NOTE

Graft Polymerization of Acrylic Acid onto Silicone Rubber Film by Preirradiation Method

INTRODUCTION

The graft polymerization reaction is a well-established method for modification of the chemical and physical properties of the polymeric matrix. Graft polymerization is also of particular interest for achieving specifically desired properties as well as for excellent membrane quality, since various commercial polymers can be used as the grafting substrate. Graft polymerization can be achieved by many methods, such as ionizing, UV, and chemical initiators. Of these, radiation grafting is one of the most promising methods since its large penetration in the polymer matrix and its rapid and uniform formation of active sites in the polymer for initiating a graft reaction occurs throughout the matrix.

Many studies have been done in our laboratory[1-6] in the application of induced graft polymerization by Co-60 γ-ray radiation and plasma treatment for generating functional polymeric membranes. The silicone rubber-*g*-poly(acrylic acid) graft copolymer (SR-*g*-AA) was never prepared or found before in the literature using the radiation graft method. In this investigation, high % graft SR-*g*-AA via the preirradiation graft method was obtained by the addition of iron powder. The % graft of acrylic acid in this investigation was compared with that of Mohr's salt system.[7,8]

EXPERIMENTAL

Film Preparation

Silicone rubber (SR) (Dow Corning HC-595, SR-A, and SR-B) was used for the film preparation. The SR-A/chloroform solution and SR-B/chloroform solution (1/15 by weight) was mixed with a stirrer and then extracted quickly by a glassy filter. The solution was then cast onto a glass plate. After slowly evaporating the solvent, the glass plate with SR was heated under 100°C for 30 min. The SR film was obtained by releasing the membrane in water and then dried at 100°C.

Graft Polymerization

The weighed SR films were irradiated in air at room temperature with a Co-60 γ-ray source at the Isotop Center in National Tsing Hua University. Graft reactions were performed by the method of Ishigaki et al.[7,8] One of the reaction kettles contained 50% acrylic acid aqueous solution and 0.25% Mohr's salt (ferrous ammonium salt). The other reaction kettle was the same as the previous one except that 0.25% of element iron powder was added. The monomer solution in the reaction kettle was deaerated by bubbling purified nitrogen. The kettle was then immersed in a thermostated water bath at 100°C. The reaction proceeded for 6 h. The acrylic acid-grafted SR film was purified by thoroughly cleaning in warm water with an ultrasonic cleaner and then dried under reduced pressure at 60°C for 48 h. The degree of grafting was calculated as follows:

$$\% \text{ Graft} = \frac{W_1 - W_0}{W_0} \times 100\%$$

where W_0 is the initial weight of the parent SR film, and W_1, the weight of acrylic acid-grafted SR film.

RESULTS AND DISCUSSION

The infrared spectra of the SR film (curve A) and the 6.25% graft SR-*g*-AA (curve B) are shown in Figure 1. A strong band absorption of the C=O band emerged at 1720 cm^{-1} and a broad absorption of the C—O band is shown at 1000–1300 cm^{-1} at curve (B). It indicated a successful structural modification of acrylic acid onto the SR matrix by the preirradiation graft method.

A high % graft of SR-*g*-AA film was obtained in the reaction system that contained iron powder in the monomer solution. As shown in Figure 2, a higher than 80% grafted SR-*g*-AA film could be prepared. It is important to note that this high % graft is 10 times higher than that of the one without the addition of iron. The iron powder in the monomer solution would react with acrylic acid in the graft polymerization step and generated ferrous acrylate, which was observed by the green color of the solution and the H_2 gas. Though the ferrous acrylate was another source of Mohr's salt, the increasing of the Mohr's salt concentration would definitely decrease the final %

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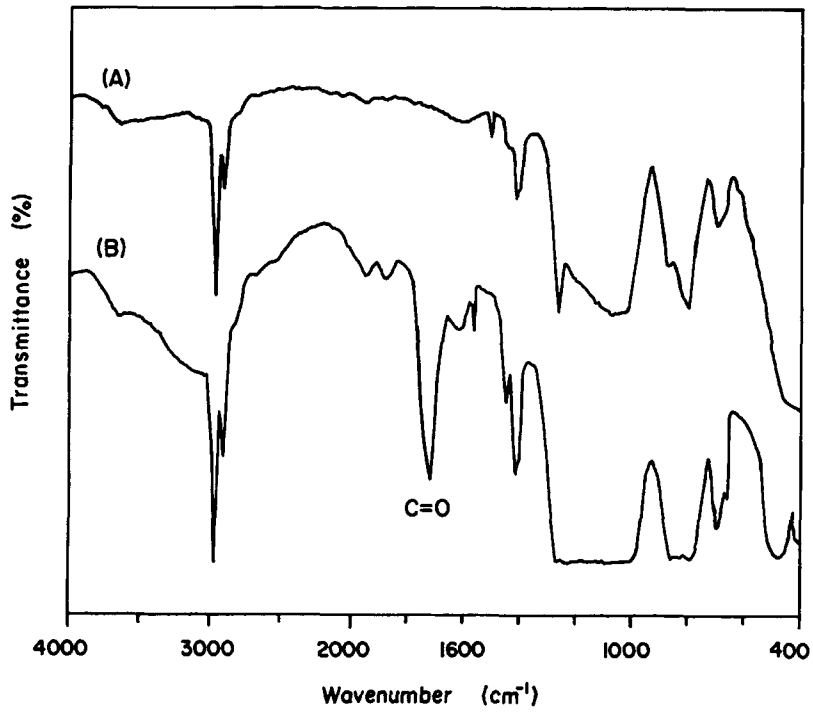

Figure 1 The infrared spectra of (A) SR film and (B) SR-*g*-AA film.

graft.[8] The increased amount of % graft in this system, therefore, resulted from the acrylate ion or the ferrous acrylate ion pair. Because of that, the activity of acrylic acid in graft polymerization would be greatly enhanced.

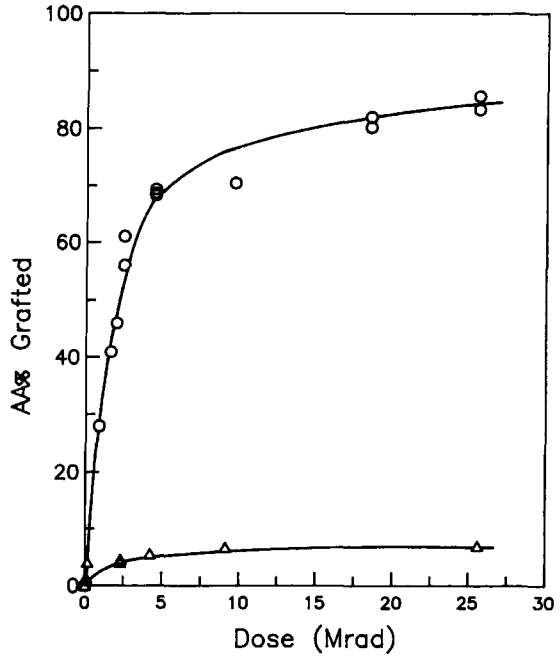

Figure 2 The % graft of acrylic acid on SR film vs. total irradiation dose: (△) 0.25% Mohr's salt; (○) 0.25% Mohr's salt and 0.25% iron powder.

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