

ACIDIC EFFECT OF RADIATION GRAFTING BETWEEN ACRYLONITRILE AND WOOL*

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ABSTRACT

The acidic effect in grafting of acrylonitrile onto wool fibre under mutual irradiation has been studied. The reactivity of various acids towards graft copolymerization was found as the order: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl} > \text{HClO}_4 > \text{HOAC}$.

Keywords: Graft copolymerization Wool fibre Mutual irradiation Acid effect

1 INTRODUCTION

In recent years, chemical modification of fibre through graft copolymerization has received considerable interest^[1,2]. Radiation grafting is a uniform and clean method, and the degree of grafting can be easily controlled. A number of vinyl monomers such as styrene, methyl methacrylate, and acrylonitrile have been grafted onto wool by mutual radiation method^[3,4]. Recently, the effect of acids on radiation grafting of methyl methacrylate onto wool fibre has been studied by Misra and Rawat^[5]. In present article the effect of acids on grafting of acrylonitrile (AN) onto wool fine fibre initiated by gamma radiation is investigated.

2 EXPERIMENTAL

The Xinjiang fine wool fiber was purified by continuous soxhlation in petroleum ether, then washed with warm acetone, followed by distilled water and air dried. Monomer AN was washed with 10 % NaOH and distilled under reduced pressure. The middle fraction was collected and its boiling point is 77.3–77.5°C.

The pure fine wool (0.1 g) was immersed in 20ml water-methanol system in 50 ml reaction tube. Definite amount of monomer and acids was added to the reaction tube respectively, and nitrogen was passed through the tube prior to irradiation for 5 min. Gamma irradiation was carried out using a 2×10^{15} Bq cobalt-60 source at room temperature, the graft copolymerization by mutual radiation technique was carried out at different conditions. After the completion of graft copolymerization, the

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homopolymer was removed from the grafts by solvent extraction, and the residue obtained was dried until the constant weight was maintained. The percentage of grafting and efficiency were determined from the following formula:

$$\text{grafting} = (W_2 - W_1) / W_1 \times 100 \%$$

$$\text{efficiency} = (W_2 - W_1) / W_3 \times 100 \%$$

Where W_1 , W_2 and W_3 are the weights of wool, grafted wool and monomer used, respectively.

3 RESULTS AND DISCUSSION

Evidence of grafting: 1. On comparison of IR spectra of wool and wool-g-PAN, it is observed that a strong peak at 2230 cm^{-1} in the grafted samples assigned to $-\text{C}\equiv\text{N}$ group of PAN is absent in the IR spectra of wool, which indicates the formation of the grafts^[1]. 2. Comparison of scanning electron micrographs of wool and grafted wool indicates that considerable amount of polymer is deposited onto the surface of wool fiber^[1]. Wool is a natural protein, possesses a number of pendant function groups such as $-\text{SH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$ *etc.*, which may be activated by gamma radiation to generate active sites where suitable monomer can be grafted.

Dose effect: Maximum percentage of grafting (13.27 %) is obtained at total dose of $0.88 \times 10^4 \text{ Gy}$. Further increase of dose decreases percent grafting (see Table 1), which may be explained as AN participates in hydrogen abstraction reaction.

Table 1

Total dose effect on percent grafting of PAN onto wool by mutual irradiation method*

Sample No.	Dose / 10^4 Gy	Percent grafting / %	Percent efficiency / %
1	0.12	4.78	8.79
2	0.24	8.46	13.28
3	0.48	10.31	17.53
4	0.88	13.27	18.91
5	1.05	12.62	20.15
6	1.50	10.89	16.07
7	2.50	7.53	14.50

* Wool = 100 mg, Water-methanol = 20 ml,
Dose rate = $3.4 \times 10^3 \text{ Gy/h}$, $[\text{AN}] = 0.63 \text{ mol/L}$,
Room temperature

Table 2

Effect of monomer concentration on grafting of PAN onto wool by mutual irradiation method*

Sample No.	Monomer / $\text{mol} \cdot \text{L}^{-1}$	Grafting / %	Efficiency / %
1	0.13	5.67	8.52
2	0.31	7.31	5.96
3	0.63	9.52	4.79
4	0.94	14.36	3.50
5	1.25	7.28	1.85

* Wool = 100 mg, Water-methanol = 20 ml,
Dose rate = $3.4 \times 10^3 \text{ Gy/h}$, Total dose = $2.5 \times 10^3 \text{ Gy}$,
Room temperature

Effect of concentration of monomer: Table 2 describes the effect of concentration of monomer on percentage of grafting. It is observed that grafting increases with increasing concentration of monomer. Maximum percentage of grafting (14.36 %) is obtained at $[\text{AN}] = 0.94 \text{ mol/L}$. Further increase in monomer concentration decreases grafting. This may be explained by the fact that at higher concentration of monomer

homopolymer formation as well as wastage reaction are accelerated.

Effect of acids on percentage of grafting of AN has been investigated and the results are presented in Table 3. It is observed from the table that the addition of acid has an enhancing effect on percent grafting. Maximum grafting is observed when sulfuric acid is used as additive. The reactivity of different acids towards grafting was found to follow the order: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl} > \text{HClO}_4 > \text{HOAC}$. A similar effect has been observed by Garnett *et al.*^[7-8], who reported that addition of sulfuric acid accelerated graft copolymerization of many systems. In the presence of sulfuric acid, the swelling of wool fibre occurs, which facilitates the diffusion of AN to the active sites. Though the swelling of wool fibre can arise in the presence of other acids, presence of strongly oxidizing acids such as nitric acid and perchloric acid, side reactions involving oxidation of backbone polymer can occur that may decrease grafting. Gamma irradiation of hydrochloric acid probably produces $\text{Cl} \cdot$ which does not contribute to grafting. In presence of acetic acid, various chain transfer reactions are accelerated, which lead to a decrease of grafting.

Table 3

Effect of acids on grafting of PAN onto wool by mutual irradiation method*

Acidic concentration / molL ⁻¹		0.25	0.50	0.75	1.00	1.25
H_2SO_4	Grafting / %	12.81	17.33 (13.27)* *	24.00	36.77	25.69
HNO_3	Grafting / %	13.41	20.17 (15.19)* *	25.30	17.19	9.80
HCl	Grafting / %	11.78	13.49 (9.56)* *	19.07	—	—
HClO_4	Grafting / %	15.72	18.56 (11.78)* *	14.24	—	—
CH_3COOH	Grafting / %	10.62	11.41 (8.37)* *	11.84	10.24	9.79

* Wool = 100 mg, Water-methanol = 20 ml, Dose rate = 3.5×10^3 Gy/h, Total dose = 1.05×10^4 Gy, [AN] = 0.63 mol/L, Room temperature ** Results with air

Effect of air during grafting of AN onto wool with acid was studied and the results are presented in Table 3. It is observed that in air grafting is less than that in nitrogen. This is due to the fact that oxygen destroys some active sites of wool and thus causes a decrease of grafting.

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