinyl monomers to polyvinyl alcohol(7), cotton,(8)-(10) paper(11), silk (12), starch (13) etc.

But, as no experiments has been made using methacrylamide (MAA) as monomer, the authors grafted it to silk by ammonium ceric nitrate(ACN); the effects of monomer and initiator concentration, reaction time, temperature and pH of reactants are investigated.

Silk is a sort of polypeptides mainly comprised of glycine, alanine and thyrosine; when the secondary



$$\overset{\wr}{\mathrm{NH}}+\mathrm{Ce}^{IV} \rightleftharpoons \mathrm{B}_{complex} \longrightarrow \overset{|}{\mathrm{N}}\cdot + \mathrm{Ce}^{III}$$
$$\underset{\wr}{\overset{\wr}{\mathrm{NH}}} \ldots \mathrm{CO}\cdot \qquad \mathrm{CO} + \mathrm{H}^+ \xrightarrow{n\mathrm{CH_2{=}C}<^{\mathrm{CH_3}}_{\mathrm{CONH_2}}} \text{Graft polymer}$$

amides of silk react with ceric salts, free radicals can be formed and in the presence of vinyl monomers, it is supposed that graft polymers can be occurred as follows.

2. EXPERIMENTAL

(1) Materials

MAA (EASTMAN) was recrystallized twice from benzene solution and dried in vacuum desiccator for 48 hours (m. p. 103°C).

ACN (MERCK) was used without further purification.

Silk fabric (white, plain, density; warp 120 ends/inch, weft 120 picks/inch, 50 denier) was scoured in boiling water dissolved 8 parts of monogen and 2 parts of soda ash for 100 parts of silk by weight for 2.5 hours. After sericine was removed, silk was washed with hot and cold water sufficiently, dried at 105°C until the weight is constant, then weighed; it was made the weight of silk untreated.

Schweitzer's reagent was prepared as follows; 50g. of copper sulfete was dissolved in 300 ml of hot distilled water and cooled. Copper hydroxide was precipitated by adding ammonium hydroxide dropwise, and stopped adding it just before copper hydroxide formed was dissolved again, when the colour of solution changes to blue. The precipitate was filtered off, washed with water and dissolved in 25% ammonium hydroxide.

(2) Grafting procedure

About 0.5 g of silk, accurately weighed was placed in a 500 ml of erlenmeyer with aq. solution of monomer, the pH of which was adjusted with dil. HNO_3 and warmed to 50°C in a water bath. Nitrogen gas washed twice with potassium pyrogallate was passed through the reaction apparatus at the rate of 2 l/min for 5 min. Stock solution of ACN was added and total volume of the solution was adjusted to be 100 ml. Nitrogen was passed for further 3 min, and graft polymerization was proceeded for a predetermined time. The grafted silk was taken out of the reaction vessel and washed with hot and cold water in turns to remove homopolymer and dried at 105°C until the weight is constant. Percent graft was defined as percentage of the weight increased by grafting per weight of silk untreated.

(3) Infrared spectrophotometry

Silk and 9.5% grafted silk were cutted as small as possible with scissors(16) and dried at 105°C to be anhydrous. Spectra from pellets made of KBr and powdered silk were recorded with Perkin-Elmer infrared spectrophotometer model 137 B.

(4) Ultraviolet absorption spectra of ceric-amide complexes

Ultraviolet spectra of aq. solution of ACN(0.01%), acetamide (0.2%) and ACN-acetamide mixture were recorded with Beckman spectrophotometer model DK-2 respectively. Aq. solution of ACN-acetamide mixture was made by dissolving acetamide into aq. solution of ACN (0.01%) so that the concentration of acetamide was to be 0.2%. As reference solutions, distilled water was used for aq. solution of ACN and acetamide; for ACN-acetamide mixture, aq. solution of ACN and acetamide was used respectively. HNO_3 concentration of each solution was 1.3×10^{-2} M/l.

(5) Determination of ceric ion concentration

The concentration of ceric ion in 1% acetamide aq. solution was measured at 400mμ with color-Eye model C(Instrument Development Lab. Inc.). At this wave length the absorption of acetamide was found to be negligible by preliminary examination.

3, RESULTS AND DISCUSSION

(1) Effect of grafting time on percent graft

Effect of grafting time on percent graft was shown in Fig. 1. The reactions were carried out at 50°C and the increase in percent graft with time was observed. The conc. of ACN, MAA and HNO_3 used was 2.5×10^{-3}, 1, 1.3×10^{-2} M/l respectively.

It was found by preliminary experiments that proper temperature of reaction was 50°C. At lower temperature than 30°C little graft polymer is produced and at higher temperature than 60°C ACN is reportedly unstable. (11)

On this condition, it is ascertained by blank test that thermal polymerization is not occurred, though homopolymer of MAA is produced in the presence of ceric salt.

As the reaction proceeds, the rate of grafting decreased. The reasons are the conc. of ACN, MAA and the amounts of amides on the silk decreases with time. (11)

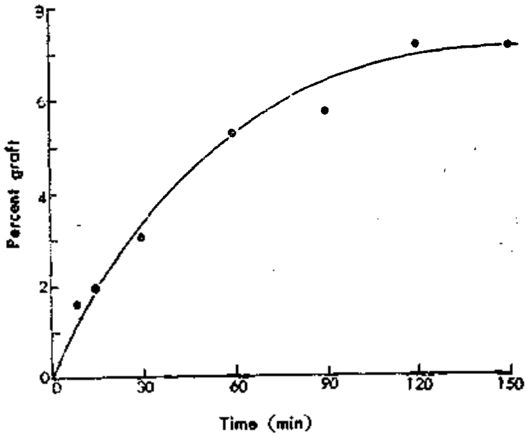


Fig. 1 Effect of Reaction Time on Grafting, MAA=1 M/l, ACN=2.5×10^{-3} M/l, $HNO_3=1.2\times10^{-2}$ M/l, Temp. =50°C

(2) Effect of HNO_3 concentration

Fig. 2 illustrates the effect of HNO_3 concentration on grafting. Percent graft reaches maximum at HNO_3 concentration of 1.3×10^{-2}M/l and decreases with increasing HNO_3 but at higher concentration than 2.1×10^{-2} M/l the amount of grafting decreases little.

It is supposed that the oxidizing rate of amide by ceric salt depends on the pH of the solution(4),(5) and the amounts of free radicals produced on the silk in a definite time depends on HNO_3 concentration; the maximum amount of grafting is obtained at optimum condition of pH. If it is true, the rate of reduction of ACN must be maximum at identical pH value, because the amounts of free radicals formed are directly proportional to the amounts of ACN decreased. In order to ascertain this fact, the concentration of ACN in 1% acetamide aq. solution of different pH value was measured at proper time intervals (see table I); the results show that the rate of reduction of ACN was maximum at 1.3×10^{-2} M/l too, although the sorts of amides are different; this causes possibly the maximum percent graft in Fig. 2 and in the case of using amides as a reducing materials, the optimum HNO_3 concentration seems to be 1.3×10^{-2}M/l.

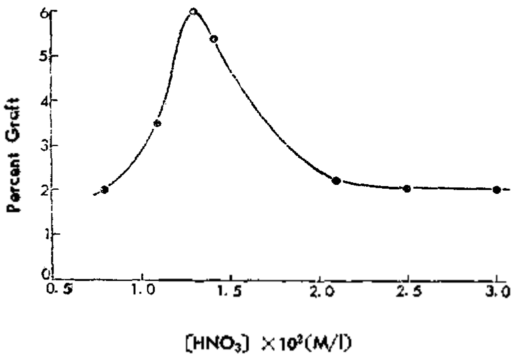


Fig. 2. Effect of HNO_3 Concentration on Grafting, MAA=1 M/l, ACN=2.5×10^{-3} M/l, Time=1 hr., Temp. =50°C

TABLE 1. Effect of HNO_3 Concentration on the Rate of Reduction of Ceric Salt in 1% Acetamide Solution (Reaction Temp. =50°C)

Conc. of $HNO_3\times10^2$ (M/l) / React. Time(Min.)	Concentration of $Ce\times10^3$ (M/l)			
	0*	0.8	1.3	2.2
0	2.50	2.50	2.50	2.50
10	2.50	1.83	1.37	1.73
20	2.50	1.60	1.25	1.60
30	2.50	1.54	1.20	1.46
60	2.50	1.49	1.14	1.37

* In distilled water without amide

(3) Effect of monomer concentration

The effect of monomer concentration on grafting is shown in Fig. 3. At higher concentration than 5%, slight increases in percent graft occurred.

In all cases, homopolymer was produced as a byproduct, but the amount was considerably decreased at lower conentration of monomer than 2%. Homopolymer was precipitated by adding methanol in the solution and its presence was confirmed.

(4) Effect of ACN concentration on grafting

Grafting was performed at various concentration of ACN from 0.1×10^{-3} to 3×10^{-3} M/l. As can be

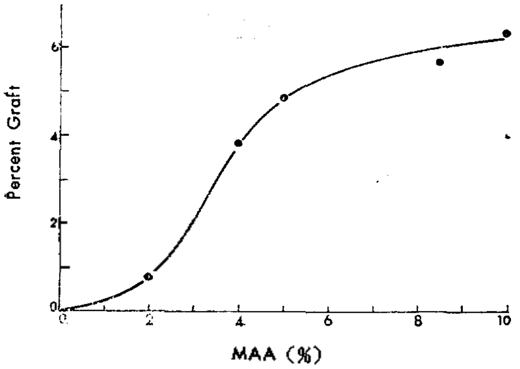


Fig. 3 Effect of MAA Concentration on Grafting, ACN$=2.5\times10^{-3}$ M/l, $HNO_3=1.3\times10^{-2}$ M/l, Time=1 hr., Temp. =50°C

observed in Fig. 4, percent graft was increased with increasing ACN concentration up to 0.3×10^{-3} M/l. But at higher concentration it was decreased until ACN concentration was 1×10^{-3} M/l, thereafter increased again. When more than 2×10^{-3} M/l of ACN was used, it increased sharply. This experimental result is a little strange. For comparison, grafting was performed at fixed ACN concentration of 0.5×10^{-3} M/l, while the amount of silk to be grafted was varied from 0.1 to 1.0 g. The results are shown in Fig. 5, where the amount of grafting reached maximum when 0.74 g of silk was used; when the ratio of ACN to silk was nearly equal to that of local maximum in preceding experiments(Fig. 4). This indicates that there exists optimum ratio between the weight of ACN and silk for a maximum percent graft.

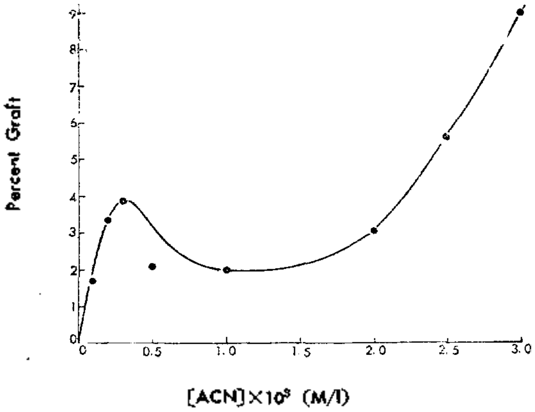


Fig. 4 Effect of ACN Concentration on Grafting, MAA=1 M/l, $HNO_3=1.3\times10^{-2}$ M/l, Reaction Time=1 hr., Temp. =50°C

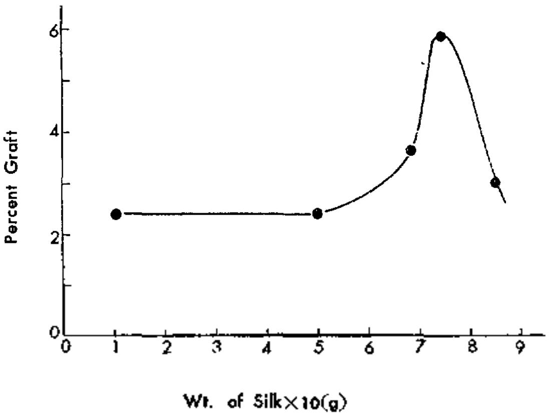


Fig. 5 Effect of the Weight of Silk on Grafting at Constant ACN Concentration, MAA=1 M/l, $HNO_3=1.3\times10^{-2}$ M/l, Time=1 hr. Temp. =50°C

The mechanism of initiation by ceric salts may be written as follows;

$$\sim CO-NH\sim+Ce^{IV}\rightleftharpoons B_{complex}\longrightarrow R_o+Ce^{III}+H^+ \quad\cdots\cdots(a)$$

where R_o is $\sim CO-\dot{N}\sim B_{complex}$ is ceric-amide complex.

Since tetravalent cerium has coordination number of six, there is a possibility that six sorts of ceric-amide complexes can be formed. But at lower concentration of amide and ACN, it is supposed that 1 : 1 complex is formed exclusively as in the case of alcohols. (15),(17)

Generally the mechanism of propagation and termindiation can be written as follows:

as follows:

$$\text{propagation; } R_o+M\xrightarrow{k_i}R_1 \quad\cdots\cdots(b)$$

$$R_n+M\xrightarrow{k_p}R_{n+1}\quad\cdots\cdots(c)$$

$$\text{termination; } R_r+Ce^{IV}\xrightarrow{k_t}Pr+Ce^{III}+H^+\quad\cdots\cdots(d)$$

$$R_r+R'_r\longrightarrow P_r+P'_r\quad\cdots\cdots(d')$$

$$R_r+R'_r\longrightarrow P_{r+r'}\quad\cdots\cdots(d'')$$

where M, R and P represent monomer, growing side chain and dead polymer (sidechain) respectively.

C. Mino(2) and R. A. Wallace(17) have shown that in the presence of ceric salt termination is occurred exclusively by the reaction (d).

The equations for reactions are therefore

$$-d[\mathrm{N}]/dt=k_i[\mathrm{N}][\mathrm{Cat}] \cdots\cdots(1)$$

$$-d[\mathrm{Cat}]/dt=k_i[\mathrm{N}][\mathrm{Cat}]+k_t[\mathrm{R}][\mathrm{Cat}] \cdots\cdots(2)$$

where [N] is the concentration of accessible secondary amides of silk and k_i is the overall rate constant of initiation.

$$-d[\mathrm{M}]/dt\fallingdotseq k_p[\mathrm{R}][\mathrm{M}] \cdots\cdots(3)$$

$$d[\mathrm{R}]/dt=k_i[\mathrm{N}][\mathrm{Cat}]-k_t[\mathrm{R}][\mathrm{Cat}] \cdots\cdots(4)$$

At steady state,

$$d[\mathrm{R}]/dt=0 \text{ and } [\mathrm{R}]=(k_i/k_t)[\mathrm{N}] \cdots\cdots(5)$$

Substitution of eq. (5) into (2) and (3) gives

$$-d[\mathrm{Cat}]/dt=2k_i[\mathrm{N}][\mathrm{Cat}] \cdots\cdots(6)$$

$$-d[\mathrm{M}]/dt=(k_ik_p/k_t)[\mathrm{N}][\mathrm{M}] \cdots\cdots(7)$$

from eq. (6) and (7), we obtain

$$d[\mathrm{M}]/d[\mathrm{Cat}]=(k_p/2k_t)[\mathrm{M}]/[\mathrm{Cat}]$$

or

$$[\mathrm{M}]/[\mathrm{M}]_0=([\mathrm{Cat}]/[\mathrm{Cat}]_0)^{k_p/2k_t}$$

where $[\mathrm{M}]_0$ and $[\mathrm{Cat}]_0$ is initial concentration of monomer and ACN respectively.

Then, from the definition of percent graft,

$$\text{Percent Graft}=([\mathrm{M}]_0-[\mathrm{M}])/W\times 100$$
$$=[\mathrm{M}]_0(1-([\mathrm{Cat}]/[\mathrm{Cat}]_0)^{k_p/2k_t})/W \times 100 \cdots\cdots(8)$$

where W is the weight of silk ungrafted.

Eq. (8) shows that percent graft in a definite reaction time reaches local maximum with increasing $[\mathrm{N}]_0$, at the range of $2[\mathrm{N}]_0>[\mathrm{Cat}]_0$ ($[\mathrm{N}]_0$ is the initial concentration of [N] and $[\mathrm{Cat}]_0 \ll 1$), if the reaction time is chosen adequately and $k_p \ll k_t$ (which is the general case); on these conditions, the plot of eq. (8) is coincident with Fig. 5 in shape. Since eq. (8) is based on an assumption that growing side chain is terminated by ceric salt, we think, the above coincidence shows our assumption is right.

In the polymerization procedure, homopolymer is produced a little.

But since monomer consumed for grafting is little comparing to its initial amount, homopolymer may be disregarded in the derivation of eq. (8); on this condition the amount of homopolymer produced as a byproduct is nearly constant throughout the experiments of Fig. 5.

(5) Solubilities and infrared spectra of silk and grafted silk

Silk and grafted silk were immersed in Schweitzer's reagent at room temperature; untreated silk was dissolved within 5 minutes, while grafted silk was not dissolved in 12 hours, but swollen.

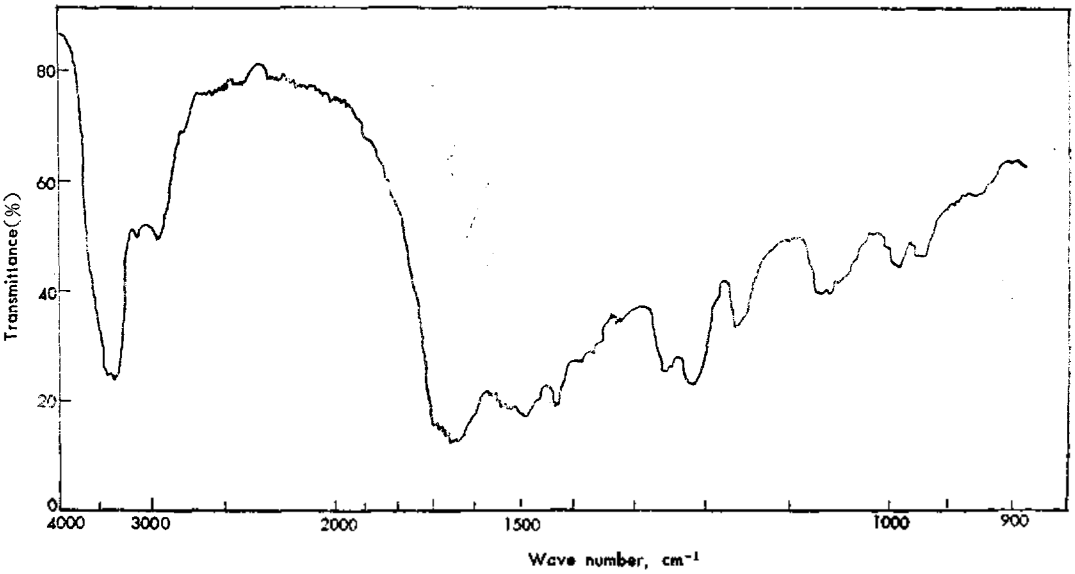


Fig. 6 Infrared Spectrum of Untreated Silk

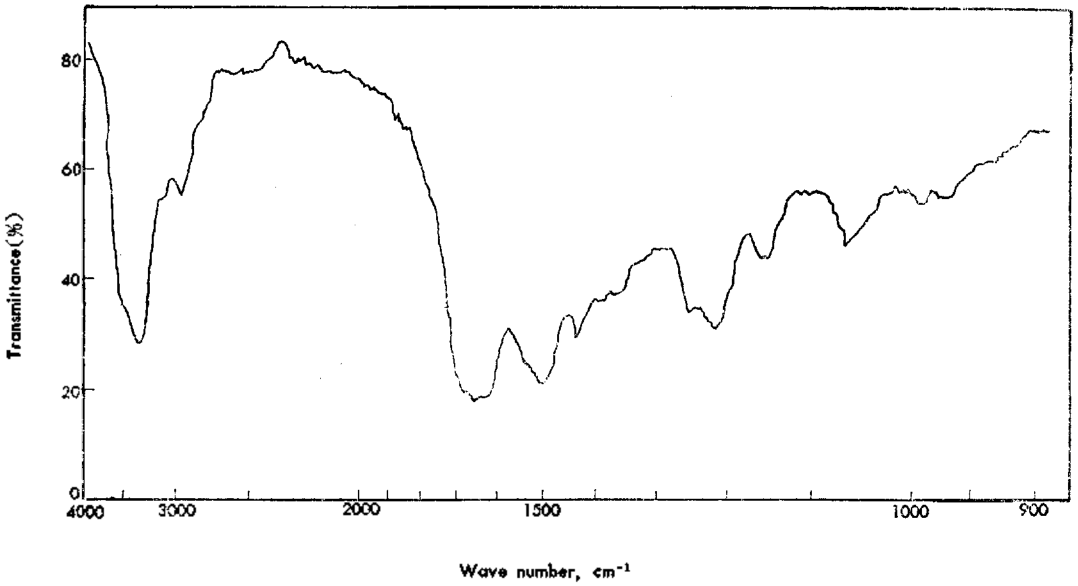


Fig. 7. Infrared Spectrum of Grafted Silk

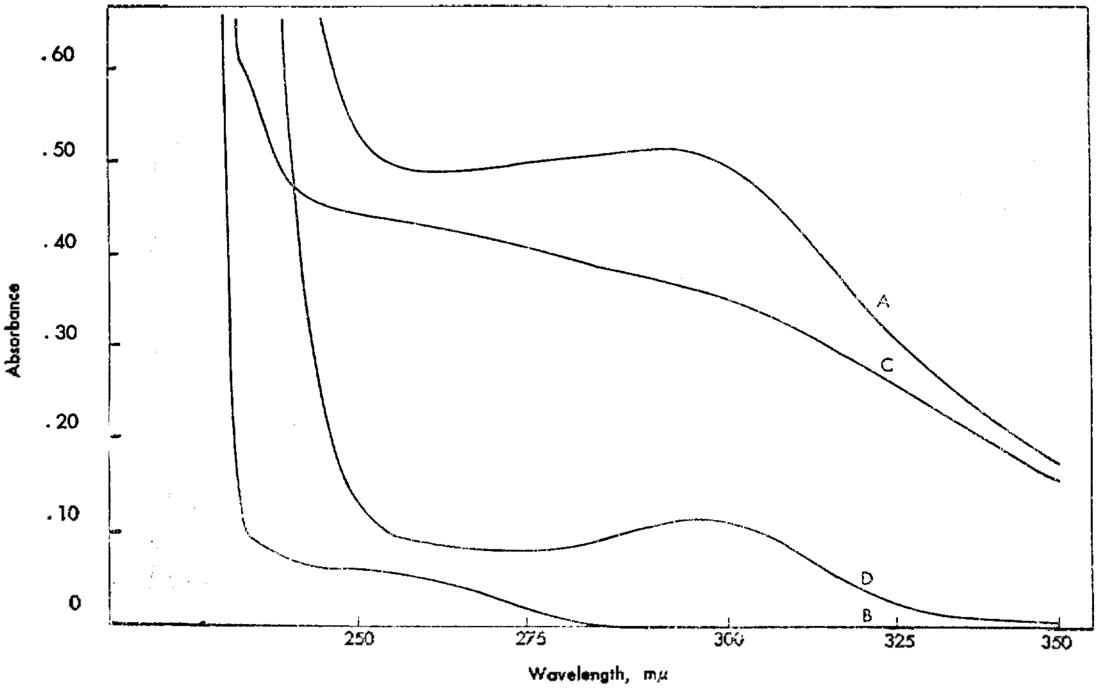


Fig. 8. Ultra Violet Absorption Spectra A=ACN, B=Acetamide, C=ACN-Acetamide Mixture (Reference Solution:B) D=ACN-Acetamide Mixture (Reference Solution:A)

The infrared spectra of silk and grafted silk are shown in Fig. 6 and 7. Grafted silk shows much less absorption at 3400 cm^{-1} assigned to N-H stretching vibration of secondary amides and at 1256 cm^{-1} probably due to amide III absorption than does untreated silk. From these results, the occurrence of true graft polymer can be certified and the sites of grafting are supposed to be the secondary amides on the silk.

(6) Ultraviolet absorption spectrum of ceric-amide complex

Duke(3) and G. Mino(6) have shown that ceric salts form complexes with alcohols, and that free radicals are formed by the disproportionation of the complexes. As the nitrogen atom of amides has one unshared pair of electrons, it can possibly form complex with ceric salts; it is supposed that amides of silk are oxidized through disproportionation of the complexes. To prove this, UV spectra were investigated (Fig. 8); in Fig. 8, curve A and C, B and D must be coincident each other respectively according to Lambert-Beers' law, if there is no chemial reaction between amide and ACN. But since they are not coincident each other, it is proved that ceric-amide complex is really occurred. From these results, it can be proved indirectly in that amides of silk form complexes with ACN.

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