# Reactor of Vapor-Phase Graft Polymerization of Reactive Monomer onto Porous Hollow Fiber

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*A novel reactor for the modification of a porous hollow-fiber membrane up to 1 m in length is presented. The polyethylene hollow fiber irradiated with an electron beam was exposed to the vapor of an epoxy-group-containing vinyl monomer (glycidyl methacrylate) in a cylindrical reactor rotated at 1 rpm. Construction of the hollow fibers resulted in a diffusion-controlled reaction system, which led to the nonuniformity of degree of grafting (dg), whereas the shuffling of the hollow fibers by rotating the cylindrical reactor provided a higher reactivity (dg = 110% for 100 min at 300 K) and uniformity (standard deviation = 4.5%) of dg.*

## Introduction

Radiation-induced graft polymerization (RIGP) is a convenient and powerful technique for modifying existing polymeric materials in that a wide range of shapes and qualities of polymers can be selected as a trunk polymer. By adopting this technique, we have to date prepared a modified porous membrane with novel surface characteristics, which collect metal ions (Konishi et al., 1992) and proteins (Shinano et al., 1993) while allowing liquid to permeate across the membranes through the pores. RIGP can be classified based on three factors: (1) irradiation source: electron beam (EB) or gamma rays; (2) irradiation opportunity: simultaneous or preirradiation grafting; and (3) monomer phase: vapor or liquid phase. Preirradiation grafting is advantageous in that it enables us to separate the two processes of irradiation and graft polymerization. We demonstrated that the radicals produced in polyethylene with EB irradiation can be stored by freezing the irradiated polyethylene below its glass transition temperature, and that the alkyl radicals can contribute to the initiation of graft polymerization (Uezu et al., 1992).

The trunk polymer irradiated with an EB is contacted with a precursor monomer and chemically modified to add the desired functional moiety. An epoxy-group-containing vinyl monomer of glycidyl methacrylate (GMA) is a feasibly convenient precursor monomer because of its high reactivity and stability (Kalal et al., 1974). The GMA-grafted membrane can be converted into a variety of specialized membranes by simple reactions of the epoxy group with amines, acids, and water: chelating membranes (Yamagishi et al., 1991), ion-exchange membranes (Tsuneda et al., 1994, 1995), pseudo-affinity membranes (Iwata et al., 1991), and hydrophilized membranes (Kim et al., 1994) are obtainable. Figure 1 shows a schematic diagram of the procedure used to prepare specialized materials by the RIGP.

In this study, we propose a novel reactor to graft-polymerize a reactive monomer onto a porous hollow-fiber membrane in vapor phase. No reports have been published on the design of the reactor for vapor-phase graft-polymerization onto a hollow-fiber trunk polymer. The reactor was designed in order to achieve uniformity of the polymer branches grafted onto the hollow fiber along its length. A porous polyethylene hollow fiber and GMA were used as a trunk polymer and a reactive monomer, respectively.

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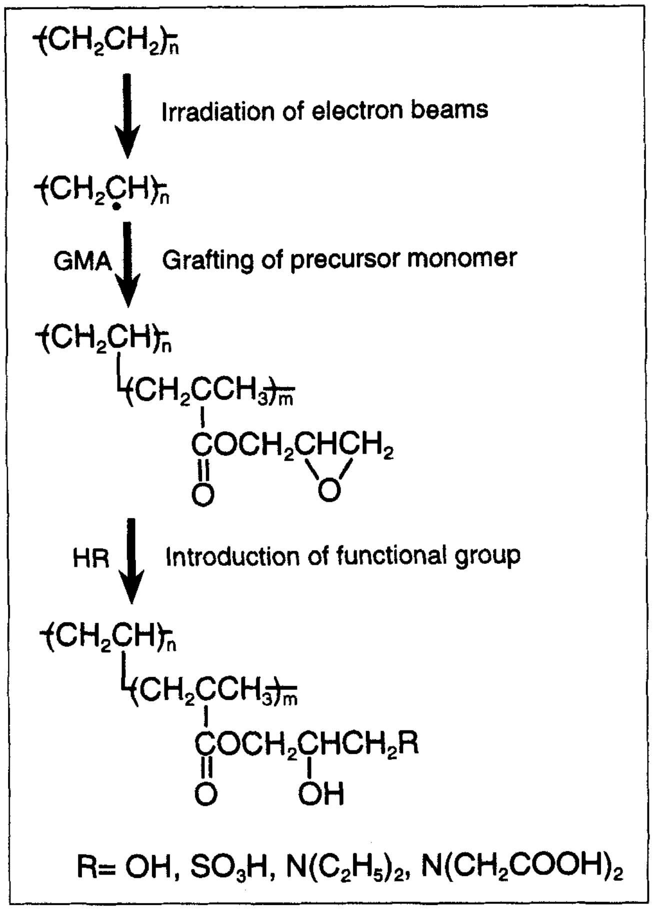

**Figure 1. Specialized membranes by radiation-induced polymerization.**

## Experimental Procedure

### *Materials*

A porous polyethylene (PE) hollow fiber (Asahi Chemical Industry Co., Ltd., Japan) was used as a trunk polymer for grafting. This hollow fiber is used industrially for microfiltration of suspended solids and bacteria, and so forth. The inner and outer diameters of the hollow fiber were 1.95 and 3.01 mm, respectively, with a porosity of 72% and nominal pore diameter of 0.34 microns. GMA ($CH_2 = CCH_3COOCH_2CHOCH_2$) was purchased from Tokyo Kasei Co., Japan, and used without further purification.

### *Reactor and grafting procedures*

The PE hollow fibers were irradiated with an EB from a cascade-type accelerator (Dynamitron, IEA-3000-25-2, Radiation Dynamics, Ltd.) at ambient temperature in nitrogen atmosphere. The accelerator was operated at a beam energy of 2.0 MeV and a current of 1 mA. The dose was 160 kGy. Immediately after EB irradiation, the hollow fiber was stored at 233 K in a freezer to reduce decay of the radical concentration (Uezu et al., 1992). Graft polymerization of GMA onto the hollow fibers was initiated within 24 h after EB irradiation.

An illustration of a novel reactor for vapor-phase graft polymerization is shown in Figure 2. The cylindrical main body of the reactor was made of Pyrex glass with an inner diameter of 11. 5 cm and 120 cm long. A driving roll and two back-up rolls made of rubber were used to rotate the cylinder at 1 rpm. An approximately 1-mm-mesh cylindrical cage made of polypropylene, of diameter 7 cm, was positioned coaxially with the cylinder. This cage held the irradiated hollow fibers. Nonwoven fabric, which was made of 5-mm thick polypropylene (Mitsubishi Kasei Co., Ltd., Japan), was applied to the entire surface of the inner wall of the cylinder to ensure a constant evaporation area for GMA monomer during graft polymerization. GMA liquid (200–300 mL) in a glass ampule was degassed for 5 min using a vacuum pump, and subsequently transferred to the cylinder. The GMA liquid was uniformly blotted on the nonwoven fabric. Graft polymerization in vapor phase was initiated at an ambient temperature (295–300 K).

Table 1 summarizes the reaction and operating conditions for each trial. After a prescribed time (0.42–2.5 h), the hol-

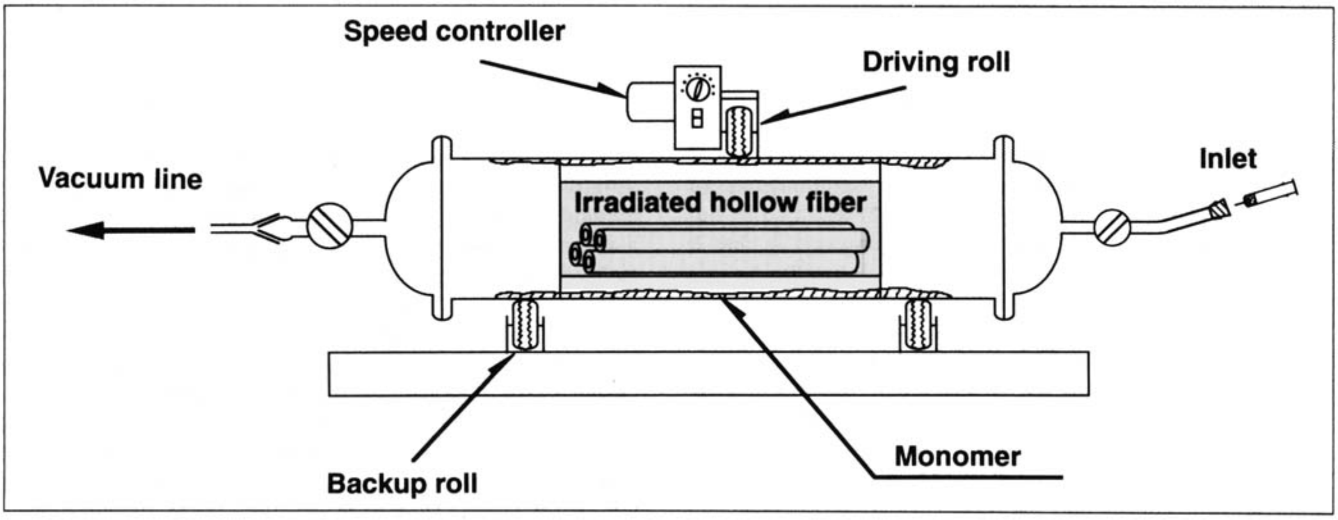

**Figure 2. Novel reactor for vapor-phase graft polymerization.**

**Table 1. Reaction and Operating Conditions of Vapor-Phase Graft Polymerization**

| | |
|---|---|
| Reaction temperature | 295–300 K |
| Reaction time | 0.42–2.5 h |
| Hollow fibers charged | |
| Number | 25–300 |
| Length | 10, 25, 100 cm |
| Rotation rate of reactor | 1 rpm |
| Initial amount of monomer | 200–300 mL |

low fibers were removed from the cylinder and immersed in dimethylformamide (DMF) for 2 h to remove traces of homopolymer. After repeated washing with methanol, the hollow fibers were dried under reduced pressure and weighed. The degree of GMA grafting ($dg$) was defined as

$$dg(\%) = 100 \frac{\text{wt. of grafted polymer}}{\text{wt. of trunk polymer}} = 100 \frac{W_1 - W_0}{W_0}, \quad (1)$$

where $W_0$ and $W_1$ are the weights of the original and resultant hollow fibers, respectively.

### *Grafting onto bundled hollow fibers*

A bundle of hollow fibers, 10 or 25 cm long, was placed in the reactor cage. The details of the bundle are denoted by ($L/N$), where $L$ and $N$ are the length and number, respectively, of the hollow fibers charged. The number of hollow fibers in the bundle ranged from 20 to 300. The filling factor ($ff$), defined as the ratio of the number of hollow fibers to the corresponding number of closely packed hollow fibers, ranged up to 1. Examples of cases of various $ff$'s for the bundled hollow fibers are illustrated in Figure 3a. After the reaction for a prescribed time (0.42–2.5 h), the grafted hollow fibers were partitioned in the radical direction of the bundle and each fraction was weighed. For normalization, the radial profile of $dg$ was divided by the $dg$ of the outermost layer of the bundle.

To prevent radial diffusion of the monomer, a bundle of hollow fibers was wrapped with nonporous PE film of 25-micron thickness (Mitsubishi Rayon Co., Ltd., Japan). Vaporized GMA entered the bundle exclusively from both ends. The bundle of GMA-grafted hollow fibers was axially cut in 1-cm lengths, and the weight of each was measured.

### *Grafting onto hollow fibers without bundling*

GMA was grafted onto the hollow fibers in the cage without bundling (Figure 3b). The uniformity of the $dg$ of the resultant hollow fibers was evaluated by calculating the standard deviation (SD) defined as

$$(\text{SD}) = \left\{ \frac{1}{N} \sum_{i=1}^{N} (dg_i - \overline{dg})^2 \right\}^{1/2}, \quad (2)$$

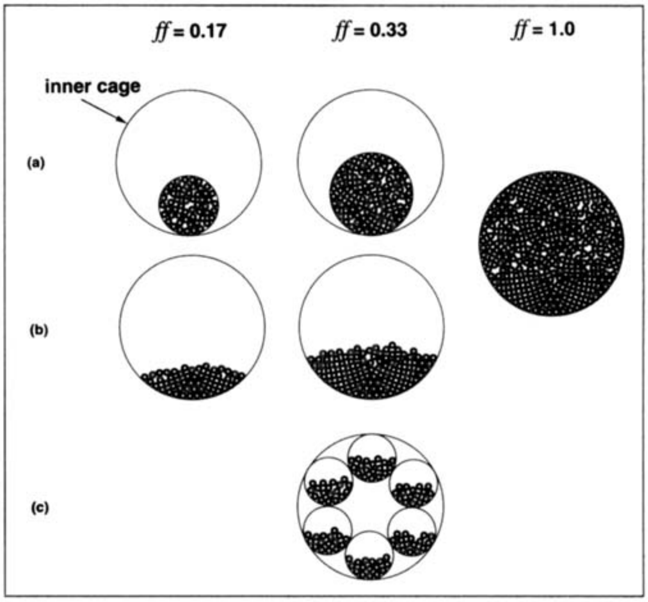

**Figure 3. Loading patterns of hollow fibers.**

(a) Bundled hollow fibers. (b) Hollow fibers without bundling. (c) Hollow fibers divided into six cages.

where $\overline{dg}$ is the averaged $dg$, and $N$ is the total number of the hollow fibers. The initial length of the original hollow fiber was set to 25 or 100 cm. Because grafting caused stretching of the hollow fiber, a cage that was 10% longer was used. Also, the 100-cm-long hollow fibers were divided into six cylindrical mesh cages 2-cm in diameter to keep the rotation of the cylindrical reactor (Figure 3c) from twisting the hollow fibers.

## Analysis

The bundle of the irradiated hollow fibers was regarded as a cylinder with radius and length $R$ and $L$, respectively. Five assumptions were adopted for brevity of analysis:

1. A steady concentration profile of the vaporized monomer is achieved.
2. The axial profile of the monomer concentration is uniform.
3. The overall rate of graft polymerization, $R_A$ [g/(kg·s)], obeys a first-order relationship with monomer concentration, $C_A$ [g/m$^3$]:

$$R_A \rho = k_1 C_A, \quad (3)$$

where $k_1$ [1/s] is the overall reaction-rate constant and $\rho$ [kg/m$^3$] is the density of the trunk polymer. We adopted gram of grafted polymer per kg of the trunk polymer per second as the unit of $R_A$.

4. The system is isothermal.
5. The diameter and length of the bundle are constant.

The following equation describes the concentration profile of the monomer in a cylindrical reactor for vapor-phase graft polymerization:

$$\frac{d^2C_A}{dr^2}+\frac{1}{r}\frac{dC_A}{dr}-\frac{k_1}{D_e}C_A=0, \tag{4}$$

where $D_e$ is the effective diffusion coefficient of the monomer in the bundle.

Boundary conditions are

$$\text{at}\quad r=0\qquad \frac{dC_A}{dr}=0 \tag{5}$$

$$\text{at}\quad r=R\qquad C_A=C_{A0}, \tag{6}$$

where $C_{A0}$ is the monomer concentration on the surface of the bundle. The equation was analytically solved:

$$C_A=C_{A0}\frac{I_0\left(\Lambda\frac{r}{R}\right)}{I_0(\Lambda)} \tag{7}$$

$$\Lambda=\sqrt{\frac{k_1}{D_e}}R, \tag{8}$$

where $I_0$ is the modified Bessel function of the first kind.

## Results and Discussion

### *Overall rate of graft polymerization*

Figure 4 shows the *dg* for the hollow fiber located in the outermost shell of the bundle (10/52) as a function of reaction time. A constant grafting rate in this range of reaction times indicated that monomer concentrations were constant on the outermost shell of the bundle. Therefore the boundary condition of Eq. 6 was experimentally satisfied. A *dg* of about 200%, which means that the hollow fiber has tripled in weight, was obtained after a reaction time of 150 min. The formation of the polymer branches in the matrix of the trunk polymer induced swelling of the entire volume, resulting in retention of the porous structure of the hollow fibers.

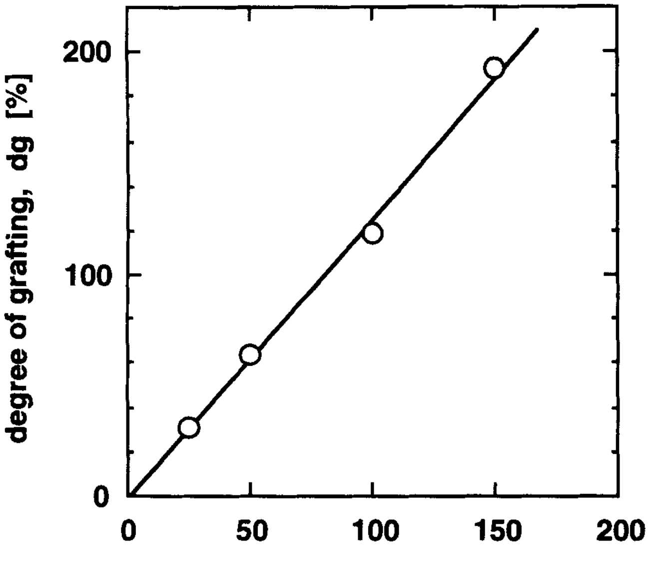

**Figure 4. Degree of grafting for the hollow fiber located in the outermost shell of the bundle (10/52) as a function of reaction time.**

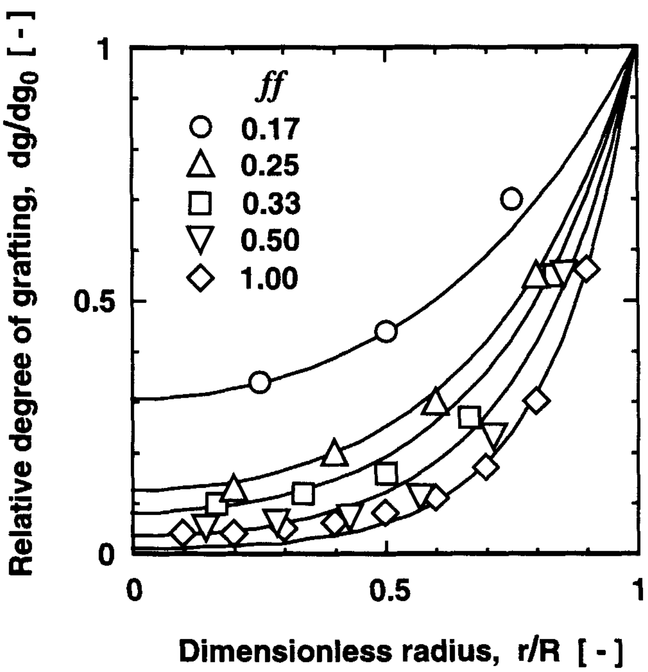

**Figure 5. Radial profile of degree of grafting for the bundle (25/*N*).**

### *Analysis of dg distribution in bundled hollow fibers*

An axial profile of *dg* for the bundle (10/52) was determined by wrapping the bundle with a nonporous polyethylene film, which was capable of preventing the radial diffusion of the monomer into the bundle. GMA was grafted from both ends onto the only 2-cm-depth of the hollow fibers with a low *dg* of 20%. In practice, the contribution of the axial diffusion of the monomer to grafting at both ends will be negligible because the hollow fibers are as long as 1 m.

A radial profile of *dg* for the bundle (25/*N*) is shown in Figure 5, where the number of the hollow fibers, *N*, ranged from 10 to 100. Since the overall rate of graft polymerization is assumed to be proportional to the monomer concentration, the profile of *dg* in the bundle is equivalent to that of the monomer concentration. The theoretical curve (solid line) calculated by Eq. 7 as shown in Figure 5 was fitted to the data to obtain the value of Λ. The ratio of the reaction-rate constant to the effective diffusion coefficient of vaporized GMA, ($k_1/D_e$), is tabulated for each trial in Table 2. The ratio $k_1/D_e$ was almost constant and independent of the number of hollow fibers. This indicates that the reaction model suggested here was applicable. From the following, the $D_e$ of GMA in the bundle was estimated to be $1.8\times10^{-3}$ $m^2/s$:

Table 2. Ratio of the Reaction-Rate Constant to the Effective Diffusion Coefficient of GMA

| $N$ | $ff$ | $R$ $\times 10^2$ m | $\Lambda$ | $k_1/D_e$ $\times 10^{-4}$ $\mathrm{m}^{-2}$ |
|---|---|---|---|---|
| 50 | 0.17 | 1.22 | 2.5 | 4.2 |
| 75 | 0.25 | 1.48 | 3.6 | 5.9 |
| 100 | 0.33 | 1.72 | 4.1 | 5.7 |
| 150 | 0.50 | 2.08 | 5.0 | 5.8 |
| 300 | 1 | 2.98 | 6.4 | 4.6 |

$$D_e = \{\epsilon + (1-\epsilon)(\epsilon_p/\tau)\} D_{AA} \qquad (9)$$

where the void fraction including lumen of the bundle, $\epsilon = 0.68$; porosity of the original hollow fiber, $\epsilon_p = 0.72$; tortuosity estimated from the flat membrane with the same porous structure, $\tau = 3.6$; and self-diffusion coefficient of GMA, $D_{AA} = 2.48 \times 10^{-3}$ $\mathrm{m^2/s}$ at 300 K (Brodkey and Hershey, 1988). The tortuosity of the bundle was assumed to be unity. Thus, the overall reaction-rate constant, $k_1$, was 36 $\mathrm{s^{-1}}$ at 300 K.

### *Improvement of uniformity by shuffling hollow fibers*

The fixed location of the hollow fibers in the bundle caused the radial distribution of the monomer concentration, resulting in nonuniformity of *dg*. There are two approaches to overcoming this problem: (1) establishment of the reaction conditions with a lower value of $k_1/D_e$, and (2) shuffling the hollow fibers in the reactor. A lower value of $k_1/D_e$ results in a lower production rate of the specialized porous membrane, which is not practical; therefore, we chose shuffling the irradiated hollow fibers by rotating the cylindrical reactor. Figure 6 shows the *dg* distribution for shuffling the hollow fibers, compared to that for bundling of the hollow fibers. By attaining greater uniformity, the dispersion of *dg* was clearly improved by shuffling. The averaged *dg* also increased markedly. The SD of *dg* is shown in Figure 7 as a function of *ff*. Uniform preparation was attainable below $ff = 0.3$, where the hollow fibers were satisfactorily shuffled in the reactor as judged by direct observation.

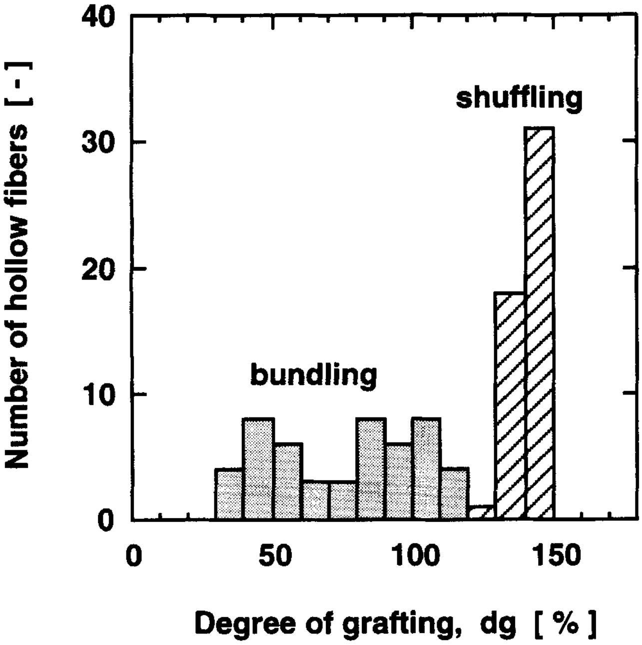

Figure 6. Degree of grafting distribution: bundling vs. shuffling.

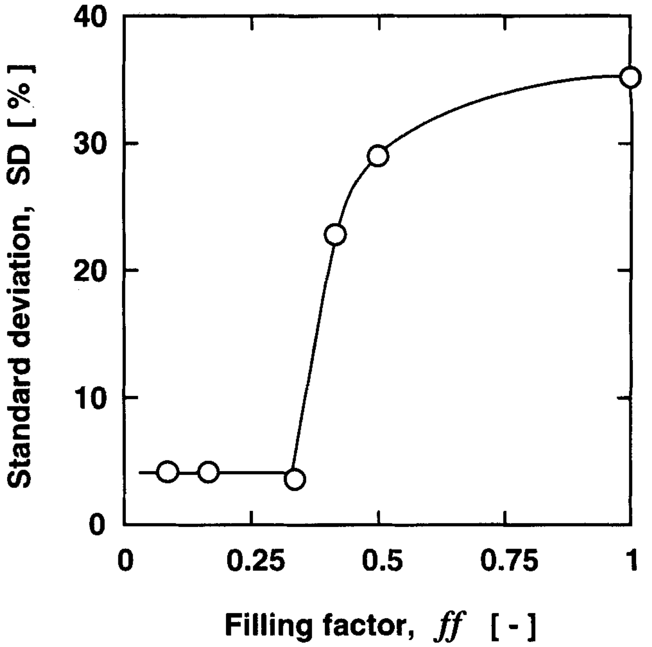

Figure 7. Standard deviation of degree of grafting for shuffling hollow fibers as a function of filling factor.

For practical use, the membrane module requires a minimum length of 1 m and SD of less than 10%. However, shuffling the hollow fibers of 1 m length by rotating the cylindrical reactor causes the hollow fibers to twist during graft-polymerization. To overcome this drawback, the internal cage was partitioned by six additional cages with smaller diameters. The hollow fibers were charged into each cage at $ff = 0.67$. The averaged *dg* and SD were 92% and 8.8%, respectively, which meets the requirements for a commercial reactor for vapor-phase graft polymerization.

## Acknowledgment

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## Notation

$dg_0$ = degree of grafting at the outermost shell of the bundle, %
$r$ = radial coordinate, m
$t$ = reaction time, s

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