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Radiation-Induced Impregnation Grafting of Acrylic Acid onto Polyester Fibers

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When polyester fiber is impregnated with pure acrylic acid (AA) or AA-water and irradiated with γ-rays from a Co-60 source or electron beam from a Van de Graaff accelerater at room temperature almost all impregnated monomer is converted to unextractable PAA, it is to say apparently grafted. However, the degree of apparent graft is several percent, which is too low, since according to our previous experiments about 15% apparent graft is desirable to make polyester fiber so hydrophilic as cotton.

When pre-swelling with a suitable liquid is carried out and the impregnated liquid is replaced with AA or AA-water twice larger of AA can be impregnated and converted to unextractable PAA by irradiation. Chlorinated hydrocarbons such as ethylene dichloride and 1,1,2,2,-tetrachloroethylene are found to be more suitable as pre-swelling agent than conventional swelling agents such as benzyl alcohol, dimethyl formamide dimethyl sulfoxide or nitrobenzene.

When fibers with some additional AA besides really impregnated AA was irradiated in the presence of Mohr's salt after appropriate pre-swelling, apparent graft higher than 20% can be easily realized at room temperature with high monomer-utilization.

I. INTRODUCTION

We have studied hydrophilization of polyester fibers by radiation-induced grafting of acrylic acid.[1,2] It was found that sodium salts of the acrylic acid graft fibers having 10 to 20% apparent graft (weight increase based on the weight of original fiber) showed nearly the same moisture regain as cotton fibers.[2] There is difficulty owing to useless formation of homopolymer in the conventional grafting process.

When polyester fibers are immersed in an aqueous solution of acrylic acid and irradiated with γ-rays, grafting of acrylic acid takes place usually accompanied by the formation of a large amount of the homopolymer in the liquid phase outside of the fibers. Although an addition of ferrous sulfate to the aqueous solution is very effective to suppress such useless formation of homopolymer,[3,4] it is very difficult to inhibit totally the formation of homopolymer in the grafting of acrylic acid.

Therefore, studies on impregnation grafting method is taken up. Polyester fibers are immersed either in acrylic acid or its aqueous solution, taken out from immersion liquid, freed from acrylic acid outside of the fibers and then subjected to irradiation up to complete polymerization of the monomer impregnated. The fibers are subjected finally to a conventional extraction with hot water. Unless all acrylic acid polymerized inside of the fibers are not extracted off, the whole monomer is not "truely graft-polymerized" but "apparently graft-polymerized" and the purpose of our impregnation grafting is accomplished.

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As a degree of apparent graft of 10 to 20% is required for making the fibers hydrophilic, the fiber should be impregnated with said amount of acrylic acid in aid of an appropriate swelling agent prior to irradiation.

The present study has been performed to know how and in what extent the above expectation is realized.

II. EXPERIMENTAL PROCEDURES AND RESULTS

1. Samples and Reagents

Polyester fibers used were commercially available filaments (75 deniers/30 filaments) containing 0.5% of TiO_2 as a delusting agent. The fibers were washed with 0.5% aqueous solutions of a nonionic detergent and sodium bicarbonate, respectively at 80°C for 1 hour and washed repeatedly with distilled water at 80°C.

Acrylic acid was purified by a conventional distillation procedure at a reduced pressure. Ethylene dichloride and other solvents employed as swelling agents were of reagent-grade and used without further purification.

2. Impregnation Grafting of Acrylic Acid to Polyester Fibers without Pretreatment

Impregnation grafting has been carried out using either pure acrylic acid or binary mixtures of acrylic acid and water without any pretreatment with swelling agent. The results are shown in Table I.

The amounts of impregnated liquid in the fibers *i.e.* the pick up, A in % are also shown in Table I. A's are 7 to 8% for pure acrylic acid and 10 to 12% for mixtures of 7/3 and 6/4, respectively.

The fibers impregnated were placed in a test tube of 1 cm inside-diameter, flushed with nitrogen gas for 2 minutes and irradiated with γ-rays at 3.2×10^5 Mrad/hr from a Co-60

Table I. Impregnation Grafting of Acrylic Acid onto Polyester Fiber
Impregnation: 22°C, 16 hr.
Irradiation: γ-rays, 0.32 Mrad/hr, 7.5 Mrad, 22°C.

AA/H_2O by vol.	Pick up[a], %, A	Weight increase %, C	Apparent graft %, D[b]	Apparent graft %, E[c]	C[d] $\frac{A\times f}{\times 100}$	D[d] $\frac{A\times f}{\times 100}$	E[d] $\frac{A\times f}{\times 100}$	Dyeing test,[e] Rating
10/0	7.0	1.8	1.7	1.4	25.7	24.3	20.0	V
〃	7.6	2.0	1.6	1.6	26.3	21.0	21.1	V
〃	7.9	4.6	3.9	3.8	58.2	49.4	48.1	III
7/3	10.3	3.6	3.4	3.2	49.9	47.2	44.4	V
〃	11.7	4.2	4.0	3.7	51.3	48.8	45.2	V
〃	9.5	3.2	3.1	3.0	48.1	46.6	45.2	V
6/4	10.9	5.2	5.0	4.8	73.3	70.5	67.7	IV
〃	10.6	5.5	5.2	5.1	80.3	75.9	74.5	IV

a) Pick up of acrylic acid or acrylic acid water mixture
b) After extraction with hot water
c) After extraction with hot 1% $NaHCO_3$ solution
d) For AA/H_2O=10/0, 7/3 and 6/4, f=1, 0.71 and 0.65, respectively
e) I: excellent, II: good, III: fair, IV: poor, V: very poor

source of 2,000 Ci at 22°C to a dose of 7.5 Mrad. Because other experiments exhibited that above dose is enongh to polymerize totally acrylic acid in bulk or in a queous solution. The irradiated fibers were dried in a vacuum oven at 75°C for 20 hours to remove unreacted acrylic acid and water, and the weight increase, C in % due to the monomer polymerized on the fibers was determined. The percentage of acrylic acid recovered is expressed by the equation, $C/A \times f$, where f is weight fraction of acrylic acid in impregnating liquid which is determined with a titration-method using alkali-solution. The values of f for the pure acrylic acid and 7/3 and 6/4 mixtures were 1.0, 0.71 and 0.65, respectively. The values of $C/A \times f$ were not greater than 58% for pure acrylic acid, and 80% for the most favourable cases of the 6/4 mixture. The irradiated fibers were washed with water at 80°C for 2 hours and the weight increase of the fibers due to polyacrylic acid unextractable with hot water was defined as degree of apparent graft, D in %. Only a small amount of polyacrylic acid was extracted with water at 80°C, particularly in the case of fibers impregnated with the 6/4 mixture. The percentage of monomer-utilization, $D/A \times f \times 100$ was found to be 70 and 76%.

As previously reported,[1] acrylic acid homopolymer formed on the surface of the fibers or in the space between fibers is readily washed out with 1% aqueous solution of sodium bicarbonate, though it is not easily with hot water. For the present grafting method acrylic acid polymer, an apparent graft, D is expected to be inside of the fibers. To ascertain this expectation the graft fibers were treated with 1% aqueous solution of sodium bicarbonate at 80°C for 2 hours and washed with water followed by treatment with 2% aqueous solution of acetic acid at room temperature to recover acid-form of the grafts. The treatment with the bicarbonate solution is called "alkali-treatment" hereafter.

The degree of apparent graft after alkali-treatment is expressed by E and shown in Table I. As seen in the table, only a very slight weight change in grafts was brought about with alkali-treatment. The observation is in agreement with the results in the previous report that acrylic acid polymerized in drawn partially crystalline polyester fibers was not readily extracted with a conventional extraction procedure.

Tests were also carried out to dye the grafts after alkali-treatment with cationic dyestuff, Sevron Brilliant Red B. The dyeing condition is as follows:

Sevron Brilliant Red B	2% owf
Sodium sulfate	10% owf
Acetic acid	0.3% owf,

weight ratio of fibers to the volume of dyeing solution is 1 : 100 and dyeing was performed at 98°C for 2 hours. Dyeing features were estimated with naked eyes as numerical ratings from I to V, I being very poor and V homogeneous dyeing to deep color. Ratings are also shown in Table I. The graft fibers with an apparent graft less than 5% show poor dyeing results. In the Table I it is also seen that the amount of acrylic acid impregnated in the fibers is very small by this procedure where no particular swelling agent was used. The degree of apparent graft is less than 6% and the monomer-utilization for apparent graft is not high enough.

3. Impregnation Grafting of Acrylic Acid after Pretreatment with Various Swelling Agents

It is expected that the impregnation process of acrylic acid is more effective to polyester

Table II. Impregnation Grafting of Acrylic Acid onto Polyester Fiber after Pretreatment with Various Swelling Agents.
Pretreatment: 70°C, 1 hr
Impregnation: 7/3 AA-water mixture 25°C, 16 hr.
Irradiation: γ-rays, 0.32 Mrad/hr, 7.5 Mrad 24°C.

Swelling agent	Deg. of swelling %	Pick up %, A	Weight increase %, C	Apparent graft %, D	Apparent graft %, E	C $\frac{A\times0.7}{\times100}$	D $\frac{A\times0.7}{\times100}$	E $\frac{A\times0.7}{\times100}$	Dyeing test, Rating
Benzyl alcohol	20.0	15.5	9.5	8.0	6.9	87.6	73.5	63.6	II–III
Dimethyl formamide	19.9	16.1	8.9	7.6	6.2	78.8	67.3	54.9	II–III
Dimethyl sulfoxide	17.6	15.7	3.9	4.1	4.0	35.5	37.3	36.4	III–IV
Ethylene dichloride	16.5	16.6	11.1	10.3	9.5	95.7	88.8	81.9	I
Nitrobenzene	15.1	20.9	10.3	8.7	6.8	70.5	59.6	46.6	II

fibers which have been subjected to pretreatment with an appropriate swelling agent. However, it cannot be expected that the better swelling agents always result higher grafting (in the present case, "matrix-polymerization" in fibers).

For the present purpose, acrylic acid should be polymerized inside of the fiber-matrix to form polymers of higher molecular weight, which are entangled tightly with each other and with polyester molecules of the matrix so that they cannot be extracted with hot water.

Grafting to the fibers pretreated with various swelling agents was carried out with the following procedure: polyester fibers immersed in a selected swelling agent at 70°C for 1 hour subjected to centrifugation of 5,000 rpm for 10 minutes to remove excess liquid and weighed to determined the degree of swelling. The fibers pretreated with a swelling agent were then immersed in the 7/3 mixture of acrylic acid and water at 25°C for 16 hours to replace the swelling agent with the mixture, followed by the irradiation as described in the preceding paragraph. The results are shown in Table II. From the table it can be seen that the swelling agent having a strong swelling power is not always suitable for conducting the grafting. Ethylene dichloride which does not show the strongest swelling power among the swelling agents tested is most favourable for the grafting with regard to the amount of grafting and monomer-utilization. Dimethyl sulfoxide is a better swelling agent than ethylene dichloride to polyester, but the degree of apparent grafting is only 4%. Benzyl alcohol and dimethyl formamide are also stronger in swelling power than ethylene dichloride, but they show lower apparent graft, lower monomer-utilization and poorer dyeability, compared with ethylene dichloride.

4. Impregnation Grafting after Pretreatment with Ethylene Dichloride

Grafting was carried out using ethylene dichloride as a swelling agent in some details. The results are shown in Table III.

The polyester fibers were swelled with ethylene dichloride and then impregnated with pure acrylic acid, 6/4 and 7/3 mixtures by replacing with ethylene dichloride. For monomer solution of different concentration percentages of pick up, A show nearly the same value of 17%. As weight increase, C after irradiation are also nearly the same for monomer solution of different concentrations, the amount of acrylic acid recovered on the fibers is the largest for 6/4 mixture. After irradiation acrylic acid homopolymer was

Table III. Impregnation Grafting of Acrylic Acid onto Polyester Fiber by Two-Step Methods
Pretreatment: ethylene dichloride, 70°C, 1 hr; pick up of ethylene dichloride 16–18%.
Impregnation: AA or AA-water mixture 22°C, 16 hr.
Irradiation: 0.32 Mrad/hr, 7.5 Mrad, 22°C.

AA/H_2O by vol.	Pick up %, A	Weight increase %, C	Apparent graft %, D	Apparent graft %, E	C $\frac{A\times f}{\times 100}$	D $\frac{A\times f}{\times 100}$	E $\frac{A\times f}{\times 100}$	Dyeing test, Rating
10/0	17.0	13.8	10.2	8.2	81.2	60.0	48.2	I
〃	16.3	11.9	10.0	7.4	73.0	61.3	45.3	I
〃	17.4	11.9	9.8	7.0	68.4	56.3	40.2	I
7/3	16.3	10.6	9.4	9.4	91.4	81.0	81.0	II
〃	16.8	11.3	10.2	10.2	95.0	85.7	85.7	I
〃	16.8	11.3	11.2	7.9	95.0	94.1	66.4	I
6/4	15.4	9.4	8.6	8.4	95.9	87.7	85.7	II
〃	18.0	11.6	10.8	9.3	100	93.1	80.0	I
〃	17.8	11.6	10.5	9.1	102	92.1	80.0	I

For AA/H_2O=10/0, 7/3 and 6/4, f=1.0, 0.71 and 0.64.

extracted with hot water and further with alkali. The higher the content of acrylic acid the larger the amount of homopolymer is. As the acrylic acid polymerized inside of the fibers in the presence of water has very high molecular weight[3] and the extent of entanglement becomes considerable for the polymer molecules of higher molecular weight, only small amount of acrylic acid polymer is extracted. The fibers of 9 to 10% apparent graft are produced with monomer-utilization of above 80% even after alkali-treatment. The graft fibers are readily and homogeneously dyed with cationic dyestuff.

The results shown in Table IV were obtained with 6/4 mixture by irradiation of electron beams from a Van de Graaff accelerator in place of γ-rays. Weight increase, C above 7% is obtained at a dose of above 2 Mrad. Acrylic acid recovered on the fibers is 94% based on the weight of impregnated amount of 6 Mrad and the degrees of apparent graft are 10

Table IV. Impregnation Grafting of Acrylic Acid onto Polyester Fiber by Irradiation with Electron Beams.
Pretreatment: ethylene dichloride, 70°C, 1 hr; pick up of ethylene dichloride 16–18%.
Impregnation: 6/4 AA-water mixture 22°C, 16 hr.
Irradiation: V.d.G. electrons, 1.5 MeV, 50 μA, 0.5 Mrad/hr, 25°C.

Pick up %, A	Dose Mrad	Weight increase %, C	Apparent graft %, D	Apparent graft %, E	C $\frac{A\times f}{\times 100}$	D $\frac{A\times f}{\times 100}$	E $\frac{A\times f}{\times 100}$	Dyeing test, Rating
16.3	1	6.1	4.9	5.1	58.5	47.1	48.8	III
17.1	〃	6.5	5.3	5.3	59.5	48.6	48.8	
17.9	2	9.0	8.0	5.7	78.6	69.6	49.8	II
15.7	〃	7.2	5.9	6.0	71.7	59.0	59.8	
17.7	4	9.4	8.6	7.8	83.0	76.1	68.8	I–II
16.8	〃	7.9	7.0	7.4	73.5	64.8	68.8	
16.3	6	9.8	8.9	8.0	93.8	85.6	76.7	I
18.5	〃	11.1	10.3	9.0	93.8	87.3	76.1	

f=0.64.

and 9% for the fibers after washing with hot water and alkali-treatment. Fibers of 8 to 9% apparent graft show satisfactory results of the dyeing test.

5. Impregnation Grafting after Pretreatment with Monomer Mixture Containing Mohr's Salt

Above experiments clearly show that the fibers with about 10% apparent graft are readily prepared, but it is difficult to prepared fibers with higher apparent graft such as 15 to 20% which is necessary to obtain hydrophilic fibers like cotton, since the amount of acrylic acid impregnated in the fibers limits the attainable degree of apparent graft.

To enhance the degree of apparent graft the following procedure was tried. After immersion in monomer solution, removing of the monomer solution are conducted so lightly that a small amount of the solution still remains between the fibers, and the fibers thus treated are irradiated for the grafting. If the polymerization outside of the fibers is either inhibited or retarded, additional amount of acrylic acid may diffuse into the fibers from the space between the fibers and sufficient amount of grafting can be attained.

From such a point of view a small amount of Mohr's salt was added to the monomer solution as an inhibiter and it was carried out by the following procedure. Fibers which had been impregnated with ethylene dichloride were immersed in acrylic acid-water mixture containing a small amount of Mohr's salt (5×10^{-3} mole/l), subjected to lightly squeezing between two pieces of filter paper and then irradiated for the grafting. The results are shown in Table V. By this procedure graft fibers of 15 to 20% apparent graft were readily obtained and exhibited excellent dyeability. It is remarkable that more homopolymer is dissolved by extraction with hot water and alkali when compared with experimental results in Table IV. This increase in the soluble homopolymer can be attributed at least partly to the decrease of molecular weight caused by the presence of Mohr's salt. Another series of experiments, details of which are omitted in this paper, showed that an addition of Mohr's salt reduced the molecular weight of acrylic acid polymer by 20 to 30 times.

Similar experiments were also carried out using electron beams from a Van de Graaff

Table V. Impregnation Grafting of Acrylic Acid onto Polyester Fiber by Two-Step Method with Excess Acrylic Acid.
Pretreatment: ethylene dichloride, 70°C, 1 hr; Pick up of ethylene dichloride 16–18%.
Impregnation: aqueous solution of acrylic acid containing Mohr's salt, 5×10^{-3} mole/1, 25°C, 16 hr.
Irradiation: γ-rays, 0.32 Mrad/hr, 7.5 Mrad, 22°C.

AA/H_2O by vol.	Pick up %, A	Weight increase %, C	Apparent graft %, D	Apparent graft %, E	C $\frac{A\times f}{\times 100}$	D $\frac{A\times f}{\times 100}$	E $\frac{A\times f}{\times 100}$	Dyeing test, Rating
9/1	33.6	28.6	15.8	11.4	94.6	52.2	37.7	I
〃	33.9	26.2	13.5	11.1	85.8	44.3	36.3	I
8/2	36.8	25.5	13.9	10.7	86.6	47.1	36.4	I
〃	41.3	32.5	23.4	15.6	98.4	70.8	47.3	I
7/3	35.0	23.2	21.0	15.7	94.7	85.7	64.1	I
〃	36.7	22 6	20.9	12.9	88.0	81.4	50.1	I
6/4	35.3	21.6	18.1	11.6	100	84.1	53.9	I
〃	32.0	20.7	16.5	13.8	106	84.4	70.7	I

For AA/H_2O=9/1, 8/2, 7/3 and 6/4, f=1.0, 0.90, 0.81, 0.72 and 0.63.

Table VI. Impregnation Grafting of Acrylic Acid onto Polyester Fiber by Irradiation with Electron Beams.
Pretreatment: ethylene dichloride, 70°C, 1 hr, pick up of ethylene dichloride 16–18%.
Impregnation: aqueous solution of acrylic acid containing Mohr's salt, 4×10^{-3} mole/l, 20°C, 4 hr.
Irradiation: V.d.G. electrons, 1.5 MeV, 50 μA, 0.5 Mrad/sec.

Pick up %, A	Dose Mrad	Weight increase %, C	Apparent graft %, D	Apparent graft %, E	C $\frac{A\times f}{\times 100}$	D $\frac{A\times f}{\times 100}$	E $\frac{A\times f}{\times 100}$	Dyeing test, Rating
52.4	1	32.8	25.7	24.8	94.8	74.3	71.6	I
48.6	〃	31.7	23.7	22.4	98.8	73.8	69.8	
53.2	2	36.3	28.4	28.5	104.0	80.9	81.2	I
42.6	〃	27.7	22.5	21.5	98.5	80.1	76.5	
44.1	4	29.4	24.8	22.9	100.0	85.2	78.0	I
46.3	〃	31.5	25.5	24.6	103.0	83.3	80.5	
50.6	5	31.9	25.8	24.2	95.6	77.3	72.5	I
51.0	〃	33.8	28.0	27.1	103.0	83.1	80.5	
53.9	6	28.7	27.8	26.2	94.5	78.1	73.6	I
46.3	〃	31.5	23.8	23.6	99.3	77.8	77.2	
f=0.66								
Without pretreatment								
32.4	3	10.8	4.8	0	55.6	24.7	—	III
36.8	6	18.3	15.8	1.1	82.9	71.5	5.0	III
219	3	58.1	22.1	14.3	44.2	16.8	10.9	I
211	6	73.0	35.7	25.6	57.7	28.2	20.2	I
f=0.60								

accelerator. The results are given in Table VI. Acrylic acid impregnated in the fibers was almost completely polymerized with a dose of 1 Mrad. Grafts above 25% were readily obtained with 70 to 80% monomer-utilization.

For comparison the fibers without ethylene dichloride pretreatment were subjected to grafting using monomer mixtures containing Mohr's salt. Fibers with weight increase less than 30% resulted in apparent graft of below 2%, whereas the fibers impregnated with a larger amount of monomer mixture such as 210 to 230% gave a considerable high value of apparent graft, but monomer-utilization was very low.

6. Swelling of Polyester Fibers with Various Chlorinated Hydrocarbons

The swelling power to polyester fibers was studied chlorinated hydrocarbons since ethylene dichloride was very suitable for promoting graft-polymerization to the fibers as explained in the preceding paragraph.

The fibers were immersed in chlorinated hydrocarbons at 30°C for 1 or 24 hours and at 70°C for 1 hour, subjected to centrifugation at 5,000 rpm for 10 minutes, and the weight of fibers was measured to determine the degree of swelling. The results are shown in Table VII. Mono-chlorobenzene and o-dichlorobenzene swelled polyester moderately at 70°C. Among chlorinated ethanes having the same number of chlorine atom or atoms the one of higher molecular symmetry exhibited strong swelling power. The degree of swelling

Table VII. Swelling of Polyester Fiber in Various Chlorinated Hydrocarbons.

Chlorinated hydrocarbon	b.p. °C	Degree of swelling at following temperature and time		
		30°C, 1 hr	30°C, 24 hr	70°C, 1 hr
Monochlorobenzene	132	0.5	3.0	14.9
o-Dichlorobenzene	180.4	2.0	3.0	9.0
Methylene chloride	40.2	12.2	12.3	—
Chloroform	61.2	11.3	9.9	—
Carbontetrachloride	76.7	1.1	0.6	0.6
Ethylidene dichloride	57.3	1.7	10.6	—
Ethylene dichloride	83.5	11.5	12.5	14.2
1,1,1-Trichloroethane	74.0	0.7	1.1	1.1
1,1,2-Trichloroethane	113.5	5.7	14.9	29.1
1,1,1,2-Tetrachloroethane	129.5	1.8	3.0	4.6
1,1,2,2-Tetrachloroethane	146	1.0	9.8	46.4
Pentachloroethane	162	1.1	1.9	5.2
cis-1,2-dichloroethylene	60.8	11.1	14.8	—
trans-1,2-dichloroethylene	48.4	12.3	13.6	—
Trichloroethylene	87.0	1.9	12.6	13.4
1,1,2,2-Tetrachloroethylene	121	0.4	2.2	3.4
n-propyl chloride	46.7	2.2	4.2	—
iso-propyl chloride	34.8	1.9	2.6	—
n-butyl chloride	68.5	0.8	1.9	2.6

in 1,1,2,2-tetrachloroethane at 70°C was the highest among those of chlorinated hydrocarbons studied. On the other side the swelling of polyester in tetrachloroethylene, trans-1, 2-dichloroethylene and trichloroethylene exhibited a degree of swelling higher than 10%.

7. Impregnation Grafting after Pretreatment with 1,1,2,2-Tetrachloroethane and Other Chlorinated Hydrocarbons

As 1,1,2,2-tetrachloroethane was found to be the most effective swelling agent to polyester, impregnation grafting was carried out with γ-rays. The results are shown in Table VIII.

As may be seen from the table the results are similar to that obtained using ethylene dichloride except with slightly small values for monomer-utilization. There are values of $C/A \times f$ which exceed 1. This unreasonable result may be attributed to either selective absorption of acrylic acid to polyester fibers or evaporation of water during nitrogen-flushing.

Table IX shows the grafting results obtained with monochlorobenzene, o-dichlorobenzene, chloroform and 1,1,2,2-tetrachloroethylene.

The swelling of polyester fibers with these four chlorinated hydrocarbons is so small that the amount of acrylic acid impregnated is small and the degree of grafting is low. For the case of chloroform it is noteworthy that the weight of the grafts decreased considerably by alkali-treatment.

Table VIII. Impregnation Grafting of Acrylic Acid onto Polyester Fiber. Two-Step Method Using 1,1,2,2-Tetrachloroethane as a Swelling Agent.
Pretreatment: $(CHCl_2)_2$, 70°C, 1 hr; Pick up of $(CHCl_2)_2$, 48–55%
Impregnation: AA-water mixture, 22°C, 16 hr
Irradiation: γ-rays, 0.32 Mrad/hr, 7.5 Mrad, 22°C

AA/H_2O by vol.	Pick up %, A	Weight increase %, C	Apparent graft %, D	%, E	C[a] $\frac{A\times f}{\times 100}$	D[a] $\frac{A\times f}{\times 100}$	E[a] $\frac{A\times f}{\times 100}$	Dyeing test, Rating
10/0	30.4	23.8	13.3	10.3	78.3	43.8	33.9	I
〃	30.7	26.1	14.5	12.9	85.0	47.2	42.0	I
8/2	26.1	20.8	15.8	15.4	99.6	76.1	74.0	II
〃	22.6	17.2	13.6	13.0	95.2	79.1	72.0	II
7/3	22.1	16.1	12.6	12.0	104	78.4	74.5	II
〃	24.0	18.5	14.1	13.2	109	76.4[b]	72.4[c]	I
6/4	23.1	15.8	11.8	11.4	114	74.7[b]	72.2[c]	II
〃	23.0	15.8	11.7	10.4	115	74.1[b]	65.8[c]	II

a) For AA/H_2O=10/0, 8/2, 7/3 and 6/4, f=1.00, 0.80, 0.71 and 0.62 (f's were calculated based on the assumption that no selective absorption takes place.)
b) D/C×100
c) E/C×100

Table IX. Impregnation Grafting of Acrylic Acid onto Polyester Fiber Pre-treated with Various Chlorinated Hydrocarbons.
Pretreatment: 70°C, 1 hr.
Impregnation: 7/3 AA-water mixture, 25°C, 16 hr.
Irradiation: γ-rays, 0.32 Mrad/hr, 7.5 Mrad, 24°C

Swelling agent	Deg. of swelling %	Pick up %, A	Weight increase %, C	Apparent graft %, D	%, E	C $\frac{A\times 0.7}{\times 100}$	D $\frac{A\times 0.7}{\times 100}$	E $\frac{A\times 0.7}{\times 100}$	Dyeing test, Rating
Mono-chloro-benzene	14.9	14.3	9.5	8.2	7.2	95.0	82.0	71.9	III
o-Dichloro-benzene	9.0	14.1	6.0	4.2	4.1	60.8	42.6	41.5	III
Chloroform	8.0[a]	15.0	11.1	9.6	0.5	106	91.5	—	I–II
1,1,2,2-Tetra-chloroethylene	3.4	11.5	5.0	4.3	3.0	62.5	53.4	37.3	III

a) Swelling temperature, 61°

8. Microscopic Obsevration of Graft Fibers

The cross-section of graft fibers was prepared, dyed with Sevron Brilliant Red B and color microphotograph was taken to observe the microstructure of the graft fibers. Three typical patterns will be shown in this paper. The first graft fiber with 7.9% apparent graft was prepared under conditions similar to that shown in Table III. Figure 1 shows the microphotograph. As may be seen from the picture the cross-section is dyed quite homogeneously, it means that the fiber is grafted with acrylic acid homogeneously.

For comparison two graft fibers prepared by immersion method which has been previously reported,[3] were also examined. The degrees of apparent graft were 8.4 and 20.1% respectively and the microphotographs are shown in Figs. 2 and 3. As may be seen

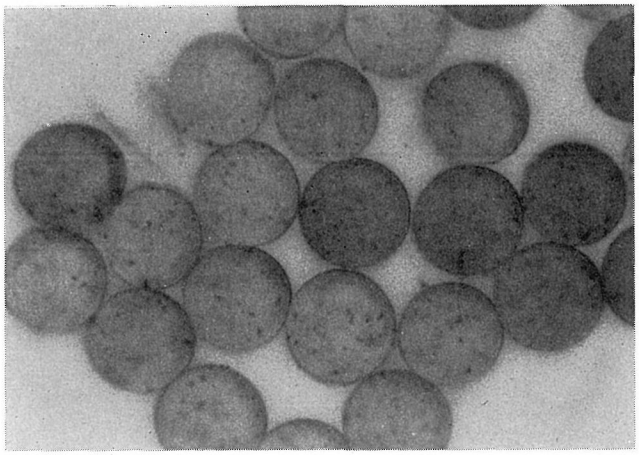

Fig. 1. Microphotograph of polyester fiber grafted with acrylic acid by two-step impregnation method at 23°C using ethylene dichloride as a pre-swelling agent. Total dose 6 Mrad; apparent graft 7.9%.

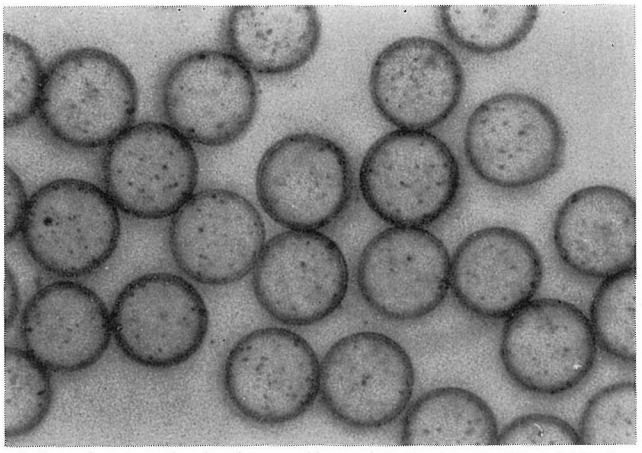

Fig. 2. Microphotograph of polyester fiber grafted with acrylic acid by immersion method at 23°C. Total dose 3.2×10^5 rad; apparent graft 8.4%.

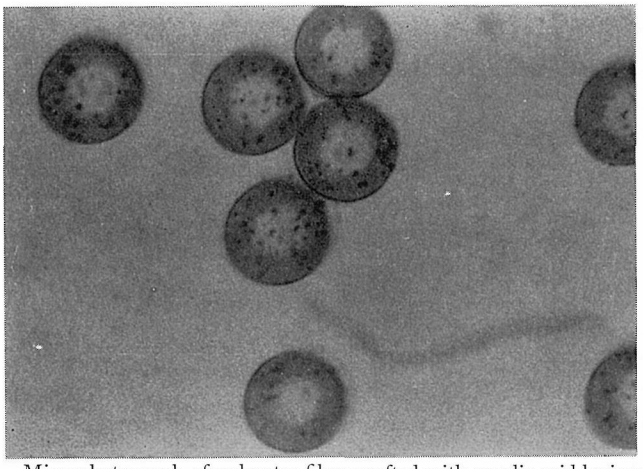

Fig. 3. Microphotograph of polyester fiber grafted with acrylic acid by immersion method at 23°C. Total dose 8.0×10^5 rad; apparent graft 26.1%.

only periphery of fibers are grafted though the degrees of apparent graft are higher than the case of impregnation grafting after pre-swelling.

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