

Graft Polymerization of Acrylic Acid onto nylon 6

Jae Ho Choi and Chong Kwang Lee

KAERI

(Recd 76. 6. 28)

Abstract

Acrylic acid has been grafted onto nylon fabric with ceric salts and γ -rays from Co-60 as initiators.

The distribution of molecular weight of the grafted polyacrylic acid has been determined and it was found that the ratio of weight-average and number-average molecular weight was higher in room temp. than in low temp. (-184°C).

The weight-average molecular weight of the polyacrylic acid was calculated from viscosity measurements in sodium hydroxide solution.

The factors affecting graft polymerization of acrylic acid onto nylon were examined.

A possible mechanism that the oxidation of nylon probably takes place at the methylene group attached to nitrogen to give a free-radical was discussed.

요 약

Ceric 염과 γ -선을 계기로 하여 Nylon 직포에 Acrylic acid를 접목반응 시켰다.

접목반응된 Polyacrylic acid의 분자량 분포를 측정된 결과 양 평균분자량과 수 평균분자량의 비는 낮은온도(-184°C)에서 보다는 상온에서 더 높았다는 것을 알았다.

Polyacrylic acid의 양 평균 분자량은 Sodium hydroxide 용액에서 점도를 측정하여 계산하였다.

Nylon에 Acrylic acid가 중합반응될 때에 중합반응에 영향을 주는 요소들을 시험하였다.

Nylon의 산화반응은 질소원자에 인접해 있는 methylene group에서 일어나 free-radical이 만들어 진다는 메카니즘을 논의 하였다.

Introduction

Relatively few detailed studies has been published on the chemical methods using ceric salts¹⁾, potassium permanganate and

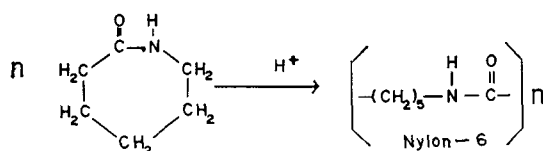
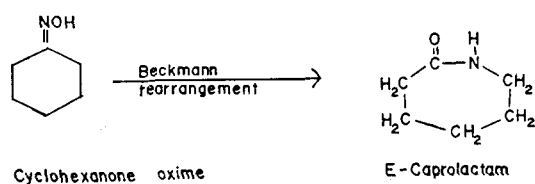
potassium persulfate²⁾ as initiators, although grafting initiated by high-energy radiation has been achieved with a number of common monomers, including acrylic acid³⁾, acrylamide⁴⁾, acrylonitrile⁵⁾, styrene⁵⁾, 4-vinylpyridine⁴⁾, vinyl acetate⁵⁾, and N-vinylpyr-

rolidone⁶⁾.

There is little published information on the oxidation of nylon by a free-radical mechanism, but it appears that primary attack occurs principally at the methylene group adjacent to the amide nitrogen atom with hydrogen peroxide⁷⁾ and potassium persulfate⁸⁾.

The polyamide selected for this work was nylon 6 fabric produced by acid-catalyzed polymerization of ϵ -caprolactam, which, in turn, is prepared by the Beckmann rearrangement of cyclohexanone oxime.

The method of the preparation of nylon 6 is as follows.



Acrylic acid diffuses and polymerizes easily into the nylon and as a result forms grafts composed of long polymeric chains.

In radiation-grafting, acrylic acid was grafted to nylon fabric by the direct radiation grafting technique⁹⁾ where the fabric is irradiated while swollen in monomer, the molecular weight of the polyacrylic acid in the graft product was determined by viscosity of an aqueous solution of sodium salt¹⁰⁾.

In this work a possible mechanism for the oxidation of nylon, initiated by ceric salts, has been studied and the distribution of molecular weight of the grafted polyacrylic

acid, initiated by radiation, has also been investigated.

The factors affecting graft polymerization of acrylic acid onto nylon, initiated by ceric salts, have also been considered.

Experimental

1. Materials

Nylon fabric was purified by treating with a mixture of 1% solution of sodium carbonate and 3% solution of sodium-dodecyl benzene sulfonate at 80°C for 2–3 hrs.

And it was treated with solution (0.5g/l) of sulfuric acid at 70°C for 40min. and treated with 1% solution of sodium thiosulfate and then washed thoroughly with distilled water.

Acrylic acid monomer was purified in the usual manner¹¹⁾ by distilling under vacuum (20mmHg, 56°C) and used immediately after distilling or stored at -10°C.

Ceric ammonium sulfate, ferrous ammonium sulfate, ferrous ammonium sulfate, propionic acid, perchloric acid, formic acid, sulfuric acid, sodium carbonate, calcium chloride, phenol, calcium hypochlorite, sodium thiosulfate, acetic acid, sodium hydroxide, and hydrochloric acid were reagent grade.

2. Preparation of Samples

Purified nylon fabric was cut into strips 4×8cm, and weighed exactly.

In radiation-grafting, the sample fabric was immersed in an aqueous solution of acrylic acid at room temperature.

The immersed fabric was irradiated with γ -rays from Co-60.

Control of the amount of acrylic acid grafted was achieved by adjustment of the

concentration of acrylic acid or the radiation dosage.

In the chemically-initiated grafting, the sample fabric was treated with a solution of acrylic acid in dilute mineral acid containing ceric ammonium sulfate, and all graft polymerizations and oxidations were carried out in stoppered flasks, which were immersed in a thermostat away from direct sunlight and shaken periodically.

The solutions were not de-aerated.

3. Irradiation

The irradiation was carried out in a Gamma-cell, an 25,000 Curie Co-60 irradiation facility, located at Korea Atomic Energy Research Institute.

The total irradiation dose of a sample was regulated by controlling the total exposure time.

All experiments were conducted in air.

Details of a similar irradiation facility are described elsewhere¹²⁾.

4. Determination of Graft Percentage

In radiation-grafting, the irradiated samples were soaked in 0.1% solution of sodium hydroxide to extract the homopolyacrylic acid formed on the surface of the fabric, and then extracted continuously in the same concentration of sodium hydroxide at 100°C.

The extracted product was converted to the free acid form from the sodium salt by heating at 90°C with 5% solution of acetic acid, and washed with distilled water, and dried at 105°C.

In the chemically-initiated grafting, the product was washed with cold water, steeped in 1-N sulfuric acid for 30 min., and again washed with distilled water.

And the product was then steeped in dilute

solution of ammonia for 30min., again washed with water, and dried at 105°C, and weighed to determine the extent of grafting.

The weight increase after treatment was taken to be weight of polyacrylic acid grafted to the nylon.

The per cent of grafting was calculated as follows.

$$\% \text{ grafting} = \frac{\text{bone dry weight of grafted product} - \text{bone dry weight of original nylon}}{\text{bone dry weight of original nylon}} \times 100$$

5. Molecular Weight Measurements

The molecular weight of polyacrylic acid was determined by viscometry in sodium hydroxide solution¹⁰⁾ in a Cannon-Fenske viscometer at 25°C.

The weight-average molecular-weight was estimated from the intrinsic viscosity by use of the equation $[\eta] = KM^\alpha$, the constants $K = 4.22 \times 10^{-4}$ and $\alpha = 0.64$ recommended by Immergut¹³⁾.

6. Separation of Acrylic Acid Homopolymer

A 1g sample was placed in a glass-stoppered Erlenmeyer flask and 50g of 85% formic acid added. After the sample was dissolved completely, 50ml of water was added dropwise to the solution from a buret. The solution was stirred with a magnetic stirrer during addition of the precipitant.

The final mixture was allowed to stand overnight at room temperature to accomplish complete precipitation of the nylon homopolymer and the N-AA graft copolymer. The precipitate was collected by filtration, washed free of acid, dried at 80°C and weighed.

The polyacrylic acid homopolymer content

of the sample was calculated from the difference in weight between the final precipitate and original sample.

7. Separation of Ungrafted Homopolymer and Graft Copolymer

A 6g sample was added to 200ml of 10% Na_2CO_3 solution and heated at 90°C for 15min. After washing free of carbonate ion with distilled water, the sample was heated at 90°C for 15min. in 10% calcium chloride solution.

The sample in the form of the calcium salt was washed free of chloride ion and dried at 50°C . The sample was then combined with 30ml of phenol at 80°C and stirred for 15min.

The mixture was filtered through coarse fritted glass.

Extraction of the residue with fresh 30ml portions of phenol was repeated until a drop of the phenol extract no longer formed a precipitate when added to 10ml of acetone.

The combined phenol extracts were added to a volume of acetone equal to ten times the volume of the extract. After precipitation was complete, the residue was collected by filtration and washed free of phenol with acetone.

The nylon homopolymer content of the original sample was calculated from the weight of the phenol-soluble fraction.

The phenol-insoluble residue (graft copolymer) was washed free of phenol with acetone and converted to the free acid form from the calcium salt by heating at 90°C with 200ml of acetic acid solution.

After washing free of excess acid with water, the product was dried to constant weight at room temperature in a vacuum desiccator. The graft copolymer content of the original sample was calculated from the

weight of this fraction.

8. Separation of Polyacrylic Acid Branches from Nylon Backbone of Graft Copolymer

An amount of graft copolymer heated with concentrated hydrochloric acid in an evacuated sealed tube for a period of 20–24 hr.

After cooling to room temperature, the sample was diluted with water and placed in a cellophane dialysis tube. The sample was dialyzed for a period of 4 days in a stream of distilled water.

The contents of the tube were transferred to a titration flask and titrated with standard NaOH as a phenol-phthaleine indicator. The amount of polyacrylic acid present was calculated from this titration.

The sample was then evaporated to a volume of about 5ml and 40ml of 4N NaOH added. The final solution was used for viscosity measurements to determine the molecular weight of the polyacrylic acid.

Results and Discussion

1. Graft Polymerization of Acrylic Acid

The relation between the amount of acrylic acid grafted on nylon fabric and the concentration of acrylic acid at room temperature is shown in Figure 1.

(A) in Figure 1 was the case when the sample fabric immersed in acrylic acid solution was irradiated with γ -rays from Co-60 at a dose of 6 Mrad.

(B) in Figure 1 was the case when the fabric was treated with a mixture of acrylic acid and ceric ammonium sulfate at room temperature.

In radiation-grafting, the per cent of grafting increases almost linearly with in-

creasing concentrations of monomer. This can be attributed to the fact at higher levels of grafting the reaction becomes diffusion controlled.

It was reported by Magat and Zimmerman³⁾ that measurements of the diffusion coefficient of diffusion of aqueous acrylic acid into nylon have yielded a value of $D=5 \times 10^{-9}$ cm²/sec. at room temperature with an activation energy of diffusion of 7.5 Kcal., corresponding to a temperature coefficient of 1.5 for every 10°C increase in temperature.

Diffusion rates are somewhat concentration dependent, faster penetration being observed at higher bath concentrations.

In the chemically-initiated grafting, treatment of nylon fabric with acrylic acid (5–30%) and ceric ammonium sulfate (0.01–N CAS in 1–N H₂SO₄) produced a non-linear increase in the yield of grafted polymer with increasing concentrations of mono-

mer.

The non-linearity is attributed to restricted swelling, and hence limited accessibility, of the nylon at low monomer concentrations. The reason for the low yields of grafted polymer at high concentrations of acrylic acid is not known exactly, but it is not due to slower oxidation of nylon.

It is supported by observing that the concentration of ceric ions consumed in 2 hrs. at 50°C by nylon fabric in aqueous propionic acid increases with propionic acid concentration over the range of 0–20% (Table 2).

And also it is supported by observing the curves for the oxidation of nylon fabric with a 0.05–N mineral acid at 50°C (Fig. 5).

It is thought that the reason for the decrease in grafting beyond an optimum concentration of acrylic acid is possibly caused by the degradation of nylon substrate or the polyacrylic acid homopolymer formed on the surface of the fabric in the range of high concentration of acrylic acid.

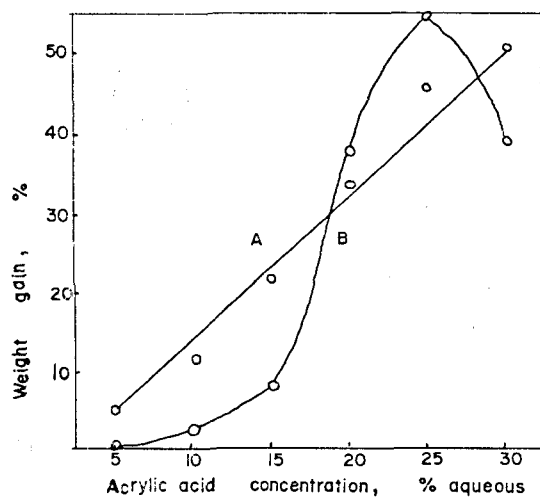
2. Molecular Weight of Grafted Polyacrylic Acid

The separation scheme of grafted polyacrylic acid is outlined in Figure 2.

The polyacrylic acid homopolymer fraction is separated by solution of the graft in 85% formic acid and precipitation of the ungrafted nylon and graft copolymer by addition of water.

The polyacrylic acid homopolymer fraction remains in solution.

The precipitation curves of nylon and nylon-acrylic acid grafts from formic acid solution are shown in Figure 3. Curve 1 in Figure 3 is the precipitation curve for nylon in formic acid-water mixtures in the absence of polyacrylic acid.



- A = irradiated (6 Mrad) with γ -rays from Co-60 at room temp.
- B = Grafted onto nylon 6 with ceric salt as initiator (at room temp).

Fig. 1. Effect of initiators on grafting of acrylic acid at room temp.

At a solvent composition of 25% water, nylon is completely soluble, but as the water content is increased to 34%, precipitation becomes 99% complete.

This shows that nylon and polyacrylic acid solution can be separated by precipitation of the nylon. The nylon precipitates quantitatively, leaving the polyacrylic acid in solution.

It is interesting to note that this separation is accomplished if the coagulant is added to polymer solution and not if the polymer solution is added to the coagulant.

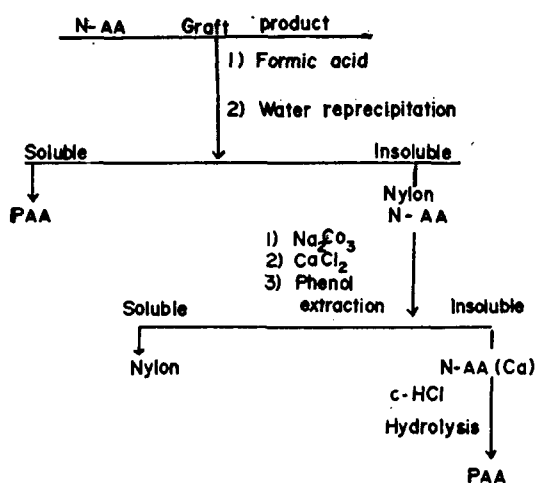


Fig. 2. Separation scheme

If nylon and polyacrylic acid in 85% formic acid is poured into water with rapid stirring, the polyacrylic acid is almost quantitatively coprecipitated with nylon.

Coprecipitation can usually be avoided by slow addition of the coagulant to the polymer solution.

Precipitation occurs by a process of nucleation and aggregation of the insoluble phase which precipitates in essentially pure form, leaving the soluble materials in solution.

Curve 2 in Figure 3 is the precipitation curve for a sample of N-AA based on a 18%

polyacrylic acid graft.

It is seen that at a solvent composition of 34% water, which gives 99% precipitation with nylon, less than 1% of the N-AA graft is precipitated. On further addition of water a single fraction precipitates.

It was thought that nylon could be separated from the graft by control of the amount of water added as coagulant.

When a mixture of nylon and N-AA graft is dissolved in formic acid, the two components coprecipitate according to curve 3, indicating that no separation can be achieved by this method.

A more effective way of separating the ungrafted nylon from the graft is performed by treating the mixture with calcium chloride. The calcium salt of the graft is insoluble in phenol at 80°C, while the ungrafted nylon is extracted.

The per cent of polyacrylic acid in the graft is obtained from the weight gain of the nylon on grafting.

The polyacrylic acid portion of the graft is hydrolyzed away from the nylon by treatment with concentrated HCl at 100°C.

The hydrolysis products are removed by dialysis, and the weight-average molecular weight of the polyacrylic acid is determined by viscosity of an aqueous solution of its sodium salt¹⁰⁾.

The results are shown in Table 1.

(a) in Table 1 was the case when the sample fabric was soaked in 15% acrylic acid solution at room temperature and then irradiated at room temperature (5.3 Mrad).

(b) in Table 1 was the case when the sample fabric was soaked in 15% acrylic acid solution at room temperature, cooled to -184°C and irradiated (5.3 Mrad), then allowed to warm to room temperatures.

The number-average molecular weight re-

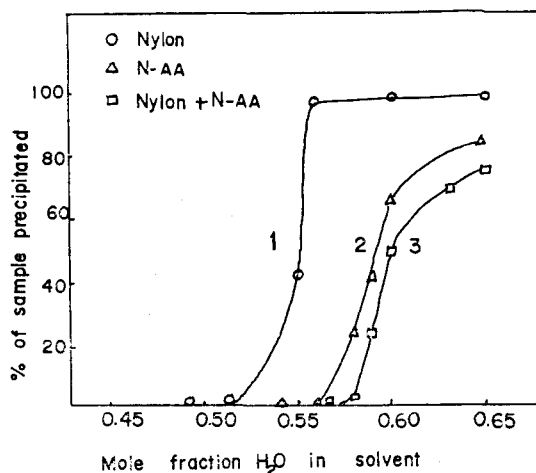


Fig. 3. Precipitation of nylon and nylon-acrylic acid grafts from formic acid solution

ported by Zimmerman³⁾ was used to investigate the molecular weight distribution of the polyacrylic acid.

The fact showing higher ratio of M_w to M_n in room temp. than that in low temperature reflects a broader molecular weight distribution.

This can be accounted for radicals trapped in extreme low temperature during the preparation of N-AA by the one-step grafting process.

If the irradiation is carried out at -184°C on nylon presoaked in acrylic acid at room temperature, very little branching of polyacrylic acid is obtained. The ratio of weight-average to number-average molecular weight in this instance was 1.5.

3. Effect of Mineral Acid-Ceric Salt Combination

The extent of grafting onto nylon depends not only on the concentrations of ceric salt and mineral acid but also on the particular combination of ceric salt and acid employed.

The results for three combinations, over a

range of monomer concentrations, are shown in Figure 4.

(A) of Figure 4 was the case when nylon fabric was treated for 1 hr. at 50°C with acrylic acid (5–30%) in 0.01-N ceric ammonium sulfate (CAS) in 1-N sulfuric acid.

(B) of Figure 4 was the case when the fabric was treated with acrylic acid in 1-N perchloric acid under the same condition.

The yields of grafted polymers increased with rise in the acrylic acid concentrations up to 25%, then fell sharply.

Table 1. Molecular weight

Sample No.	Weight gain (%)	Mol. wt. of grafted polyacrylic acid		
		\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
1 ^{a)}	17	31,700	14,000 ^{c)}	2.3
2 ^{b)}	12	19,300	13,000 ^{c)}	1.5

- a) Soaked in 15% acrylic acid solution at room temp. and irradiated at room temp. (5.3 Mrad)
 b) Soaked in 15% acrylic acid solution at room temp., cooled to -184°C and irradiated (5.3 Mrad), then allowed to warm to room temp.
 c) Data reported by Zimmerman

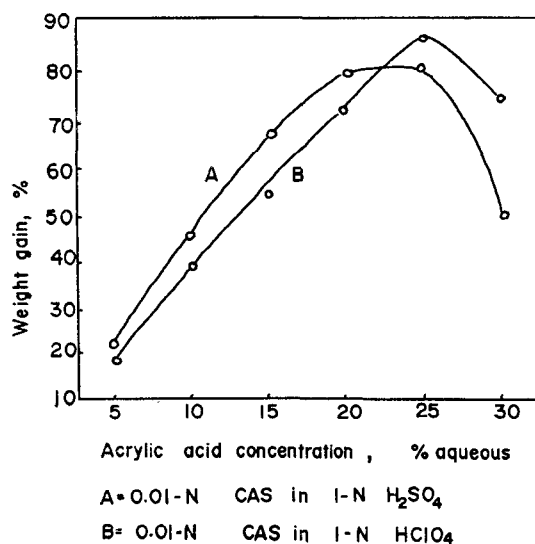


Fig. 4. Effect of initiators on grafting acrylic acid at 50°C for 1 hr

Table 2. Effect of propionic acid on the oxidation and grafting of nylon by ceric salts

Propionic acid conc. (%)	Ce ⁴⁺ consumed with the oxidation and grafting (Normality × 10 ³)		Ce ⁴⁺ consumed with the oxidation (Normality × 10 ³)		Ce ⁴⁺ consumed with grafting (Normality × 10 ³)	
	CAS/H ₂ SO ₄	CAS/HClO ₄	CAS/HClO ₄	CAS/HClO ₄	CAS/H ₂ SO ₄	CAS/HClO ₄
0	3.44	4.67	3.1	3.65	2.44	1.02
5	3.67	4.80	1.69	4.45	1.98	0.33
10	4.34	4.89	2.64	4.73	1.70	0.16
20	4.67	4.93	3.08	4.86	1.59	0.07

Ceric salt concentration: 0.005-N

Mineral acid concentration: 0.5-N

Acrylic acid concentration: 5%

It is thought that the reason for the low yield of grafted polymer in the range of high concentration of acrylic acid is possibly caused by the degradation of nylon substrate or the polyacrylic acid homopolymer as already mentioned in Figure 1.

No thermally-initiated graft polymerization occurred at 50°C in the absence of ceric salt.

4. Effect of Propionic Acid on Grafting

Nylon fabric was treated for 2 hrs. at

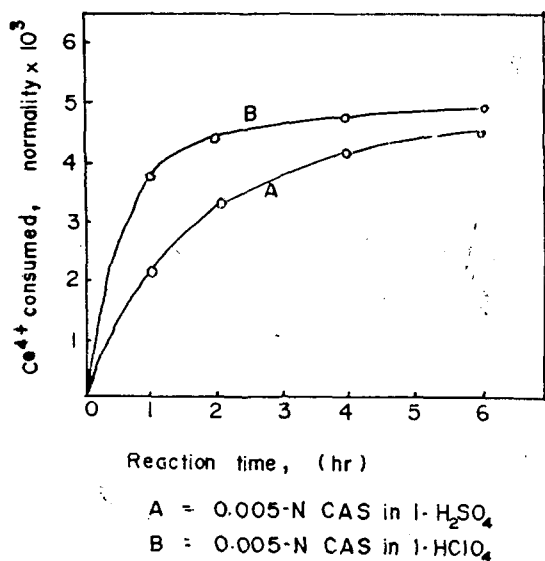


Fig. 5. Oxidation of nylon at 50°C with different ceric salts

50°C with acrylic acid (5%) in 0.01-N ceric ammonium sulfate(CAS) in 0.5-N mineral acids.

Propionic acid was added to the system to investigate the effect on either of oxidation and grafting of nylon.

The results are shown in Table 2.

It is seen that the concentration of ceric ions consumed in grafting followed by oxidation increases with increasing propionic acid concentration over the range of 0–20%. A possible amount of propionic acid oxidized in control runs was negligible.

By considering the amounts of ceric ions consumed, it is found that nylon is oxidized by solutions of ceric salts in dilute mineral acid at a rate depending on the particular acid added, and that the rate can be increased by the addition of propionic acid.

5. Mechanism of Oxidation

The curves for oxidation of nylon fabric with 0.005-N solutions of ceric salts in 1-N mineral acids (Figure 5), in conjunction with the results for oxidations in the presence of propionic acid (Table 2), strongly suggest that attack by ceric salts cannot be attributed solely to oxidation of terminal amino groups.

Thus, the amount of ceric ions consumed in

sulfuric acid or perchloric acid for 2 hrs. in oxidation process was fully equivalent to the amount required for complete conversion of accessible basic and-groups to carboxyl groups.

By considering the amounts of ceric ions consumed, it is assumed that nylon is oxidized by ceric ions, and that further oxidation of aldehyde to carboxyl end-groups may involve a free-radical intermediate, and initiation of graft polymerization could occur at either of the free-radical stages.

Although our results form an insufficient basis for detailed conclusions regarding the mechanism of oxidation, those are in keeping with the report of Haworth¹⁾ who suggested that initial attack could take place at the methylene group attached to nitrogen to give a free radical.

Webb⁷⁾ and Needles⁸⁾ have shown that primary attack occurs principally at the methylene group adjacent to the amide nitrogen atom with hydrogen peroxide or potassium persulfate, and that the terminal carboxyl groups should also resist oxidation, which must therefore occur mainly at the

amide links.

In the light of these and our own findings it is proposed that the mechanism of oxidation by ceric ions proceeds in a manner similiar to those found by Haworth et al.¹⁾ The diagram of the mechanism of oxidation is shown in Figure 6.

Conclusions

Acrylic acid has been grafted onto polyamide in the form of nylon cloth with ionizing radiation and ceric salts as initiators.

Acrylic acid is probably strongly sorbed from its aqueous solutions by nylon fabric and the resulting high concentration of monomer in the fabric will favour rapid polymerization.

In radiation-grafting, the per cent of the grafting increases almost linearly with the increase of monomer concentration, but in chemically initiated grafting, the yields of grafted polymer show a non-linearity.

When a mixture of nylon and nylon-acrylic acid graft is dissolved in formic acid, no separation can be achieved.

And so a effective way of separating the ungrafted nylon from the graft is performed by treating the mixture with calcium chloride.

It was found in radiation-grafting that the difference in polymerization temperature affected very markedly on the molecular weight distribution.

Addition of propionic acid at a given monomer concentration facilitated the oxidation of nylon.

Our results represent a step towards elucidation of the mechanism of the reactions between polyamides and ceric salts that are responsible for initiating graft polymerization

Although there are a few reports of amides

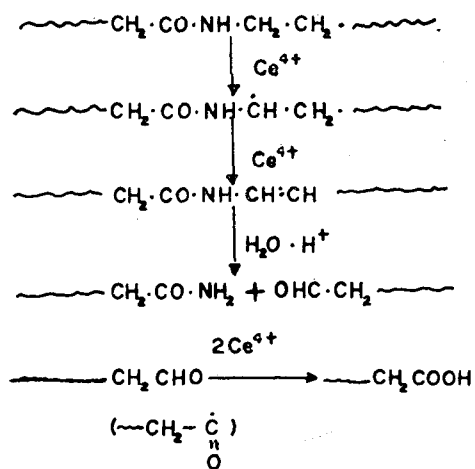


Fig. 6. Mechanism of oxidation

being oxidized by ceric salts, analogy with their oxidation by persulfate favours attack at the methylene group adjacent to amide nitrogen.

The radical thus formed would then initiate polymerization or undergo further oxidation to an enamide, followed by hydrolytic chain-fission to primary amide and aldehyde end-groups.

Oxidation of the aldehyde, again by a free-radical mechanism, would finally yield carboxyl end-groups.

References

- 1) Susan Haworth and J.R. Holker, *J. Soc. Dyers Colourists*, 82(7), 257-4 (1966)
- 2) Sakurada, I., and Sakaguchi, Y., *Sen-i, Gakkaishi*, 20, 613 (1964)
- 3) Nagat, E.E., and Zimmerman, J., *J. Polymer Sci.*, Part C, No. 4, pp. 615-629 (1963)
- 4) Sykes, J.A.W., and Thomas, J.K., *J. Polymer Sci.*, 55, 721 (1961)
- 5) Armstrong, A.A., and Rutherford, H.A., *Text. Research J.*, 33, 264 (1963)
- 6) Levine, C.A., and Traylor, T.G., *J. Applied Polymer Sci.*, 5, 606 (1961)
- 7) Webb, M.W., and Swallow, J.E., *J. Applied Polymer Sci.*, 8, 2067 (1964)
- 8) Needles, H.L., and Whitfield R.E., *J. Org. Chem.*, 29, 3632 (1964)
- 9) Chapiro, A., *Radiation Chemistry of Polymer Systems*, New York. Interscience, pp. 596-691 (1962)
- 10) Kawaga, I., and R. M. Fuoss, *J. Polymer Sci.*, Vol. 18, pp. 535-542 (1955)
- 11) R. Y. M. Huang, and B. Immergut, *J. Polymer Sci.*, Part A, Vol. 1, pp. 1257-1297 (1963)
- 12) Rice, F.G., *Ind. Eng. Chem.*, 52, 5, 52A (1960)
- 13) J. Brandrup and E.H. Immergut, *Polymer Hand Book*, W-pp. 21 (1963)