

Postirradiation Polymerization of Acrylic Acid and Vinyl Pyrrolidinone on Polypropylene

Limited research work on γ -irradiation polymerization of various monomers on polypropylene (PP) has been published. Among the polymerization studies, either preirradiation^{1,2} or mutual^{3,4} irradiation processes were employed to polymerize such monomers, as acrylamide,² acrylic acid,² acrylonitrile,³ ethyl acrylate,³ methyl acrylate,³ methyl methacrylate,⁴ vinyl acetate,³ 4-vinyl pyridine,¹ and 1-vinyl-2-pyrrolidone.² In a more recent study,⁵ a modified mutual irradiation technique was found to be very effective in polymerizing acrylic acid, methyl acrylate, and methyl methacrylate in PP fibers. This modified procedure employs the immersion of substrates in a concentrated monomer for a prolonged period of time prior to the mutual irradiation of substrates in a dilute solution of the same monomer.

Very little information is available in the literature on postirradiation polymerization of monomers on PP. Previous research has indicated that *n*-butanol could serve as a swelling agent to promote acrylic acid incorporation in PP.⁵ *n*-Butanol, however, was found not to improve the polymerization yield of acrylic acid in the modified mutual irradiation procedure. In a postirradiation process, the ultimate polymerization yield is limited to the available monomer in the substrate. The effect of a swelling agent on monomer retention in the host substrate can be an important consideration in postirradiation polymerization. This note elucidates data on the postirradiation polymerization of acrylic acid (AA) and vinyl pyrrolidinone (VP) on PP and examines the role of *n*-butanol on the polymerization.

The material studied was polypropylene fabric from Testfabric, Inc. The fibrous substrates were rinsed with distilled water and dried in a vacuum oven at 60°C overnight. The initial dry weight W_i was obtained after drying in a vacuum oven at 105°C for 2 h. The swelling treatments were performed in a temperature-controlled silicone oil bath. Excess solvent was removed by blotting the specimens between filter paper to obtain the solvent incorporated weight W_s .

Acrylic acid was purified by passing through activated neutral alumina. The stabilizer in VP was filtered through #50 Wattman paper. The samples were then immersed in concentrated monomer solutions for predetermined time periods. A 10:1 monomer-sample ratio, (milliliters per gram), based upon the initial sample weight, was employed. The samples were again blotted and weighed to obtain the monomer incorporated weight W_m .

Each sample was immediately placed in a test tube, flushed with nitrogen for 30 min, and stoppered. Polymerization was induced by a cobalt 60 γ source. A total dose of 3.0 Mrad was obtained by irradiating at a dose rate of 9.2 rad/s for 4 days. Immediately after irradiation, samples were first rinsed and then extracted with proper solvents for 4–6 h. Methanol was used to extract specimens polymerized with AA, whereas water was used to extract those modified with VP. The polymerized weight W_p was measured after each sample was dried at 60°C overnight and at 105°C for 2 h in a vacuum oven. The polymerized samples were then conditioned at 21°C and 65% RH for 4 days to get the conditioned weight W_c .

The solvent uptake δW_s , monomer uptake δW_m , polymerization yield P , and moisture regain MR were calculated according to

$$\delta S, \% = \frac{W_s - W_i}{W_i} \times 100\%$$

$$\delta M, \% = \frac{W_m - W_i}{W_i} \times 100\%$$

$$P, \% = \frac{W_p - W_i}{W_i} \times 100\%$$

$$MR, \% = \frac{W_c - W_p}{W_i} \times 100\%$$

All polymerization data reported were averages of five specimens with their standard deviation values in parentheses. A total of 10 specimens were used in determining the tensile properties of single fibers.

n-Butanol was used as a swelling agent in the postirradiation process. Monomer exchange periods were evaluated for both AA and VP at 4 and 6 days (Table I). The shorter exchange time, that is, 4 days, was sufficient for either monomer. The polymerization yield of AA in PP yarns by postirradiation (60–69%) came out to be similar to those by the modified mutual irradiation (58–67%).⁵ However, the moisture regain values by the postirradiation method is about one-half of those by mutual irradiation. These differences in MR indicate that there may be differences in how AA polymerized in the yarns in the two processes.

Figure 1 shows the scanning electron micrographs (SEM) of PP fibers polymerized with AA and VP after *n*-butanol treatment. Heavy coatings on the fiber surfaces are apparent and similar with both monomers. Though polymerization yields of VP were slightly less than those of AA, VP resulted in much higher *MR* values than AA. This is consistent with the more hydrophilic nature of VP than AA.

n-Butanol was then eliminated in postirradiation polymerization of AA and VP in PP yarns and fabrics. Without any solvent pretreatment, substantial *P* and *MR* values were also obtained by postirradiation (Table II). Higher *M*, *P*, and *MR* values on yarns than on fabrics may reflect the better monomer accessibility of the yarns. Even though the addition of *n*-butanol increased *P* tremendously, *MR* was only slightly better than when *n*-butanol was not used. Surface morphology by SEM did not show any noticeable difference whether *n*-butanol treatment was used or not. It is thought that there may be a very high extent of cross-linkage among the newly formed AA or VP polymers when *n*-butanol was present, thus reducing the attraction to water moisture.

Single-fiber tensile properties of polypropylene fibers were also examined (Table III). Breaking load and elongation were slightly lowered by the polymerization of VP. The yield load and yield elongation were considerably decreased. The difference between the polymerized substrates whether they were solvent treated or not was not apparent. It is thought that the tensile properties are mostly affected by the polymerization process but little by the solvent treatment. The considerably lower load and extension at yield suggest that polymerization occurs in the amorphous regions of the fibers, with possible cross-linking.

In summary, the choice of a polymerization procedure is important in obtaining a high polymerization yield of VP and AA in polypropylene fibers. The use of a swelling agent, *n*-butanol, was effective in increasing both monomer uptake and polymerization yield by postirradiation but only increased the moisture regain slightly more than when *n*-butanol was absent. The postirradiation technique, which resembles a pad-cure textile finishing process, is the simplest procedure and also produces reasonably good polymerization yield and moisture regain values. The untreated PP yarns do not absorb moisture at all. Postirradiation poly-

TABLE I
Polymerization of AA and VP on PP Yarns After 4 and 6 Days of Monomer Exchange Periods^a

Monomer		δS^b	δM	<i>P</i>	<i>MR</i>
Type	Days exchange				
AA	4	58.7 (19.3)	86.2 (12.2)	68.5 (1.3)	2.82 (0.3)
	6	59.2 (11.4)	92.9 (7.0)	60.0 (3.9)	2.69 (0.07)
VP	4	67.7 (16.1)	81.1 (6.2)	58.2 (0.8)	6.97 (0.7)
	6	49.6 (2.6)	65.4 (9.4)	49.2 (7.8)	6.83 (1.1)

^a Yarns were treated with *n*-butanol at 80°C for 30 min.

^b *S* denotes the percentage of solvent incorporation with respect to the substrate weight.

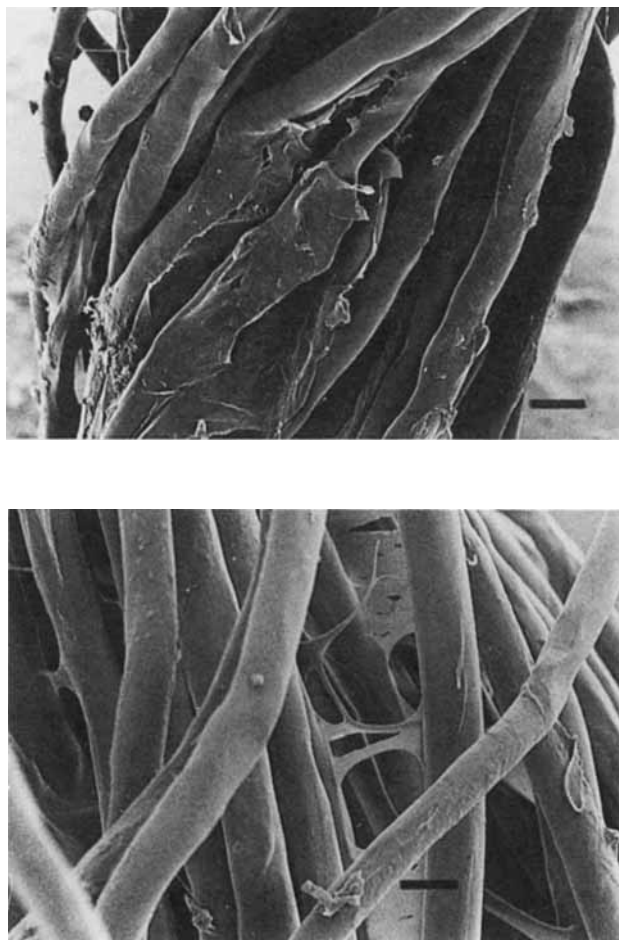


Fig. 1. PP fibers polymerized after *n*-butanol treatment. (a) With VP; bar = 39 μm . With AA; bar = 24 μm .

TABLE II
Polymerization of AA and VP on Yarns and Fabrics Without Solvent Treatment^a

		δM	P	MR
AA	Yarn	59.2 (0.8)	32.0 (9.5)	2.23 (0.41)
	Fabric	46.5 (3.3)	22.6 (8.7)	1.72 (0.46)
VI	Yarn	76.6 (28.9)	44.8 (15.8)	5.38 (0.87)
	Fabric	49.0 (6.1)	12.0 (7.2)	2.59 (1.00)

^a Monomer exchange time is 2 days.

TABLE III
Single-Fiber Tensile Properties of Modified^a Polypropylene Fabrics

Solvent treatment	Monomer	Breaking load (g)	Breaking extension (%)	Yield load (g)	Yield extension (%)
None	None	16.6 (1.4)	25.5 (4.5)	8.6 (0.9)	9.7 (1.5)
None	VP	15.2 (0.7)	21.1 (5.2)	2.4 (0.5)	2.1 (2.4)
<i>n</i> -Butanol ^b	VP	14.5 (0.3)	22.1 (3.7)	2.5 (0.2)	2.6 (1.5)

^a Irradiation at 3.0 Mrad.

^b At 100°C for 30 min.

merization of AA improves the *MR* of PP yarns to 2.2%, whereas that of VP on PP yarns resulted in a much higher value of 5.4%. The modified mutual-irradiation technique⁵ approximately doubled both polymerization yield and moisture regain compared with postirradiation polymerization of AA onto PP fibers, but it is also a more lengthy process than the postirradiation process.

References

1. S. Munari et al., *Eur. Polym. J.*, **4**, 241 (1968).
2. S. Sundari, *J. Appl. Polym. Sci.*, **22**, 3163 (1978).
3. A. A. Armstrong, Jr., and W. K. Walsh, Modification of Textile Fiber Properties by Radiation-Induced Graft Polymerization, Office of Technical Services, Dept. of Commerce, Washington, D.C., 1962.
4. B. J. Burchill, D. M. Pinkerton, and R. H. Stacewicz, *J. Polym. Sci. Symp.*, **55**, 303 (1976).
5. C. Pugh and Y.-L. Hsieh, *J. Appl. Polym. Sci.*, **29**, 3641 (1984).

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