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Radiation-Induced Graft Copolymerization of Mixtures of Acrylic Acid and Acrylonitrile onto Cellulose

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ABSTRACT

Graft copolymerization of mixtures of acrylic acid and acrylonitrile (AN) onto irradiated cellulose was studied. The effects of radiation dose, temperature, duration, and concentration of the monomers were investigated. The extent of grafting was found to increase with radiation dose, temperature, and duration. Grafting was higher with increasing AN concentrations.

INTRODUCTION

The modification of cellulose fibers through graft copolymerization of vinyl monomers has evoked considerable interest in recent years [1-7]. Generally, only a single monomer is grafted onto cellulose, but grafting from a mixture of monomers may be much more beneficial [8]. The property imparted by each of these monomers may produce a synergistic effect.

Acrylic acid is grafted to impart high sorbency, and polyacrylonitrile would improve rot resistance. Combined grafting of both may produce a cellulose having high water sorbency and improved

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resistance against moth and fungus. This type of special cotton may be useful for surgical and other applications.

EXPERIMENTAL

Whatman filter paper was used as the cellulose base. The filter papers were washed thoroughly with benzene and methanol before grafting. Freshly distilled acrylic acid (AA) and acrylonitrile (AN) were used. The treated and dried cellulose samples were first irradiated in air at various doses and then immersed in the monomer blend at the desired temperature under nitrogen for different time intervals. The grafted cellulose samples were washed with hot solvents (water for poly(acrylic acid) and DMF for polyacrylonitrile) in a Soxhlet apparatus for many hours to remove homopolymers. Knowing that complete removal of homopolymer is difficult, this solvent treatment was repeated to constant weight after drying. The weight loss on extraction was taken to be due entirely to homopolymer. The grafted samples are hygroscopic; hence, they were always kept in vacuum desiccators. The increase in weight of the cellulose was taken as the extent of grafting:

$$\text{wt\% graft} = \frac{\text{increase in wt of sample}}{\text{initial wt of cellulose}} \times 100.$$

The grafted copolymer samples were analyzed for their composition by determining the acrylic acid content, by reaction with dilute NaOH. A 100-mg sample was kept overnight at 0-5°C in 0.1 N NaOH solution, and the unreacted NaOH was determined by backtitration with dilute HCl. The acrylonitrile content in the grafted copolymer was then taken to be the difference between wt% total graft and wt% acrylic acid.

RESULTS AND DISCUSSION

Figure 1 shows the effect of radiation dose on the extent of grafting. The cellulose samples were irradiated with 2.0, 4.8, and 8.0 Mrd doses in air and heated at 60°C in a 5-M acrylic acid and 5-M acrylonitrile mixture for 7 h under nitrogen. The amount of polymer grafted was found to increase with increasing radiation dose. ESR studies of irradiated cellulose samples showed that free radicals were formed in the cellulose, and that more radicals were formed at higher doses. The amount of grafting rose rapidly and linearly up to about 5 Mrd, and the curve tended to level off after that. Homopolymers of these

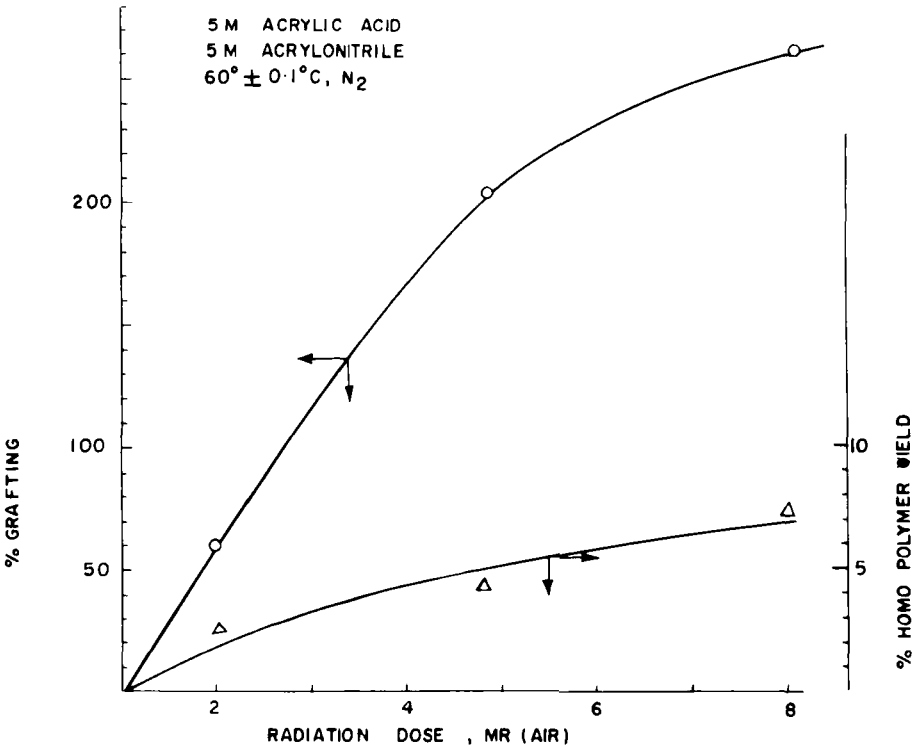

FIG. 1. Effect of radiation dose on grafting.

monomers were also formed during grafting, and the homopolymer yield also increased with the radiation dose.

When cellulose is irradiated in air, peroxides are formed which, on heating, decompose to yield free radicals which initiate the graft copolymerization. The samples were irradiated with 8 Mrd in air followed by heating at various temperatures in the solution of monomers under nitrogen for 7 h (see Fig. 2). Grafting increased with temperature; between 40 and 60°C there was a steep rise in grafting. The greater decomposition of peroxides at higher temperatures probably accounted for the higher extents of grafting.

To study the effect of duration, the cellulose samples were irradiated and polymerization was carried out under nitrogen for 1, 3, 7, and 14 h (Fig. 3). The rate of grafting was high in the first hour and then slowed down, especially for the sample with the lower irradiation dose.

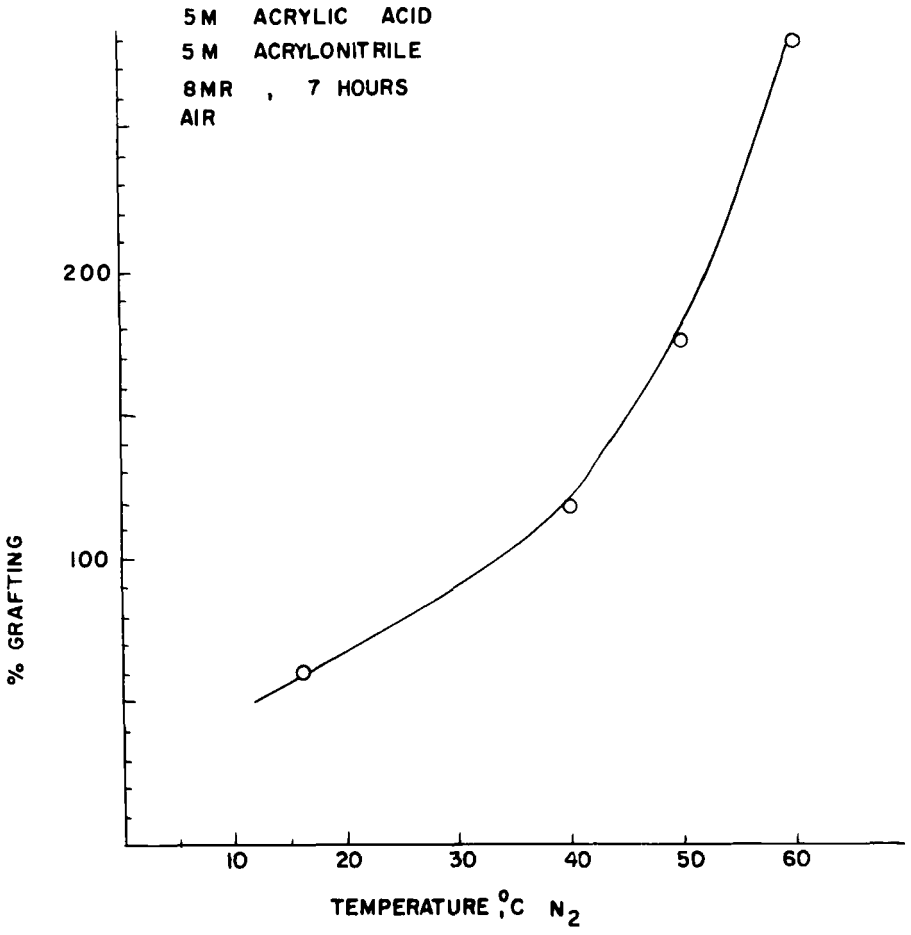

FIG. 2. Effect of temperature on grafting.

The extent of grafting with varying acrylic acid and acrylonitrile concentrations is shown in Fig. 4. The grafting was maximum for pure acrylonitrile. On increasing the concentration of acrylic acid, wt% grafting decreased linearly. Evidently the rate of grafting of acrylic acid is lower than that of acrylonitrile. The linear fall of grafting shows that the relative rates of conversions of the two monomers remained constant.

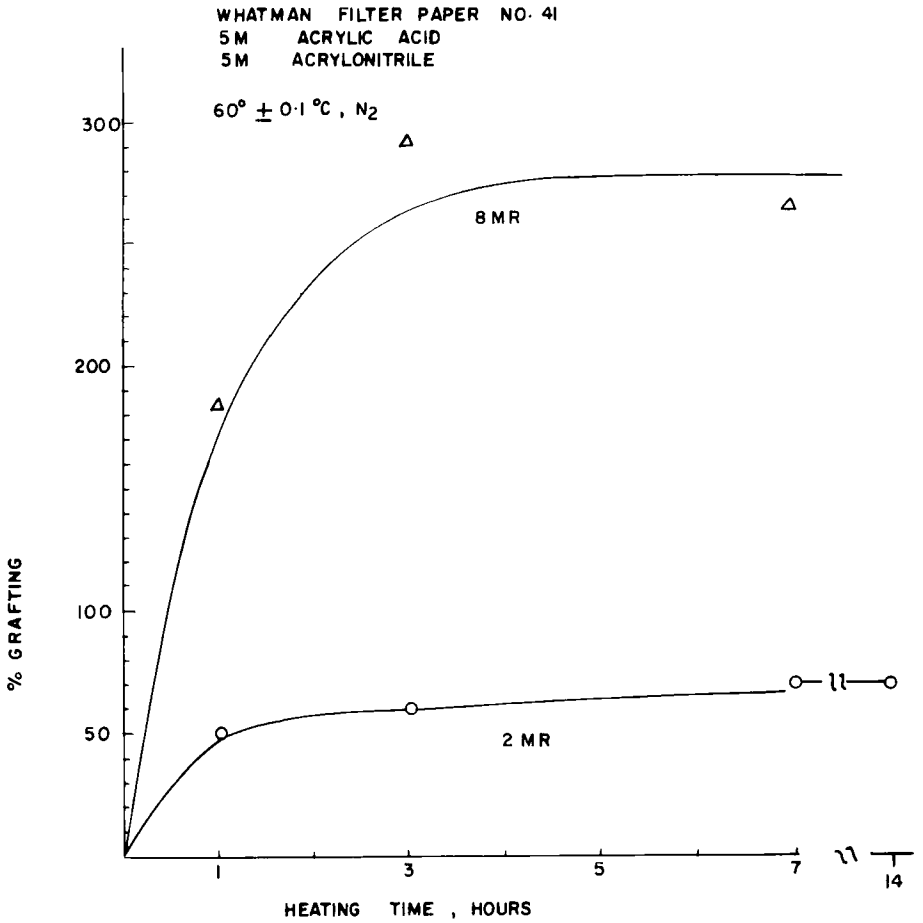

FIG. 3. Effect of heating time on grafting.

The contents of AA and AN in the grafted samples obtained with varying monomer ratio are given in Table 1 and the dashed line in Fig. 4. The extents of AA and AN grafting on the cellulose are seen to be proportional to their concentrations in the monomer mixture.

The nature and composition of the graft copolymer are being studied further and will be reported later.

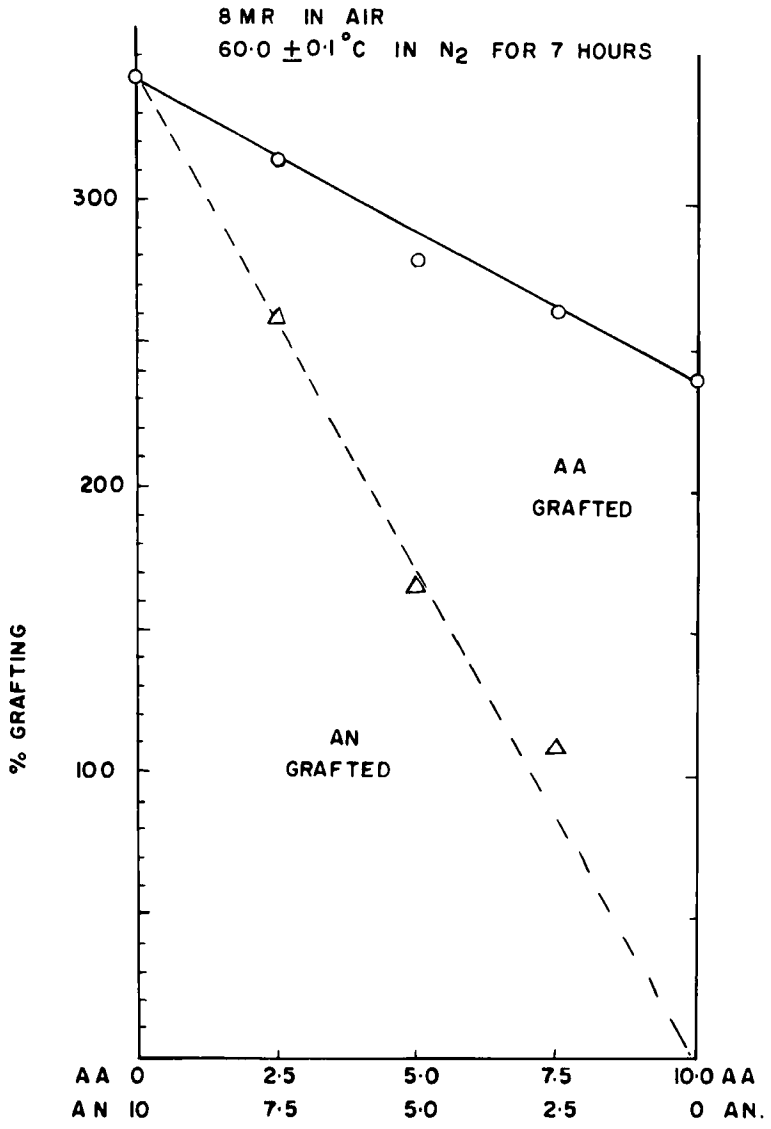

FIG. 4. Effect of comonomer composition on grafting.

TABLE 1. Effect of Monomer Composition

Monomer molar concentration in feed		Composition of grafted cellulose, %		
AA	AN	P(AA)	P(AN)	Total % grafting
0	10.0	0	343	343
2.5	7.5	53	261	314
5.0	5.0	112	168	280
7.5	2.5	154	108	262
10.0	0	239	0	239

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