

# Grafting onto Polyester Fibers. IV. Synergism during Graft Copolymerization of Binary Mixtures of Vinyl Monomers onto Polyester Fibers

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## Synopsis

Graft-copolymerization reactions of binary mixtures of vinyl monomers (acrylamide–acrylic acid and acrylonitrile–acrylic acid) with polyester fibers have been studied by chemical initiation technique using benzoyl peroxide as an initiator. The total graft add-on was determined gravimetrically, while the modified Kjeldahl's method for *N*-estimation was employed to determine acrylamide and acrylonitrile grafts in their mixtures with acrylic acid grafts. Synergism of very high order was noticed during the graft-copolymerization reactions. In the case of the acrylamide–acrylic acid system a very high order of synergism (129.15%) was noticed at equimolar proportions of the monomers in the grafting bath. Both acrylamide and acrylic acid showed synergistic influence over each other during graft-copolymerization reactions. In the case of the acrylonitrile–acrylic acid system, however, the presence of acrylonitrile reduced the graft yield of the acrylic acid component showing a negative synergism; but acrylic acid enhanced the acrylonitrile graft yield to a considerable extent. The results have been explained in terms of reactivity ratios of the monomers. The conductivity results of the monomer mixtures also supported the experimental results.

## INTRODUCTION

Results of the graft-copolymerization reaction of individual vinyl monomers onto polyester fibers have been reported earlier from these laboratories.<sup>1-3</sup> Grafting of fibers in the presence of mixtures of vinyl monomers is important since different types of polymer chains containing various functional groups can be introduced in the fiber structure. The conditions of grafting reactions can be manipulated and graft copolymers of desired properties obtained. Grafting using mixtures of monomers can also influence the extent of grafting of the individual monomers onto the fibers, especially when the phenomenon of synergism occurs during such reactions. Such grafting reactions can also give more economical grafts under the most favorable reaction conditions. It is, therefore, obvious that the subject of grafting with mixtures of monomers would attract attention of a number of research workers in this field.

A literature survey indicates that a number of Japanese researchers are working in the field of introducing mixed copolymers into polyester fibers using graft-copolymerization reactions of two or more vinyl monomers.<sup>4-11</sup> Most of these publications, however, are in the form of patent literature, and, therefore, detailed information about highly favorable changes taking place in the characteristics of the grafted polyester fibers, as well as the basic understanding of

the graft-copolymerization reactions using mixtures of vinyl monomers, is lacking.

The present communication describes the results of graft-copolymerization reactions of binary mixtures of acrylamide-acrylic acid and acrylonitrile-acrylic acid monomers with polyester fibers.

## EXPERIMENTAL

**Materials.** "Jailene" polyester fibers (1.5 D × 38 mm) manufactured and kindly supplied by Swadeshi Polytex, Ltd. (Ghaziabad, India) was used after purification by treatment with acetone for 8 h in a Soxhlet apparatus. Reagent-grade acrylic acid and acrylonitrile were freed from the inhibitors by vacuum distillation and simple distillation, respectively. Acrylamide, 1,2-dichloroethane, benzoyl peroxide, benzene, acetone, ethanol, acetic acid, dimethylformamide, sulfuric acid, etc., were of chemically pure grade. The cationic dye—Sandocryl Blue B3G (C.I. Basic Blue 3)—and acid dye—Polar Red RS (C.I. Acid Red 114)—obtained from Sandoz (India) and Amar Dyechem Ltd. (India), respectively, were purified according to the standard procedures before use.<sup>12,13</sup>

**Grafting with Individual Monomers.** Polyester was first swollen at 95°C for 3 h in a solvent/nonsolvent system consisting of 1,2-dichloroethane/water (20/80, v/v). Dichloroethane was then removed from the fiber completely by treatment with boiling water. This fiber was then used for subsequent graft copolymerization.

In the case of acrylamide-acrylic acid monomer mixtures, the composition of the mixtures tried were 100:0, 70:30, 50:50, 30:70, and 0:100, respectively. Benzoyl peroxide (0.125 g) was dissolved in pure crystallizable benzene (10 mL) and distilled water (90 mL) was added to it. Then the additions of the two monomers were made in order to have above proportions, keeping the total concentration of monomers at 5% (w/w). The grafting was carried out in the temperature range of 68–91°C for different intervals of time up to 12 h. The samples were then washed with boiling water.

In case of the acrylonitrile-acrylic acid mixture, the proportions used were 100:0, 80:20, 70:30, 50:50, 40:60, 30:70, 20:80, and 0:100, respectively. The medium for dispersing benzoyl peroxide was acetone (10 mL) and the grafted samples were washed first with dimethylformamide for 2 h at 70°C, followed by washing with boiling water for several hours.

The samples were then dried at 110°C for 2 h and then cooled in P<sub>2</sub>O<sub>5</sub> desiccator. The amount of graft add-on was determined gravimetrically.

**Estimation of Individual Grafts.** This was done by estimating *N*-content of the grafted samples containing acrylamide-acrylic acid and acrylonitrile-acrylic acid grafts using the modified semimicro Kjeldahl's method.<sup>14</sup>

From the *N*-content, the amount of acrylamide or acrylonitrile content in the fiber sample was given by the formula: AAm or AN graft content (%) = *N*-content (%) × *M*/14, where *M* = molecular weight of acrylamide or acrylonitrile. The individual graft add-on was calculated as follows: AAm or AN graft add-on (%) = [100 + (G%)]/100 × AAm or AN graft content (%), where *G* is the total graft add-on (%) in the fibers grafted with respective mixtures of monomers.

**Determination of Specific Conductivity.** Conductivity of solutions [5% (w/w) total strength] of mixtures of acrylamide:acrylic acid and acrylonitrile:

TABLE I  
Optimization of Conditions of Grafting of AAm:AA (50:50) Mixture onto Polyester Fibers

Temperature 81°C, initiator concn 0.125% (w/v)		Time 10 h, initiator concn 0.125% (w/v)		Temperature 81°C, time 10 h	
Time (h)	Graft add-on (%)	Temp (°C)	Graft add-on (%)	Initiator Concn % (w/v)	Graft add-on (%)
0.25	8.27	68	9.50	0.080	28.06
0.50	10.91	71	19.34	0.125	29.56
1	14.29	73	26.18	0.250	28.60
2	21.62	81	29.56	0.350	28.01
3	25.90	91	28.25	0.500	27.40
4	26.17			0.600	26.54
6	27.80				
8	28.16				
10	29.56				
12	29.46				

acrylic acid with different relative proportions was measured directly by using "Conductivity Bridge," Type CL01/02A (Toshniwal Bros., India) and a conductivity cell having cell constant 0.94. Conductivity was measured at room temperature and the reading obtained  $C$  was noted. Specific conductivity,  $K_s = 0.94 \times C \Omega\text{-cm}^{-1}$ .

**Determination of Monomer Reactivity Ratio.** Monomer reactivity ratios of pairs of monomers studied (acrylamide–acrylic acid and acrylonitrile–acrylic acid) were calculated from experimental results of polymerization reactions according to the procedure suggested by Mayo and Lewis.<sup>15</sup>

**Determination of Dye-Content of Dyed Substrate.** The grafted polyester fiber samples along with the control were dyed for 2% shade with acid and cationic dyes in open bath, at boil for 2 h, keeping the liquor ratio of 75 at pH 4–5. The dyed samples were soaped in 2 g/L soap solution at 70°C for 15 min.

Dye content of the dyed fibers was found by extracting the dye from a known amount of the fiber with (a) 25% aqueous pyridine for 24 h treatment in the case of acid dyes and (b) 50% aqueous acetic acid treatment at 40°C for 2 h with occasional shaking in the case of cationic dyes. From the optical density of the extract, the amount of solvent taken, the weight of dyed substrate, and the calibration curve, the dye content was determined.

## RESULTS AND DISCUSSION

In the present work, binary mixtures of acrylamide (AAm) and acrylic acid (AA) as well as acrylonitrile (AN) and acrylic acid (AA) in varying relative proportions giving a constant monomer concentration of 5% (w/w) in the grafting bath have been employed to carry out the graft-copolymerization reaction at 81°C onto polyester fibers using benzoyl peroxide as an initiator. Since the optimum conditions of the grafting reactions of the individual monomers, namely, AAm and AA, do not coincide with each other, the optimization experiments were carried out using equimolar mixture of the two monomers at 5% (w/w) total concentration in the grafting bath and the results are given in Table I. The results indicate that the highest amount of graft add-on was obtained at 81°C for

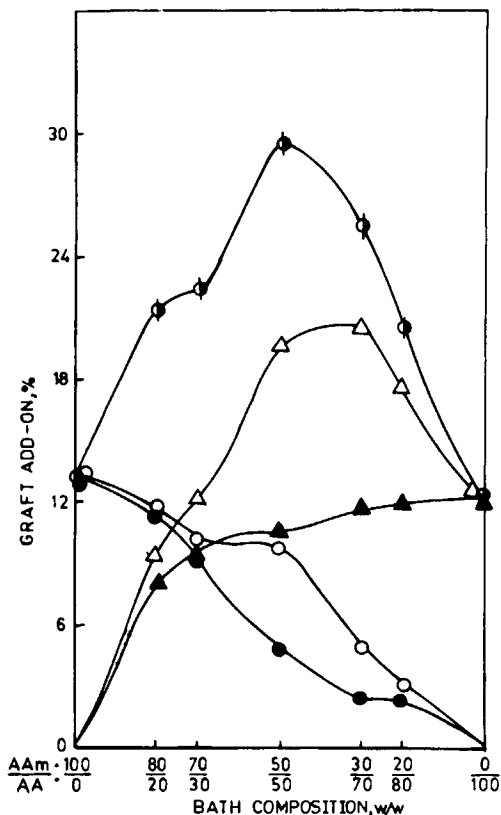


Fig. 1. Relation between graft add-on of polyester fibers grafted from mixed and individual baths of AAm and AA and bath composition: (●) AAm-AA total (mixed bath); (○) AAm (mixed bath); (△) AA (mixed bath); (●) AAm (individual bath); (▲) AA (individual bath).

10 h reaction time using the benzoyl peroxide initiator concentration of 0.125% (w/v).

The total graft add-on onto the polyester fibers has been determined gravimetrically, while the individual graft add-on of AAm-AA and AN-AA graft mixtures have been estimated using the *N*-estimation technique. The results obtained show accuracy of this method of  $99.7 \pm 0.3\%$ , justifying its usefulness in the present investigation.

The results of grafting of AAm and AA individually and in mixtures on polyester have been plotted in Figure 1. In general, the graft add-on increased with the increase in the concentration of individual monomers. Thus, individual AAm graft add-on increased from 0% to 13.56%, as its actual concentration is varied from 0% to 5% (w/w) in the grafting bath. Similarly, in case of AA alone, the steady increase from 0% to 12.24% in the graft add-on was observed when the concentration in the grafting bath was changed from 0% to 5% (w/w).

This may be attributed to the concentration effects of monomers during grafting reactions. At higher concentrations of the monomers, a greater number of monomer molecules are available for combination with the free radical on the backbone of the polymer chain. Alternatively, it also favors the production of large number of growing homopolymer chains which increase the possibility of

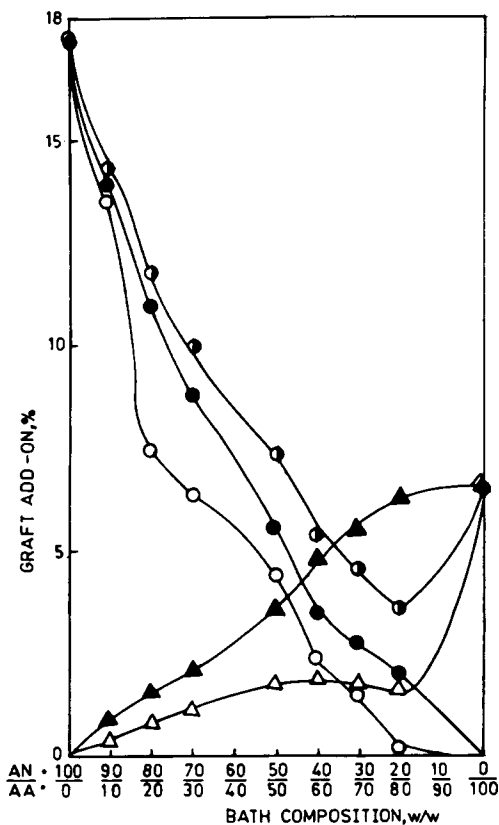


Fig. 2. Relation between graft add-on of polyester fibers grafted from AN and AA mixed and individual baths and bath composition: (●) AN-AA total (mixed bath); (●) AN (mixed bath); (▲) AA (mixed bath); (○) AN (individual bath); (▲) AA (individual bath).

H-abstraction via chain transfer to give rise to the substrate macroradical. This leads to the increased extent of chain propagation, resulting in the greater degree of graft add-on.

The results with respect to AAm-AA binary mixtures of varying proportions indicate that there is a considerable increase in the total graft add-on onto the polyester fibers, which is over and above the maximum amount of graft that could be obtained with the individual monomers, if were used at the same concentration level of 5% (w/w). Thus, when AAm and AA mixture (5% w/w) was taken in the proportion of 80:20, the total graft add-on obtained was 21.53%, as compared to only 13.56% and 12.24%, of individual monomers of 5% (w/w) each, respectively. This clearly indicates the synergistic effect when the two monomers are used together in the mixture. It may be noticed that the synergistic effect can be observed at all the proportions of monomers in binary mixtures, although the extent of synergism may vary from one mixture to another. The total graft add-on increases with the increase in the proportion of AA from 0 to 50 parts per 100 parts of AAm:AA mixture in the grafting bath, but decreases when the proportion is further increased, thus giving a maximum in the curve at 50:50 AAm:AA, corresponding to the highest amount of total graft add-on of 29.56%. With a view of expressing the synergistic phenomenon quantitatively, the percent

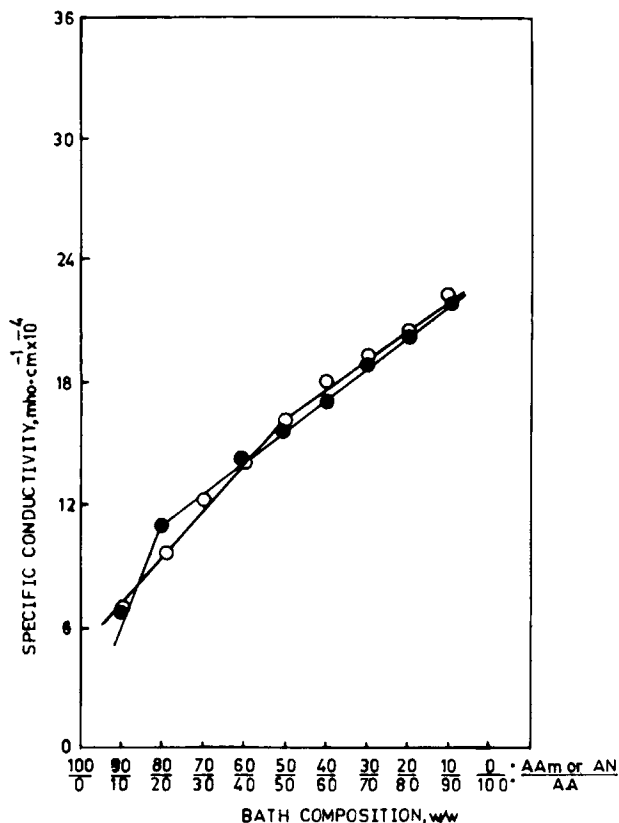


Fig. 3. Relation between specific conductivity and bath composition (5% total concentration) of AAm:AA and AN:AA monomer mixtures: (○) AAm:AA mixture; (●) AN:AA mixture.

synergistic influence was calculated by taking 13.56% and 12.24% AAm and AA grafts, respectively, as control values for 0% synergism. On this basis, the maximum graft add-on obtained of 29.56% at 50:50 AAm:AA corresponds to 129.15% synergism. Thus, it is interesting to note that instead of taking 5% (w/w) solution of AAm and AA individually, if 2.5% AAm is replaced by 2.5% AA (thus keeping the mixture at 5% total concentration) the total graft add-on is increased over twofold. The fact that the extent of synergism is dependent on relative proportions of AAm and AA in the grafting bath indicates that both the monomers contribute to the synergistic effect, although to varying extents. When the graft add-on curves for AAm, grafted individually, and that from the mixed bath are compared, then it can be seen that the synergistic effect of the presence of AA in the mixture can be noticed at almost all the proportions of the monomers in the grafting bath. Similar conclusion can be drawn for the synergistic influence of AAm on AA graft add-on onto the polyester fibers. From the above discussion, it is clear that both AAm and AA exhibit positive synergism in presence of one another giving additive effect to get the total synergistic influence of a very high order. The results of the present investigation indicate that out of the two monomers, namely AAm and AA, the latter is grafted preferentially as compared to the former. This may be attributed to the higher polarity of the  $-\text{COOH}$  groups of AA as compared to  $-\text{CONH}_2$  groups of the AAm monomer.

Similar conclusions were drawn by Odian et al.<sup>16</sup> and Garnett et al.<sup>17</sup> from their studies on polyethylene and wool substrates, respectively.

Figure 2 gives results with respect to grafting of AN-AA mixtures onto polyester fibers, with their varying proportions in the grafting bath, at 81°C for 10 h using 0.125% (w/v) benzoyl peroxide as an initiator. The results indicate that, in case of AN, the positive synergism can be witnessed at all the proportions of the mixture. Thus, the presence of AA enhances the extent of grafting of AN onto polyester fibers. The curves for AA graft, however, show exactly the reverse trend. Thus, the presence of AN in the AN:AA mixture seems to be detrimental to the graft yield of the AA component in the mixture at all the relative proportions of the two monomers (negative synergism). The resultant total graft add-on in the polyester fibers will be governed by the above two opposing types of synergism. It may be noted that the positive synergism for the AN graft is maximum at 80:20 AN:AA composition which decreases with the increase in the amount of AA in the grafting bath. Similarly, the negative synergism observed in the case of the AA graft is minimum around the same composition, which enhances with the increase in the amount of AA. Its net effect is that a marginal positive synergism is witnessed for the total graft add-on when the composition of the grafting bath varied from 90:10 to 70:30 AN:AA. Beyond this stage, a negative synergism is observed. This is expected in accordance to the finding that the presence of AN in the AN:AA mixture is detrimental to the grafting reaction of AA into polyester fibers.

### Mechanism of Synergistic Influence

Figure 3 gives the specific conductivity curves for the binary mixtures of monomers of varying proportions in aqueous solution.

During the grafting of AAm-AA binary mixtures onto polyester fibers, the synergistic influence has been witnessed giving enhanced grafting of each of the two components. Obviously, it indicates that the rate of grafting is enhanced at the expense of the rate and the extent of homopolymer formation, resulting in the increase in the efficiency of grafting. The specific conductivity results for AAm-AA binary mixtures clearly show the break at 50:50, i.e., almost equimolar proportions of the two monomers, suggesting maximum interaction between AAm and AA monomer molecules. This also implies that AAm and AA monomer molecules are present in solution with some kind of association between the two, which increases or decreases depending upon their relative proportion in the bath. Obviously, it is maximum, when they are present in 1:1 molar proportion. It is, therefore, possible that the AAm and AA monomer molecules form a labile complex, and the extent of its formation will be the highest, when the monomers are present in equimolar proportion, giving the break in the conductivity curve. The complex formation seems to have considerable influence in changing the rates of reaction during the grafting process: (i) due to the complex formation mobility of the reacting species in the solution is reduced, thereby retarding the rate of homopolymerization; (ii) when one monomer molecule diffuses inside the fiber structure, it automatically carries another monomer molecule present in the complex, thus increasing the monomer concentration in the fiber phase—a very favorable situation for higher graft-co-polymer formation; (iii) when the monomer molecule reacts with the free radical

TABLE II  
 Reactivity Ratios in Copolymerization Reaction [Temp 81°C; benzoyl peroxide 0.125% (w/v)]

AAm:AA	AN:AA
$r_1 = \frac{\text{rate constant (AAm} \rightarrow \text{AAm)}}{\text{rate constant (AAm} \rightarrow \text{AA)}} = 0.30$	$r'_1 = \frac{\text{rate constant (AN} \rightarrow \text{AN)}}{\text{rate constant (AN} \rightarrow \text{AA)}} = 0.31$
$r_2 = \frac{\text{rate constant (AA} \rightarrow \text{AA)}}{\text{rate constant (AA} \rightarrow \text{AAm)}} = 0.45$	$r'_2 = \frac{\text{rate constant (AA} \rightarrow \text{AA)}}{\text{rate constant (AA} \rightarrow \text{AN)}} = 1.34$

on the backbone of the polyester chain molecule, the chain propagation is enhanced due to the complex, and, hence, a higher amount of monomer molecules is utilized resulting in the synergistic influence.

The reactivity ratios of monomers give a good indication about their interaction with each other as well as their capability of reacting with the free radical on the backbone of the polymer chain. The reactivity ratios for the copolymerization of AAm:AA and AN:AA have been given in Table II ( $r_1, r_2$  and  $r'_1, r'_2$ , respectively). In the case of the AAm:AA monomer pair, the values of  $r_1$  and  $r_2$  are 0.30 and 0.45, respectively, both of which are  $<1$ . These values signify that AAm and AA monomer radicals prefer to react with each other rather than reacting with those of their own kind. The value of  $r_1$  (0.30) suggests that AAm reacts with AA almost three times faster than with its own molecules; similarly, the value of  $r_2$  (0.45) indicates that AA reacts with AAm about twice as fast as its own molecules. These reactivity ratios of AAm and AA clearly suggest the possibility of enhanced reaction activity between AAm and AA monomers and their graft-copolymerization reaction with the polyester fibers, giving rise to positive synergistic influence under the most favorable conditions, namely, 1:1 molar proportions in the grafting bath. The results of the present investigation can be very well understood in the light of this contention. Accordingly, positive synergistic effect on grafting onto polyester fibers has been witnessed at all the proportions of these two monomers, and maximum synergism was observed at the 50:50 proportion of AAm:AA in the grafting bath. It is interesting to note that, although AAm:AA are in equimolar proportions in the grafting bath, the amount of AA graft in the total graft mixture onto polyester fibers is almost twice as much as AAm graft (AA graft 19.74%; AAm graft 9.82%). This confirms the higher ability of AA, perhaps, due to greater polarity to go into the graft copolymer during grafting onto polyester fibers in the presence of AAm monomer.

As regards AN:AA binary mixtures, the specific conductivity curve (Fig. 3) also shows a break at 80:20 AN:AA composition in the solution, indicating that the two monomer molecules have some kind of interaction at this proportion and, therefore, it seems that there is a positive synergistic effect observed during graft copolymerization at the same proportion in the grafting bath. Results on reactivity ratios of AN and AA ( $r'_1 = 0.31$  and  $r'_2 = 1.34$ , respectively) indicate that this is the case where  $r'_1 < 1 < r'_2$ . In such cases, copolymer contains larger proportion of more reactive monomer, and, hence, the same should go in the formation of homopolymer to a larger extent. The net result, perhaps, could be that the lesser amount of the more reactive monomer is available for graft-copolymerization reaction with polyester fibers. In the present case, the positive synergistic influence has been observed with respect to AN component, when



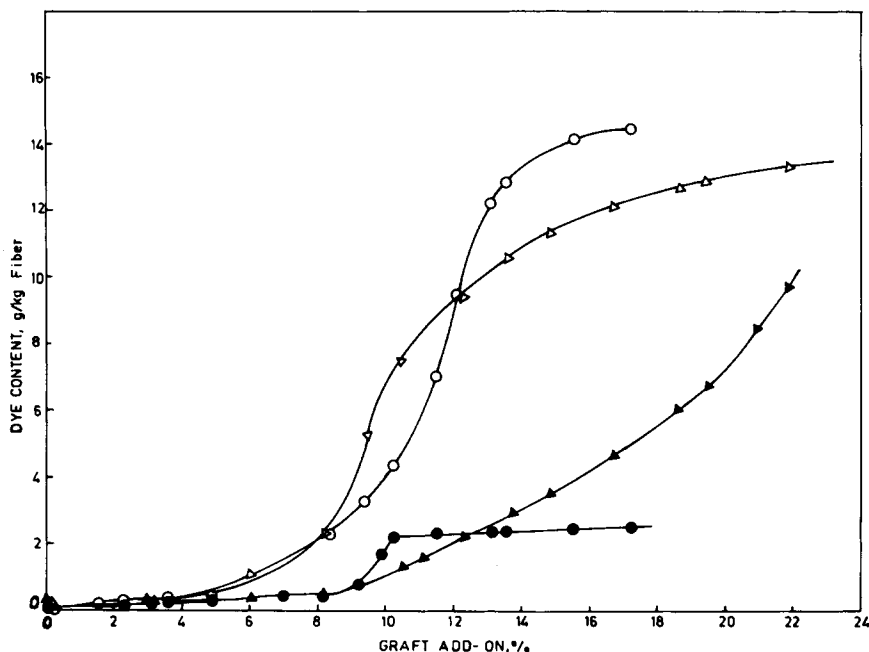


Fig. 4. Relation between acid and cationic dye content and graft add-on of AAm- and AA-grafted polyester fibers: (O) Polar Red RS, AAm graft; (●) Sandocryl Blue B3G, AAm graft; (▲) Polar Red RS, AA graft; (Δ) Sandocryl Blue B3G, AA graft.

its mixture with AA has 80:20 composition in grafting bath. In case of AA, however, there is negative synergistic influence. This means that the greater reactivity of AA ( $r_2 = 1.34$ ) has been utilized more to form the homopolymer and to certain extent to copolymerize with AN, rather than the actual graft copolymerization with polyester fibers in the presence of the AN monomer. It is significant, therefore, that out of the total graft mixture of 11.81%, the AN contribution is 11.01%, while that of AA is only 0.80% at the bath composition of 80:20 during the graft-copolymerization reaction.

#### Dyeability Method of Estimating AA Composition in Binary Mixtures of Grafts

This method is based on the dyeability of polyester fibers containing different types of grafts. The dyeability of a textile fiber can be increased by introducing suitable functional groups in the fiber structure, so that they become the centers of adsorption or reaction with the appropriate class of dye molecules. The dyeability can also be enhanced by bringing about opening up of the fiber structure, thus creating additional accessibility for the dye molecules. During the graft copolymerization reactions onto polyester fibers, both the above-mentioned criteria are relevant. Thus, the AA graft, AAm graft, or their mixture when introduced in the polyester fiber structure, will accompany  $-\text{COOH}$ ,  $-\text{CCNH}_2$ , or combination of these two groups into the polymer matrix. The dyeability of AA-containing graft is enhanced when the cationic dye is used during dyeing, while the acid dye will be intensely dyed on AAm-grafted polyester

TABLE III  
 Comparison of *N*-Estimation and Dyeability Techniques for Determining Individual Grafts in AAm-AA-Grafted Polyester Fibers<sup>a</sup>

Bath composition (w/w), AAm:AA	<i>N</i> -estimation, graft add-on (%)		Dyeability, dye content (g/kg fiber)		AA graft by dyeability technique (%)
	AAm	AA	Due to AAm	Due to AA	
100:0	13.56	0.00	C 2.40	0.00	2.40
80:20	11.95	9.58	A 12.90	0.00	12.90
70:30	10.23	12.19	C 2.35	6.25	8.60
50:50	9.82	19.74	A 8.90	1.10	10.00
30:70	4.99	20.71	C 2.20	9.40	11.60
20:80	3.06	17.60	A 4.30	2.40	6.70
0:100	0.00	12.24	C 1.60	12.80	14.40
			A 3.90	6.70	10.60
			C 0.20	13.20	13.40
			A 0.40	8.00	8.40
			C 0.15	12.50	12.65
			A 0.20	5.50	5.70
			C 0.00	9.40	9.40
			A 0.00	2.40	2.40

<sup>a</sup> C = cationic dye; A = acid dye.

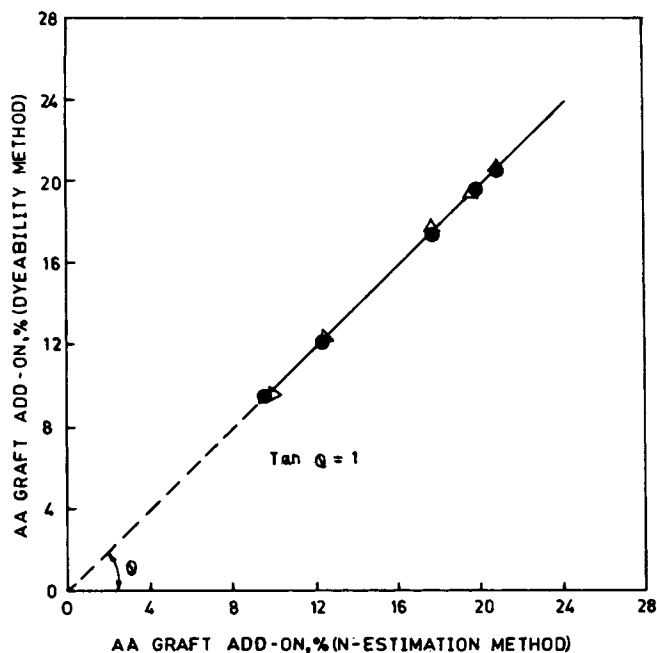


Fig. 5. Comparison between AA graft add-on in AAm-AA graft mixture obtained by dyeability and *N*-estimation techniques: (●) Sandocryl Blue B3G; (Δ) Polar Red RS.

fibers. In addition to the changes in the chemical nature of the polyester fibers, significant changes in the supermolecular structure of the polymer are also visualized during the graft-copolymerization reaction. Thus, when the AA-grafted polyester is dyed with an acid dye, theoretically, no dyeing should be possible; but, due to open structure of this grafted fibers, as compared to the control, some acid dye can penetrate inside the substrate, and the dyeing can be possible. The extent of the dyeability will be the function of amount of graft introduced in the fiber structure, since the opening up of the same will, in turn, be proportional to the graft add-on of the modified substrate.

Similar contention can be applied for dyeability of AAm-grafted polyester fibers with cationic dyes. Thus, for a polyester substrate containing both AA and AAm grafts, the dyeability with either acid or cationic dyes will be a complex phenomenon. Although most of the acid dye dyeability would be due to the presence of AAm graft, a small proportion of this dye will also be retained in the fiber structure, apparently by the AA graft. Similarly, it can be said that the cationic dye dyeability will mainly be due to the presence of the AA graft, but, to a certain extent, would be attributed to the presence of AAm graft in the mixture. Figure 4 gives the relationship between the amount of acid and cationic dye content values versus graft add-on for AAm and AA grafts (obtained from individual monomer grafting). The results indicate that, with the increase in the AA graft add-on, the cationic dye uptake is increased to a great extent. But, when the same substrate is dyed with acid dye, there is adsorption of this dye also, especially at the higher amounts of graft introduced in the fiber structure. Similarly, due to the presence of  $-\text{CONH}_2$  groups in the AAm-grafted fibers, intense shades with the acid dye could be obtained. The same substrate, how-

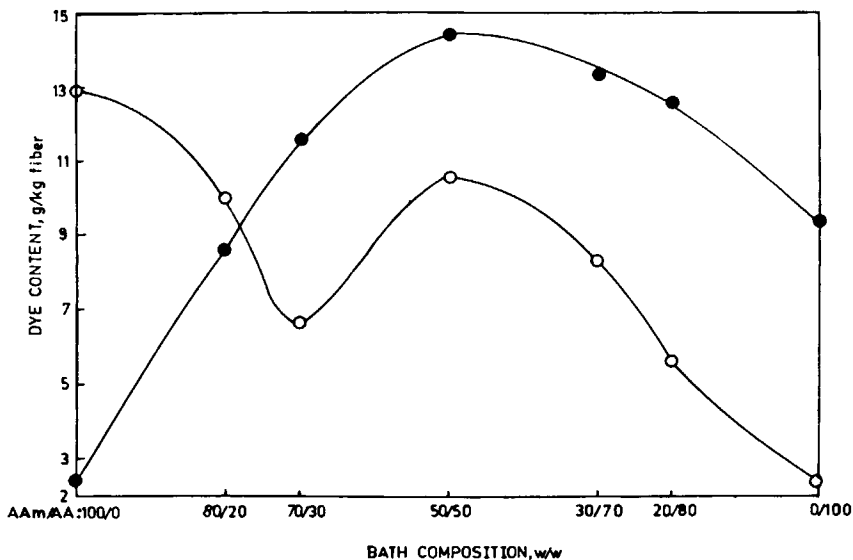


Fig. 6. Relation between cationic and acid dye content for polyester fibers and grafting bath composition of AAm:AA monomer mixtures: (●) Sandocryl Blue B3G; (○) Polar Red RS.

ever, also adsorbs a limited amount of cationic dye, especially at higher amounts of graft. These reference curves have been utilized to arrive at "true dyeability" due to AA and AAm grafts with cationic and acid dyes, respectively, by subtracting their contributions to dyeability in the case of acid and cationic dyes, respectively, from the total dye uptake. For example, for a sample containing AAm-AA graft mixture, say, the sample grafted through the bath containing 50:50 AAm:AA monomers, the total graft add-on of AAm-AA is 29.56%. The AAm graft add-on in the mixture is arrived at 9.82% by the *N*-estimation method, and, by difference, the AA component is arrived at 19.74%. In order to estimate the AA component in the above mixture using the dyeability method, the substrate was dyed with cationic dye, which gave the total dye content of 14.40 g/kg of fiber. The contribution of the AAm graft (9.82% add-on) can be read from reference curve (Fig. 4), which comes to 1.60 g/kg of fiber. By difference, the true cationic dye uptake due to the AA graft component in the fiber comes to be 12.80 g/kg of fiber. Figure 4 can again be used to get the corresponding AA graft add-on for dye content of 12.80 g/kg of fiber. The same corresponds to 19.70% AA graft add-on, which is very close to the value of 19.74% AA graft add-on obtained by *N*-estimation method. The above treatment was given to a number of substrates with varying amounts of AAm and AA grafts in the mixture and, also, using acid dye dyeability data. These results have been summarized in Table III.

In order to see the reproducibility and the validity of the new dyeability method proposed here, a correlation curve was plotted in Figure 5 for AA graft add-on, in the AAm-AA graft mixtures, obtained by *N*-estimation and the dyeability methods. The results showing a common linear plot both for acid and cationic dyes indicate that there is a very good correlation between the two methods. On extrapolation, the linear plot passes through the origin and has a slope of unity; both these facts further suggest that the proposed dyeability

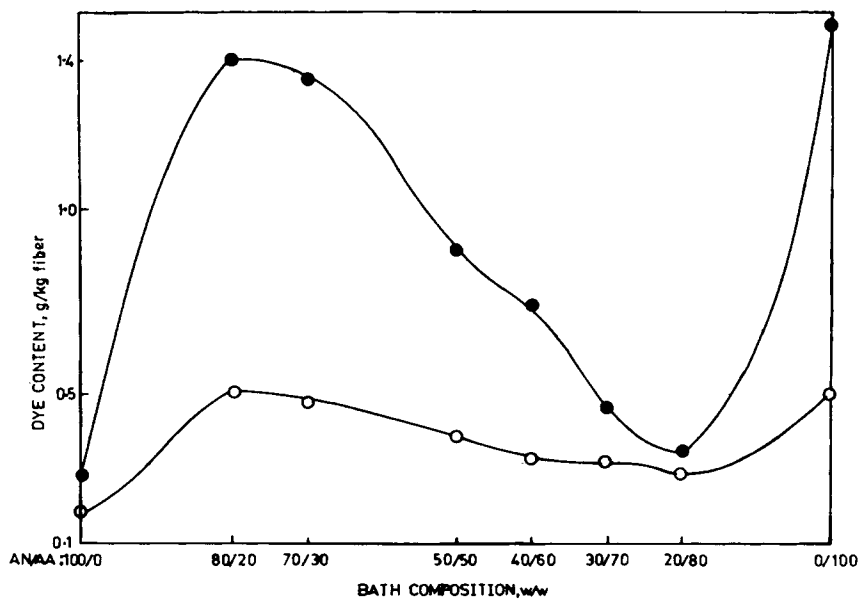


Fig. 7. Relation between cationic and acid dye content for polyester fibers and grafting bath composition of AN:AA monomer mixtures: (●) Sandocryl Blue B3G; (○) Polar Red RS.

method of estimation of AA component in AAm-AA-grafted polyester fibers is as reliable and reproducible as the well-known *N*-estimation method.

### Dyeability of AAm-AA- and AN-AA-Grafted Polyester Fibers

Figure 6 gives the relationship between total cationic and acid dye content and the composition of AAm:AA monomer mixtures in the grafting bath. It can be seen that the polyester fibers containing pure AAm graft adsorb the highest amount of acid dye, and, as the bath contains more and more AA monomer, resulting in the introduction of higher amounts of AA graft into the AAm-AA-grafted polyester fibers, the amount of the acid dye adsorbed decreases up to a bath concentration of AAm:AA 70:30. The trend is, however, reversed at 50:50 AAm:AA mixture in the bath, beyond which, again, the original trend is restored. The binary mixture of 50:50 AAm:AA composition, thus, gives a maximum in the curve with a sudden rise in the acid dye uptake, indicating a positive synergistic influence of AAm component in the AAm-AA graft mixture present in the polyester fibers. As regards the cationic dye uptake, the 50:50 composition of AAm:AA in the grafting bath gives the highest amount of dye uptake, although it contains only half the amount of AA monomer in the bath as compared to the bath containing pure AA monomers. In addition, the total amount of graft add-on can also influence the dye adsorption due to the favorable changes in the fiber structure. The results, therefore, indicate that there is synergistic effect at the same composition for the AAm and AA grafts add-on in the mixture.

Thus, the dyeability studies also confirm the positive synergistic influence of AAm and AA over each other, which is of the highest order, when they are present in 1:1 proportion in grafting bath during graft copolymerization onto polyester fibers.

Figure 7 gives the results with respect to AN-AA grafting onto polyester fibers. In general, the dye uptake values are very low, specially in case of acid dye as both AN and AA grafts or their mixtures adsorb very low amounts of this anionic dye. The AN graft adsorbs a certain amount of cationic dye, and it can be seen that the maximum amount of dye uptake is by the sample grafted from 80:20 AN:AA in the grafting bath, thus showing the synergistic influence for AN component during its grafting in presence of AA monomer onto polyester fibers. It is also interesting to note that a minimum in the curve is obtained in the case of grafting from binary mixtures of AN:AA 20:80 composition. These results confirm that the above mixture exhibits the highest amount of negative synergism in case of AA graft add-on in the binary mixture.

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