

Photoinduced Acrylamide Graft Polymerization onto Extended Hard Elastic Polypropylene

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Synopsis

Hard elastic PP films were graft polymerized with PAAm, using a photoinduction method derived by Tazuke. The graft yield (GY) was measured as a function of extension applied to the PP film during the polymerization. The GY increased stepwise when the extension increased above the yield point. This remarkable increase in GY is due to the fact that the surface of voids created by extension are involved in the graft polymerization. The GY obtained under extensions larger than the yield point was much larger than that ever achieved for the usual PP films. The residual strain after the graft polymerization increased with increase in GY, and the relationship between them changed at about 40% GY, suggesting that some change occurred in the location of grafted PAAm in PP films. The graft ratio, determined after complete extraction of PP and PAAm homopolymers, remained nearly constant with polymerization time, except at the early stage of the polymerization. The effect of extension on the graft ratio implied that the size of the voids may affect the degree of polymerization of graft PAAm when the size is comparatively small.

INTRODUCTION

Polypropylene (PP) films and fibers prepared by melt spinning under high extension force and subsequent annealing at high temperatures are called "hard elastic" ones, for they have an extraordinarily high reversible extensibility in the direction of their length,¹ that is, they can be extended more than 100% with only a few percent residual strain at room temperature, as will be shown later. In addition to high elasticity, hard elastic materials have another particular property that the value increases markedly with extension; in some cases the volume increases approximately linearly with the extension ratio. This extraordinary volume increase due to the creation of voids has been revealed by small-angle x-ray scattering,²⁻⁴ gas permeability,⁵ and form birefringence.⁶

In our previous investigation, the gas permeation of hard elastic PP film was measured as a function of extension to study how the voids created by extension act in gas permeation. We are interested in the photoinduced graftpolymerization onto PP which has been developed by Tazuke and his co-worker.⁷⁻⁹ According to them, the graft yield achieved by their method was so small that quantitative estimation was impossible, although even a small amount of graft polymer changes remarkably the surface property of the film. If the graft polymerization is made for hard elastic PP films under extension, the voids created by extension may participate in the polymerization as well as the outer surface. Since the total area of the void surface is enormous, the graft yield must increase markedly with extension. This may make the quantitative study of the graft polymerization possible, which has been difficult to do because of too small a graft yield. On the other hand, the chemically modified void surface must

change the permeation property of the film. We therefore expect that the permeation properties of the film can be widely controlled by changing the void size (extension ratio) and the degree of chemical modification. In the present article, the effect of extension on the graft polymerization is studied, and the effect of the permeation properties will be studied in a subsequent investigation.

EXPERIMENTAL

Preparation of Hard Elastic Film

A film 10 μm thick and 25 mm wide was prepared from molten isotactic PP (Sho-Allomer, MG-210) by use of an extruder equipped with a T-die. This film, as prepared, had a high degree of crystal orientation which is necessary for hard elastic materials, but not the maximum elasticity. In order to enhance the elasticity, the film was annealed at 130°C for 1 h in a circulating-air thermostat with the length of the film kept constant. The annealed film was highly elastic, as is shown by the stress-strain curve (A) in Figure 1. The density of the sample was 0.905 g/cm^3 at 25°C in a density gradient tube of ethylene glycol/isopropyl alcohol mixture. Prior to the graft polymerization, the sample was washed with acetone repeatedly.

Graft Polymerization

The graft polymerization was done by the method developed by Tazuke et al.⁷ A PP film was irradiated by ultraviolet ray in the reacting solution containing monomer and sensitizer. The reacting solution was prepared from 1 mol/L acrylamide (AAm) monomer, 0.2 mol/L benzophenone as the sensitizer, and acetone as solvent. It has been recognized by Tazuke⁷⁻⁹ that acetone is one of the most useful solvents in the graft polymerization, for it has a high stability

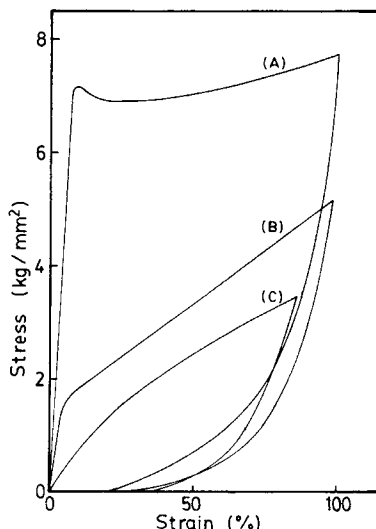


Fig. 1. Stress-strain curves of hard elastic polypropylene film measured in air (A), acetone (B), and *n*-hexane (C).

against hydrogen abstraction by excited sensitizer. In order to make the surface of voids created by the extension as well as the outer surface participate in the graft polymerization, the solvent must penetrate easily into the voids. That acetone could penetrate the film to fill the voids was ascertained by the microscopic observation that the form birefringence due to the voids disappeared in acetone. The stress-strain relationships of sample in acetone, shown in Figure 1 also implies that it penetrates into the sample. From these considerations acetone was chosen as the solvent of the reacting solution. The apparatus and the procedure of the graft polymerization were the same as these for usual PP films made by Tazuke,⁷ with the exception that in this case PP films were kept under a fixed extension during the polymerization.

Figure 2 shows a schematic drawing of the apparatus for the polymerization. A PP film was stretched to a predetermined extent and put on a Pyrex plate C to be cramped at the two ends. The plate C with the PP film was covered by a bell-shaped glass cell, and they were joined with cramps D. Then, the cell was evacuated by a vacuum pump for 30 min. The reacting solution, 50 ml, was then introduced into the cell through a Teflon cock G, and nitrogen gas was bubbled into the solution to remove the oxygen for 30 min. Finally, the sample was irradiated by ultraviolet ray from a 150-W high-pressure mercury lamp located 20 cm below plate C. Although the wavelength was widely distributed in the ray from the mercury lamp, the rays with longer wavelengths than ca. 300 nm only passed through the plate C to work for the graft polymerization. An area 2 cm × 6 cm on a film was irradiated. The irradiation time was varied, while the temperature was kept at 15°C. After being irradiated for a predetermined time, the film was washed with acetone to remove unreacted monomer and sensitizer, and then boiled in water to remove PAAm homopolymer which might be produced in the sample for 10 h.

For a more effective procedure, the graft polymerized sample was extended further than the extension given during the polymerization, for this extension made the sample more porous, and as a result made penetration of acetone and water into the film much easier. The sample was then dried in a desiccator with P₂O₅ for one day and weighed. The graft yield (GY) was defined as

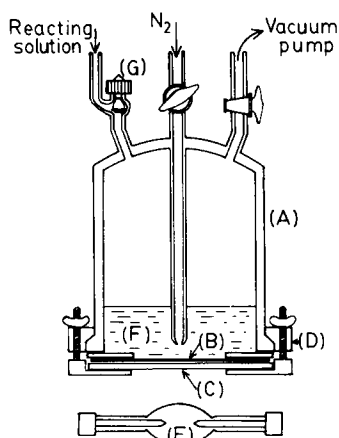


Fig. 2. Schematic drawing of apparatus for the polymerization: (A) glass vessel; (B) hard elastic PP film; (C) Pyrex plate; (D) clamp; (E) 150-W high-pressure mercury lamp; (F) reacting solution; (G) Teflon cock.

$$GY = \frac{W - W_0}{W_0} \quad (1)$$

where W_0 is the weight of PP film before the graft polymerization, and W is that measured by this weighing. Then the sample was boiled in xylene to dissolve PP homopolymer onto which PAAm had not graft polymerized. The graft ratio (GR) was determined as

$$GR = \frac{W - W_0}{W_0 - \Delta W} \quad (2)$$

where ΔW is the weight loss in boiling in xylene and $W_0 - \Delta W$ is the weight of PP which actually participated in the graft polymerization. In the case where the graft yield was too small to be estimated by weighing, GY was estimated by IR using the 3350 cm^{-1} band for NH stretching and the 1382 cm^{-1} band for CH_3 deformation.¹⁰

RESULTS AND DISCUSSION

Figure 3 shows the relationships between the graft yield GY and ultraviolet irradiation time in the AAm graft polymerization onto a hard elastic PP film under various extensions. The GY obtained without extension is as small as that found by Tazuke et al.⁷ for commercially produced PP films. The extension does not only increase the GY but also changes the shape of the curves in Figure 3. The curves are more complicated under comparatively smaller extensions; under 20% extension the rate of increase slows down as early as 2 min, and again becomes larger after about 8 min, being followed by a second slowdown. The first slowdown in GY increase must be due to the exhaustion of monomer in the voids. The smaller the size of the voids, the shorter the time for exhaustion may be. The decrease in the concentration necessarily causes monomer diffusion into the voids from the reacting solution outside the sample film. The rate of monomer diffusion must be slower under smaller extension, because of the smaller void size and the larger tortuosity.⁵

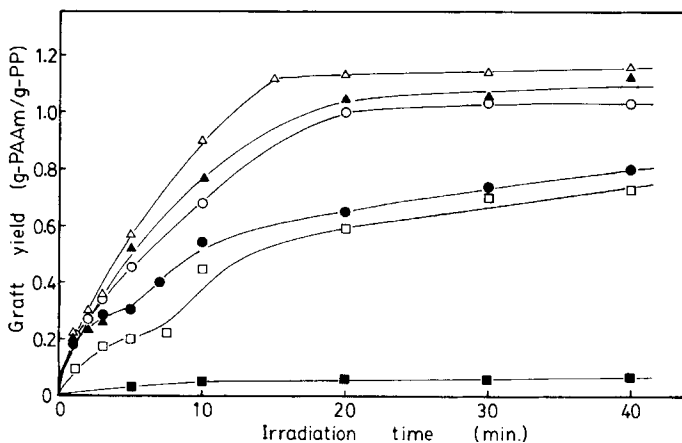


Fig. 3. Relationships between graft yield (GY) and UV irradiation time in the acrylamide graft-polymerization onto a hard elastic PP film under various extensions: (■) 0%; (□) 20%; (●) 40%; (○) 60%; (▲) 80%; (△) 100%.

At the same time, the following two important problems must be taken into consideration. The first is that monomer has a high affinity for the graft PAAM produced on the voids surfaces, and therefore the motive force for monomer diffusion into the voids increases with the graft polymerization. The second is that the progress of the graft polymerization decreases bare PP on the void surfaces, which decreases the rate of the polymerization. The relationship between the GY and the irradiation time, shown in Figure 3, may be explained by these effects. Although Tazuke⁷ noticed the appreciable induction time in the graft polymerization, the time is too short to be detected in this case.

In Figure 4 the GY obtained by 40 min of polymerization is plotted against the extension to show the large effect of extension on GY. It should be noted that such high values of GY as shown in Figure 4 have never been achieved by this photoinduced graft polymerization. The GY increases $\times 15$ stepwise at about 15% extension, which corresponds to the yield point, as seen in Figure 1. According to SAXS study,⁴ the number of voids increases with the extension, and under 100% extension voids are produced between almost all the adjacent stacked lamellae. This means that under 100% extension, the total area of void surface is comparable to that of the end surfaces of all the crystals in a sample. (The end surface is the surface perpendicular to the chains.) The total area of the end surface is approximately estimated by $(2/L\rho)$ per unit weight of sample, where L is the long spacing and ρ is the density. Since in this case L is 220 Å and ρ is 0.9 g/cm³, the total end surface area is about 10⁶ cm² per 1 g sample. This may be large enough to cause the remarkable increase in GY observed. These considerations lead us to conclude that the remarkable increase in GY under extension after the yield point is due to the fact that the void surfaces are involved in the graft polymerization. This conclusion is also evidenced by the change in the gas and solute permeabilities through the graft-polymerized samples, as will be shown in a subsequent report.

Figure 5 shows the relationships between GY and the residual strain (RS), defined by $(l' - l_0)/l_0$, where l_0 is the original length and l' is the length at free state after the graft polymerization. The RS increases with the increase in GY for the samples polymerized under a given extension. It is interesting that the

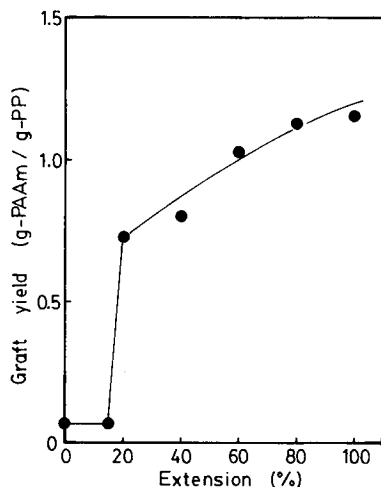


Fig. 4. Relationship between GY obtained by 40 min of polymerization and extension.

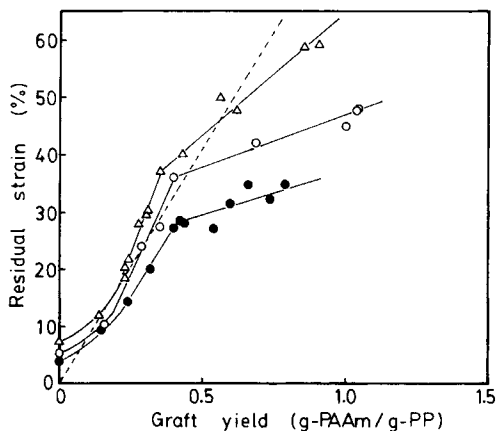


Fig. 5. Relationships between GY and residual strain for film grafted with PAAm under various extensions: (●) 40%; (○) 60%; (△) 100%.

GY-RS relations have deflection points at about 0.4 GY, for it implies that some change may occur in the location of the PAAm. The dotted line in Figure 5 gives the RS expected for an assumed PP-PAAm series model in which the sectional area of sample is not changed by the graft polymerization, and the graft PAAm contributes only the increase in the length of sample. The residual strain measured after the graft polymerization may relate not only to the location of PAAm in PP film but may also relate to the relaxation induced by the graft polymerization as observed by Miyasaka et al.¹¹ in the cellulose-PMMA graft polymerization. This problem will be discussed in the following report, using the small-angle scattering method.

Figure 6 shows the graft ratio (GR) as a function of polymerization time. The GR was determined after extraction of both PP and PAAm homopolymer by boiling in water and xylene. The extraction of PP homopolymer from high-GY samples was difficult because of the poor affinity of PAAm for xylene; the PAAm component prevented high-graft samples from swelling in xylene. Figure 6 shows that the GR increases with time for the first 10 min and then becomes nearly

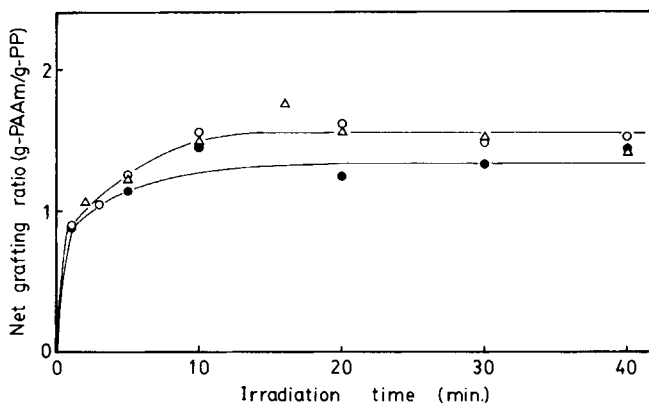


Fig. 6. Relationship between graft ratio (GR) and irradiation time for hard elastic PP films grafted under various extensions: (●) 40%; (○) 60%; (△) 100%.

constant. This increase at an early stage of polymerization may be related to the molecular weight distribution of PP. Larger-MW PP should be more involved in the graft polymerization than lower-MW PP. The graft ratio is inversely proportional to the MW when a given amount of PAAm is grafted onto a PP chain. The effect of extension on the graft ratio is small. However, the fact that in Figure 6 the GR for the 40% sample is always smaller than those for the 60 and 100% samples seems to imply that the size of the voids affects the degree of polymerization of graft PAAm when the size is comparatively small.

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