

Radiation Induced Grafting of Mixed Monomers onto Polyester and Polypropylene Fibers

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Synopsis

Grafting of the mixture of acrylamide and acrylic acid onto polyester and polypropylene fibers and mixture of acrylic acid and methacrylic acid onto polypropylene by the radiation method are reported. It is observed that when pure acrylamide was used for grafting, the grafting extent was small, whereas when the mixture was used, the amount of acrylamide content in the copolymer was found to be more than the feed ratios. The results are explained on the basis of chain transfer mechanism. With methacrylic acid and acrylic acid mixtures, the rate of grafting decreased with the increase in the concentration of acrylic acid in the feed ratio, and this has been explained on the basis of the formation of either a 3-dimensional network structure or a highly branched structure involving backbone polymer molecules with acrylic acid, which prevents the diffusion of the monomer from the solution phase to the swollen phase.

INTRODUCTION

Mixed monomers can be used in grafting onto polymers to introduce dual properties like hydrophilicity and hydrophobicity. Trivedi et al.¹ have studied the grafting of mixtures of acrylamide and acrylic acid onto polyamide and observed positive synergistic effect. Lokhande et al.² have also observed synergistic grafting when the mixtures of acrylamide and acrylic acid were gradually copolymerized onto polyester by chemical methods and studied their dyeing, moisture uptake, and electrokinetic properties. In this paper we are reporting results of the radiation-initiated grafting of mixtures of acrylamide and acrylic acid onto polyester and polypropylene and mixtures of acrylic and methacrylic acids onto polypropylene fibers.

EXPERIMENTAL

Materials

Polyester. Jailene "polyester" fibers (1.5 × 38 mm) manufactured and supplied by Swadeshi Polytex Ltd., Ghaziabad (India) were used after 8 h Soxhlet extraction with acetone. These fibers were first swollen at 95°C for 3 h in a solvent/nonsolvent system, 1,2-dichloroethane/water (20/80). Dichloroethane was then removed completely by treatment with boiling water.

Polypropylene Fiber. Type s spun from isotactic polypropylene and supplied by M/s. Montecatini Edison Group was used.

Chemicals. Acrylic acid (AA) and methacrylic acid (MAA) obtained from Aldrich Chemical Corp. were distilled before use. Acrylamide (AAM) was recrystallized from acetone and thoroughly dried.

Methods

The grafting yields were determined by gravimetric method after treatment with boiling water to remove homopolymer. The samples were dried in vacuum oven at 70°C and weighed.

Monomer Solutions. Monomer solutions of the desired concentration containing copper sulfate or ferrous ammonium sulfate were prepared in water, and the concentration of the scavenger was adjusted to M/50.

Swelling. The samples were soaked in monomer solutions or their mixtures at 70°C for 4 h for attainment of saturation swelling (monomer uptake ~ 60% of dry weight) using a fiber to liquor ratio of 1 : 10. Before swelling the sample tubes were purged with oxygen free nitrogen, and the tubes were closed. Irradiations were done at room temperature (27°C) using a cobalt-60 source.

Estimation of Acrylamide Content in the Copolymers. The acrylamide content in the copolymer was calculated from nitrogen percentage in the fibers which was estimated using semimicro Kjeldahl's method.³

RESULTS AND DISCUSSION

The results for approximately equal concentrations (mol/L) of acrylamide and acrylic acid mixtures are shown in Table I. From the results one can observe that graft yields for only acrylic acid ~ 7.3M is much higher than for mixtures, even with 7.3M AA and 7.0M AA together. In case of pure AA the acceleration as well as increase in graft is explained on the basis of chain transfer to the backbone polymer from the growing acrylic acid end.⁶⁻⁸ This shows that Fe⁺⁺ is a poor scavenger for acrylic acid chain ends. In a mixture when both acrylamide and acrylic acid are present the acrylamide chain end is scavenged by Fe⁺⁺ very efficiently, thus decreasing the total yield. The data are shown in Table II wherein acrylic acid concentration is kept constant at

TABLE I
Grafting Yields for Acrylic Acid and Acrylamide Mixtures with Polyester^a

Time of irradiation (h)	% Grafting			
	Monomer solution AAM + AA : 1.4M + 1.46M	AAM + AA, 2.8M + 2.92M	AAM + AA, 7M + 7.3M	AA 7.3M
1	—	—	—	3.3
2	1.22	—	—	6.0
3	2.54	3.67	5.38	7.2
4	—	3.80	6.15	8.65
5	4.06	5.00	13.20	19.60
6	4.40	7.00	—	—
7	4.20	—	—	—

^aScavenger used: FeSO₄; dose rate: 0.22 Mrad/h.

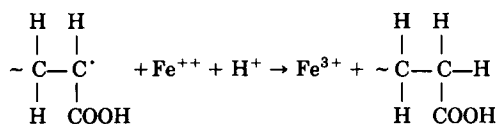
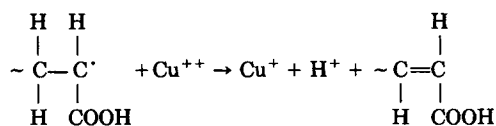
TABLE II
Grafting Yields on Variation of Acrylamide Concentration onto Polyester^a

Time of irradiations (h)	AAM: AA 1.4M: 7.3M scavenger		AAM: AA 3.5: 7.3M scavenger		AAM: AA 7.0M: 7.3M scavenger	
	FeSO ₄	CuSO ₄	FeSO ₄	CuSO ₄	FeSO ₄	CuSO ₄
1	—	—	3.6	2.5	—	1.95
1	9.36	—	—	—	—	—
2	11.56	5.13	4.7	3.3	—	2.55
3	—	—	11.21	5.0	5.38	3.3
4	17.96	6.44	—	5.1	6.15	4.5
5	26.88	7.37	—	—	13.2	5.8

^aDose rate: 0.22 Mrad/h.

~ 7.3M and the concentration of acrylamide varied from 1.4 to 7M in the presence of copper sulfate or ferrous sulfate as scavengers.

From the data one observes that as the concentration of acrylamide increases the amount of graft decreases. This indicates that acrylamide plays a negative role. Perhaps the reactivity of the polymer radical, i.e., radical on the backbone towards acrylamide, is less or chain transfer of the propagating acrylamide radical to the backbone polymer is less. It is also observed that CuSO₄ reduces the grafting yields in all the cases indicating that Cu⁺⁺ is an efficient scavenger for both types of radical ends of the copolymer. Similar observation was made in our earlier studies on the grafting of acrylic acid with polyester⁴, polypropylene,⁵ and also by Huglin and Johnson.⁹ The rate constants for reaction of hydrogen atoms with Fe⁺⁺ and Cu⁺⁺ are $2 \times 10^7 M^{-1} s^{-1}$ and $5 \times 10^7 M^{-1} s^{-1}$, respectively.⁶ The reaction mechanism suggested for scavenging is as follows:



Similar reaction scheme is also applicable with Fe⁺⁺ but the Fe⁺⁺ ends up as Fe⁺⁺⁺. This is also a good scavenger for growing chains. Huglin and Johnson⁹ in their earlier studies on grafting of acrylic acid onto nylon 6⁹ have proposed a similar mechanism.

The acrylamide content in the grafted chain is shown in Table III. For comparison purposes the grafting yield and the acrylamide content in the copolymer obtained by chemical grafting are shown in Table IV, using benzoyl peroxide as the initiator, without scavengers.

TABLE III
Acrylamide Content in the Copolymer to Various Feed Ratios^a

Feed ratio	Scavenger FeSO ₄			Scavenger CuSO ₄		
	% Graft	AAM + AA content in the copolymer		% Graft	AAM + AA content in the copolymer	
AAM : AA						
1M : 1.04M	6.15	3.02	3.13	4.55	1.33	3.17
1M : 2.09M	21.55	7.22	14.33	—	—	—
1M : 5.2M	17.96	7.32	0.64	6.44	1.44	5.00

^aScavenger : FeSO₄; dose rate : 0.22 Mrad/h; total dose : 0.88 Mrad/h.

TABLE IV
Acrylamide Content in the Copolymer for Various Feed Ratios

Feed ratio AAM/AA (M)	% Graft	Ratio of AAM/AA content in the copolymer
4 : 1.04	21.53	11.95/9.58
7 : 3.13	22.42	10.23/12.19
1 : 1.04	29.56	9.92/19.74
3 : 7.29	25.7	5/20.7
1 : 4.18	20.66	3/17.6

From the data shown in Table IV, the amount of acrylic acid entering into the copolymer is always higher than the feed ratios, since the reactivity ratios of the copolymerization is favorable towards acrylic acid addition.³ It is not possible to determine the reactivity ratios of the monomers in the presence of scavengers, since they are mostly used for preventing the homopolymerization. But it appears that, in radiation grafting, the presence of FeSO₄ as a scavenger alters the composition. The acrylamide content in the copolymer is higher than the feed ratio. It is observed that rate of grafting is much less in the mixture than with pure acrylic acid. The data obtained for individual monomers (AA and AAM) are shown in Table V. The data reveal that the amount of acrylamide grafted is quite low when compared to acrylic acid for

TABLE V
Grafting of Acrylic Acid and Acrylamide onto Polyester^a

Time of irradiation (h)	Acrylamide 3.5M	Acrylic acid 7.3M
1	—	3.3
1	—	6.0
2	1.0	7.2
3	—	8.65
4	1.8	13.20
5	2.3	19.6
6	4.4	—

^aDose rate = 0.22 Mrad/h; scavenger: FeSO₄.

the same amount of radiation received. This is attributed to the lower reactivity of the polymer radical with acrylamide than radicals with acrylic acid or alternatively the acrylamide ends are not efficient in their chain transfer to the backbone polymer to give higher grafts. But, in combination, the amount of acrylamide present in the copolymer was higher than what was expected for only acrylamide.

The reactivity ratios

$$R_2 = \frac{k(\text{AA-AA})}{k(\text{AA-AAm})}$$

and

$$R_1 = \frac{k(\text{AAm-AAm})}{k(\text{AAm-AA})}$$

The reactivity ratios r_1 and r_2 are both less than 1, i.e., 0.3 and 0.45, respectively, and hence the probability of the addition of comonomer is more than the monomer of its own kind.

Grafting of the Mixtures onto Polypropylene

Polypropylene is an aliphatic hydrocarbon and the radical yield by radiation, i.e., $G(R)$ is 6.2,¹⁰ whereas for polyester $G(R)$ is 0.1.¹¹ It is expected that the rate of grafting in polypropylene should be higher than in polyester since the rate of initiation would be higher. The results obtained with polypropylene are shown in Table VI. The total amount of graft as well as rate of grafting was almost identical with both polypropylene and polyester. Hence it is presumed that the amount of the monomer present in the swollen phase is almost identical.⁵

Tables V and VI demonstrate that the rate of grafting is not very different for the two backbone polymers used, which means that the radicals generated

TABLE VI
Grafting of Acrylic, Acrylamide, and Their Mixture
onto Polypropylene^a

Time of irradiation (h)	Pure AA 7.3M	Pure AAM 2.8M	Mixture AA : AAM, 7.3M : 2.8M
1	0.8	—	3.73
1	2.0	0.65	1.40
2	3.15	0.83	2.83
2	6.74	—	2.87
3	8.20	0.85	5.50
4	11.06	1.31	6.10
5	17.2	1.53	6.96
6	19.92	—	9.45
7	—	—	—

^aDose rate: 0.16 Mrad/h; scavenger: FeSO₄.

at the backbone polymer by radiation alone are not responsible for graft yield, but some other mechanism also should be operative.

Earlier, we had suggested in the case of polyester that the enhanced grafting is due to chain transfer to the backbone polymer.⁴ The same argument holds good even with polypropylene. However, one could expect that, under identical conditions, the amount of the total graft yield obtained is almost the same for both. Since the rates of grafting are almost equal for both the polymers, it can be said that the rate of chain transfer to the backbone polymer of polyester is higher than for polypropylene. This could be due to the difference in the chemical structure of the two polymers.

In the case of polyester $-\text{CH}_2-\text{CH}_2-$ groups are situated between two carbonyl groups which makes the C—H bond weaker. Hence, the rate of abstraction is higher resulting in larger chain transfer to the polymer. The saturation grafting in both the polyester and polypropylene fibers was previously explained as due to the formation of 3-dimensional net work structure with acrylic acid, thus preventing the diffusion of the monomer to the swollen phase from the solution phase.^{5,12}

Graft Copolymerization with the Mixtures of Methacrylic Acid and Acrylic Acid onto Polypropylene Fibers

It was found that for the same concentration of acrylic and methacrylic acid, when used individually, the saturation grafting and the rates of grafting differed considerably. For instance methacrylic acid gave grafting to the extent of 270%, whereas with acrylic acid it was between 27 and 29%.⁶

Results shown in Table VII indicate that the total graft increases with the increase in the concentration of the mixture. However, it becomes almost independent of the mixture above 1.0*M*. This shows that above this concentration the rate of grafting depends only on the rate of production of radicals on the backbone polymer.

Figure 1 shows the grafting yields for 1.46*M* solution of acrylic acid and 1.18*M* solution of methacrylic acid and their mixture onto polypropylene. From the results it is evident that the rate of grafting with methacrylic acid is very much higher than that with acrylic acid. In the case of the mixture and also with methacrylic acid an autoacceleration is observed. It appears from

TABLE VII
Grafting Yields for the Mixtures with Polypropylene^a

Times of irradiation (h)	AA : MAA 0.73 <i>M</i> : 0.59 <i>M</i>	AA : MAA 1.095 <i>M</i> : 0.785 <i>M</i>	AA : MAA 1.46 <i>M</i> : 1.18 <i>M</i>	AA : MAA 1.825 <i>M</i> : 1.375 <i>M</i>	AA : MAA 2.19 <i>M</i> : 1.57 <i>M</i>	AA : MAA 2.92 <i>M</i> : 2.36 <i>M</i>
	1.06	1.6	1.47	1.41	1.6	1.6
1	1.90	2.97	3.66	3.6	4.47	4.3
1	2.74	5.54	7.10	10.1	12.76	11.9
2	2.8	8.82	10.1	16.48	20.8	19.49
2	5.8	12.2	15.0	22.89	29.90	30.13
3	7.9	15.16	19.7	28.02	37.3	39.57

^aScavenger: CuSO_4 ; dose rate: 0.4 Mrad/h.

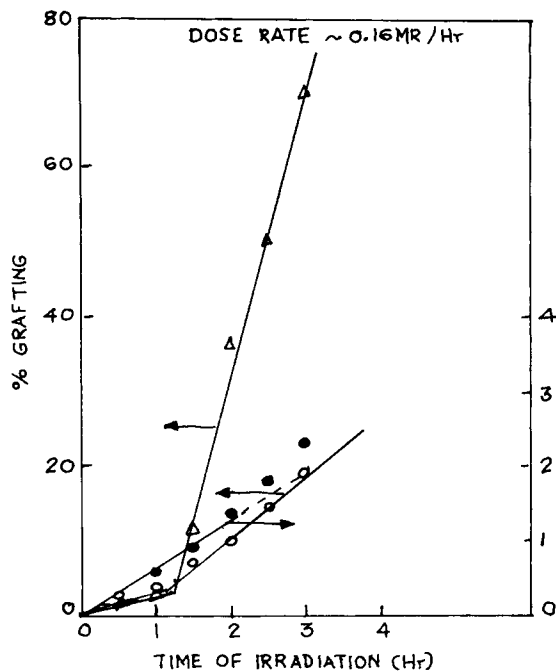


Fig. 1. Grafting of methacrylic acid (Δ), acrylic acid (\bullet), and their mixture (\circ) with polypropylene.

the graph that the initial rate of grafting 3.7%/h is the sum of the individual rates (i.e., 0.7% for acrylic acid + 3.0% for methacrylic acid).

The higher rate for methacrylic acid shown in Figure 1 is linear (38%/h), indicating that the mechanism for high rate could be due to chain transfer to the backbone polymer. Similar observations were made for the other concentrations studied. The rate of transfer is dependent only on the rate of initiation, that is, the total number of grafted chains produced initially, and not due to any other effect such as viscosity effect. However, in the presence of acrylic acid, rate of grafting decreases considerably from 38%/h to 9%/h. Even though the high rate is accounted for as due to chain transfer to the backbone polymer even with acrylic acid, the mechanism of transfer could be different. The difference in rate of grafting can be explained as due to the formation of 3-dimensional network structure in the presence of acrylic acid which decreases the diffusion of the monomer into the swollen phase from the solution phase. Alternately as suggested by Huglin and Richards,⁸ a highly branched structure in graft copolymerization of acrylic acid onto nylon 6 could also prevent the diffusion of the monomer from the solution phase to the swollen phase. This in effect decreases the total yield, and hence saturation grafting is observed.

References

1. I. M. Trivedi, P. C. Mehta, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **19**(1), (1975).
2. M. D. Teli, H. T. Lokhande, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.* **29**, 1843 (1984).

3. Anon., Indian Standards Institution, Indian Standard 5194 (1969).
4. P. D. Kale, H. T. Lokhande, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **19**, 461 (1975).
5. M. H. Rao and K. N. Rao, *Polym. Bull.* **1**, 727 (1979).
6. M. Anbar and T. Neta, *Int. J. Appl. Radio. Isotope*, **18**, 493 (1967).
7. E. E. Megat, I. K. Miller, D. Tanner, and J. Zimmerman, *J. Polym. Sci., Part C*, **4** 615 (1963).
8. M. B. Huglin and R. W. Richards, *J. Appl. Polym. Sci.*, **25**, 2513 (1980).
9. M. B. Huglin and B. L. Johnson, *J. Polym. Sci.*, **A7**, 1379 (1969).
10. S. Ohinishi, *Bull. Chem. Soc. Jpn.* **35**, 254 (1962).
11. A. Kajiura and H. Sobue, *Kogyokagaku Zasshi*, **62**, 1771 (1959).
12. M. H. Rao and K. N. Rao, *Radiat. Phys. Chem.* **26**, 669 (1985).

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