Graft Copolymerization of Acrylic Acid onto Polystyrene Using the Solid Phase Grafting Technique

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ABSTRACT: Graft copolymerization of acrylic acid (AAc) onto polystyrene (PS) by the solid phase graft copolymerization technique was studied. Benzoyl peroxide (BPO) was used as the free radical initiator. Acrylic acid was introduced into the reactor as an aqueous solution. Optimum reaction conditions to obtain maximum grafting were evaluated. The variables studied were temperature, initiator concentration, monomer concentration, acrylic acid-to-water ratio, and reaction time. The graft copolymer was characterized by infrared (IR) spectroscopy, and the graft level was quantified by the IR absorbance ratio technique and titration. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1001–1007, 1998

Key words: graft copolymerization; polystyrene; acrylic acid; infrared absorbance ratio technique; compatibilizer

INTRODUCTION

Historically, graft copolymerization of polymers with monomers has been primarily carried out in the liquid (solution, bulk, and emulsion) phase.[1–8] More recently, graft copolymers were also synthesized by the techniques of reactive extrusion[7,9] and radiation grafting.[10–15] In the former technique, the polymer is in the melt phase during the grafting reaction, whereas, in the latter technique, the polymer is generally in the form of a film. Solid phase graft copolymerization, which is a relatively new technique, has been used to graft-copolymerize monomers onto polymers[16–18] while the polymer is in the solid phase. The solid phase graft copolymerization process is a simple and easy means to modify the surface of the polymer by grafting various monomers onto its backbone. As the name suggests, the polymer remains in the solid form (or free flowing powder) during the entire reaction. This is achieved by conduct-

ing the reaction at or near the glass transition temperature (or the Vicat softening point) of the polymer. It has been reported that for radical and radiation-induced graft copolymerization, the maximum grafting yield is obtained when the reaction is performed in the temperature range of the glass transition of the polymer.[19] The grafting reactions are initiated by means of free radical initiators and are conducted at atmospheric pressures with low residence times.

The bulk and surface properties of polymers can be altered by grafting different monomers onto their backbones. Graft copolymers find a variety of applications in the plastics industry notably as compatibilizing agents,[20–24] semipermeable and ion-exchange membranes,[13–15] and semiconducting materials.[13] Polystyrene is one of the most widely used polymers in the plastics industry. It has found application in almost every aspect of human life. However, polystyrene is highly nonpolar and hydrophobic. This nonpolarity causes it to be immiscible with commercially important polar polymers, such as nylon and acrylic polymers. Introduction of acrylic acid groups in the polystyrene backbone can, however,

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improve the polarity of polystyrene and make it hydrophilic. These graft copolymers with new properties can be effectively used as blend compatibilizing agents and ion exchange agents.

The present investigation was undertaken to determine the feasibility of grafting polystyrene with acrylic acid using the solid phase graft copolymerization technique and to study the reaction condition. The polymer–monomer system chosen here is an unique one due to the absence of any published work on the grafting of acrylic acid onto polystyrene. The successful grafting of acrylic acid, a highly reactive monomer, onto polystyrene in a controlled manner by the solid phase grafting technique proves the potential of this technique to be a commercially important one to synthesize graft copolymers. The grafting reaction was carried out close to the glass transition temperature of polystyrene (100°C). The initiator chosen was benzoyl peroxide based upon its half-life at the set reaction temperatures. After some preliminary work, it was determined that using water as a solvent for acrylic acid resulted in a better grafting yield. The addition of water resulted in the reduction of homopolymerization of acrylic acid. The choice of water as solvent is a very critical aspect of this reaction process because the lack of a suitable solvent results in the rapid homopolymerization of acrylic acid and a failure of the grafting reaction.

EXPERIMENTAL

Materials

Polystyrene (PS), Huntsman Chemical Co., with a molecular weight (M_w) of 300,000 and particle size in the range of $-35 +115$ Tyler mesh was used. Benzoyl peroxide (BPO) was obtained from Aldrich Chemical Co. Acrylic acid (AAc), Aldrich Chemical Co., of 99% purity stabilized with 200-ppm methyl ethyl hydroquinone was used without further purification.

Graft Copolymerization Equipment

A four-blade, stainless-steel, 800-mL batch reactor was specially designed for this grafting process. A schematic diagram of the experimental apparatus is shown in Figure 1. The reactor vessel is cylindrical in shape. It is mounted horizontally around the reactor shaft and is supported by a back plate and a face plate. The reactor shaft is
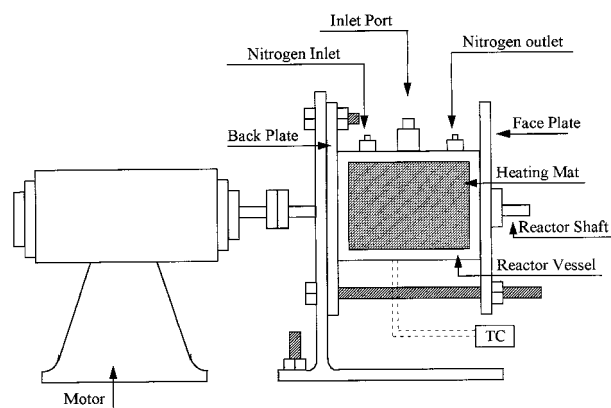
Figure 1   Solid phase graft copolymerization reactor system.

supported by a pair of stainless steel ball bearings, one in each of the back and face plate. A rubber seal between the shaft and the bearings prevented leakage of material. The reactor shaft with 4 blades was driven by a 1.5-hp variable speed motor connected to a 120 VAC output. The blades were specially designed and assembled on the shaft in such a way that the tolerance between the surface of the blade and the inner surface of the reactor vessel is minimal. This minimized the dead space in the reactor and facilitated uniform mixing of the reactants inside the reactor.

The reactor was electrically heated by flexible silicone heating tapes adhered to the outer surface of the reactor to maintain an uniform temperature distribution inside the reactor. Two detachable K-type copper constantan thermocouple with Omega proportional-integral-differential (PID) solid state relay temperature controllers were used to control the temperature. Arrangements were made to facilitate the flow of nitrogen through the reactor and the addition of reactants into the reactor through ports on the top surface of the reactor. The nitrogen flow through the reactor was monitored using a mass flow controller. The nitrogen outlet was connected to a gas bubbler containing acetone. The initiator was added into the reactor by means of a separatory funnel. The monomer solution was injected into the reactor through a syringe. Care was taken to maintain a uniform rate of injection of the monomer solution into the reactor. The equipment used in this study has several advantages in that it is very compact and energy efficient and it is easy to assemble and clean.

Experimental Procedure

A typical experimental procedure to conduct the grafting reaction was standardized after several trial runs. The standardized experimental procedure is described below. The reactor system was set up as shown in the Figure 1. The inside of the reactor was sprayed with a silicone mold release system. This prevented the polymer from sticking to the reactor walls and, hence, facilitated easy movement of the reactor parts. The reactor was preheated to 70°C. At this temperature, 100 g of PS were added to the reactor, and the nitrogen purge through the reactor was started. At this stage, the speed of the reactor shaft was 750 rpm. As soon as the polymer reached the reaction temperature, the speed of the reactor shaft was increased to 1300 rpm, and the required amount of initiator (BPO) was added to the reactor. The initiator was allowed to mix thoroughly with the polymer for 1 min, and then the monomer–water mixture was injected into the reactor. There was no appreciable change in the reaction temperature. The nitrogen purge was stopped at this time. The reaction was allowed to go through for the required time. The reaction mixture remained as a freely flowing powder so that the whole reaction took place in the solid state.

The reaction temperatures for the various experiments were chosen to be on or about the glass transition temperature of polystyrene as the maximum grafting yield is obtained when the reaction is performed in the temperature range of the glass transition of the polymer used.[19] Since the glass transition temperature of polystyrene is 100°C, the temperature range for the grafting reaction was set between 95 and 110°C.

The graft copolymer thus obtained was then washed by continuous extraction with distilled water for 24 h and then dried to remove residual water. It was then further purified by dissolving it in refluxing dimethyl formamide and then precipitating out with water. The precipitate was filtered and then washed with water twice to remove unreacted acrylic acid and homopolymer of acrylic acid. The second purification step was done to remove any acrylic acid that had dissolved in the PS during the reaction. The above extraction procedure was repeated twice. The graft content of the copolymer was determined after every step. There was no difference in the graft level indicating complete separation of the unreacted monomer and its homopolymer and, hence, complete purification of the graft copolymer.
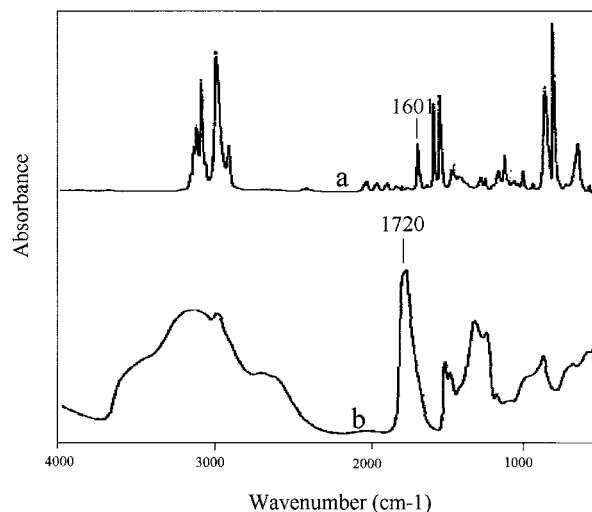
Figure 2 IR spectra of (a) polystyrene and (b) poly-(acrylic acid).

Characterization and Quantification of the Graft Copolymer

The graft copolymer was characterized and quantified by infrared (IR) spectroscopy. IR spectra of the graft copolymer and polystyrene were recorded with a Bio-Rad FTS-7 Spectrometer using KBr disc coated with the polymers. The graft content was quantified by the IR absorbance ratio technique.[24] This was done by plotting the concentration ratio of PS and poly-(acrylic acid) against the absorbance ratio of the characteristic peaks of the 2 polymers. The vibrational C=C band of the phenyl group of polystyrene (1600 cm^{-1}) and the C=O stretching band of the carboxylic acid group of poly-(acrylic acid) (1720 cm^{-1}) were the characteristic peaks chosen. Figure 2 shows the IR spectra of polystyrene and poly(acrylic acid), and Figure 3 represents the calibration curve to determine the acrylic acid content in the graft copolymer. The graft content was also determined by titration of the graft copolymer in dimethyl formamide solution with 0.01N NaOH using phenolphthalein as indicator. The titration was done to verify the graft percentages obtained by the IR absorbance ratio technique. The values obtained by the 2 analysis techniques were very close ($\pm 5\%$), and, hence, the graft percentages obtained by the IR absorbance ratio technique have been used in the data presented in the next section.
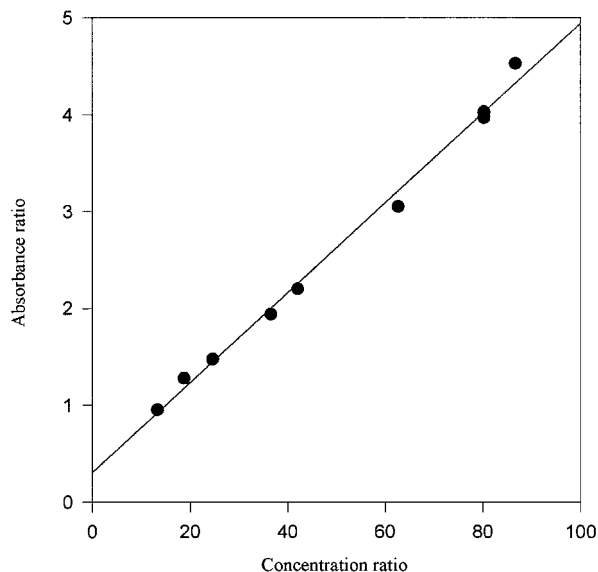
Figure 3 IR calibration curve for determination of the percentage grafted in PS-*g*-AAc.

RESULTS AND DISCUSSION

IR Spectroscopy

Figure 4 shows the spectra of PS and PS-*g*-AAc. The appearance of the new band at 1710–1730 cm^{-1} in the graft copolymer is due to the asymmetrical C=O stretching band of dimers of acrylic acids. The presence of acrylic acid on the polymer backbone is further accentuated by the increase in the intensity of the peaks at 3000–3200 cm^{-1} due to the hydroxyl groups in acrylic acid.
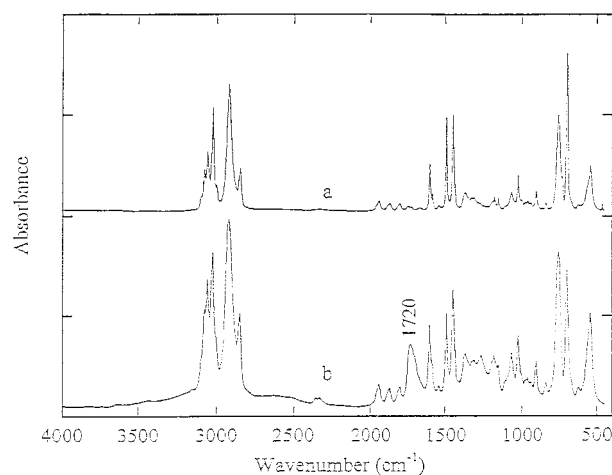
Figure 4 IR spectra of (a) PS homopolymer and (b) PS-*g*-AAc (4 wt %).
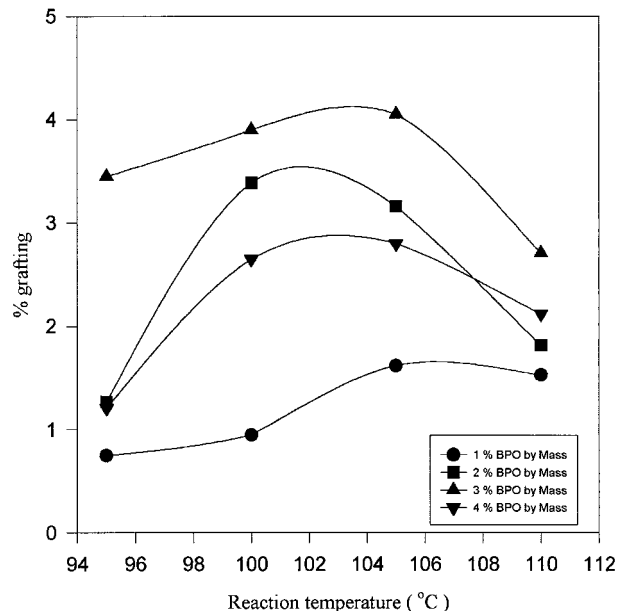
Figure 5 Effect of temperature on the percentage of grafting. Reaction time = 20 min; monomer concentration = 7.37×10^{-4} mol/g PS; monomer-to-solvent ratio = 0.265 mol AAc/mol H_2O.
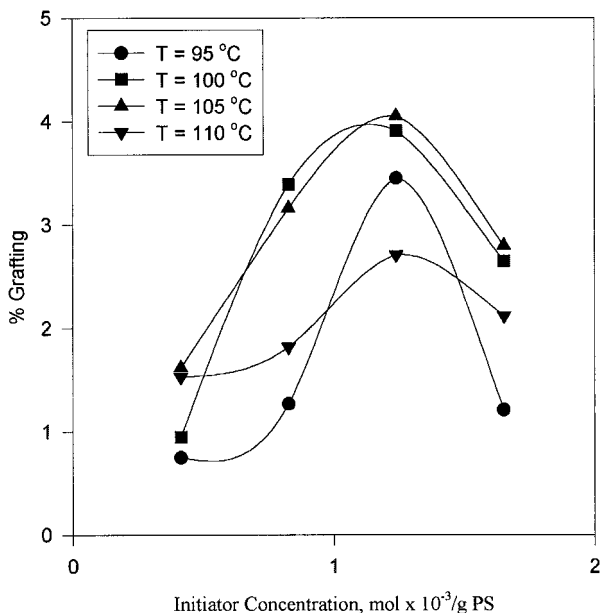
Effect of Reaction Temperature

The effect of temperature on the graft copolymerization of PS with acrylic acid was studied at 95, 100, 105, and 110°C (Fig. 5) at 4 different initiator concentrations. There is a gradual increase in the percent grafting as the reaction temperature is increased from 95 to 105°C. This behavior is as expected because as the temperature increases, the number of free radicals generated by the thermal decomposition of the initiator increases, resulting in more reactive sites along the polymer chains. Another effect of increasing the temperature is that it enhances the diffusion of the monomer into the polymer.

At 110°C, the graft level decreased substantially. This is because at that temperature the half-life of BPO becomes very low, resulting in the depletion of the free radicals very rapidly and a decrease in the number of reactive sites on the polymer backbone. Also at higher temperatures, AAc has a higher tendency to homopolymerize resulting in a decrease in the graft level.

Effect of Initiator Concentration

The concentration of initiator is a very critical parameter in most graft copolymerization studies. The effect of BPO was studied in the range
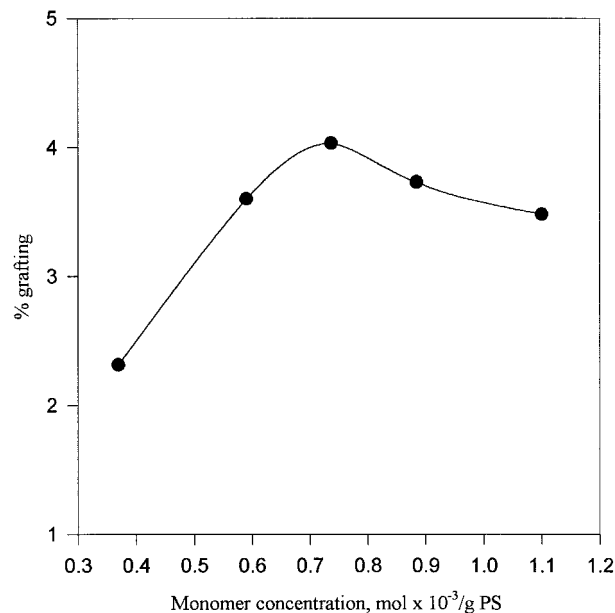
Figure 6 Effect of initiator concentration on the percentage of grafting. Reaction time = 20 min; monomer concentration = 7.37×10^{-4} mol/g PS; monomer-to-solvent ratio = 0.265 mol AAc/mol H_2O.

Figure 7 Effect of monomer concentration on the percentage of grafting. Reaction time = 20 min; initiator concentration = 1.24×10^{-4} mol/g PS; monomer-to-solvent ratio = 0.265 mol AAc/mol H_2O; temperature = 105°C.

4.13×10^{-5}–1.65×10^{-4} mol/g PS (Fig. 6) at 4 different temperatures. The percent grafting increased with increase in concentration of initiator from 4.13×10^{-5} to 1.24×10^{-4} mol/g PS for all temperatures. This trend can be explained by the fact that the amount of free radicals generated increases on increasing the concentration of BPO, resulting in the increase in grafting. However, at concentrations higher than 1.24×10^{-4} mol/g PS, the % grafting decreased. This is because as the initiator concentration increases, there would be a tendency for the chain transfer to the monomer to be more pronounced, facilitating the homopolymerization of acrylic acid and a decrease in grafting level.
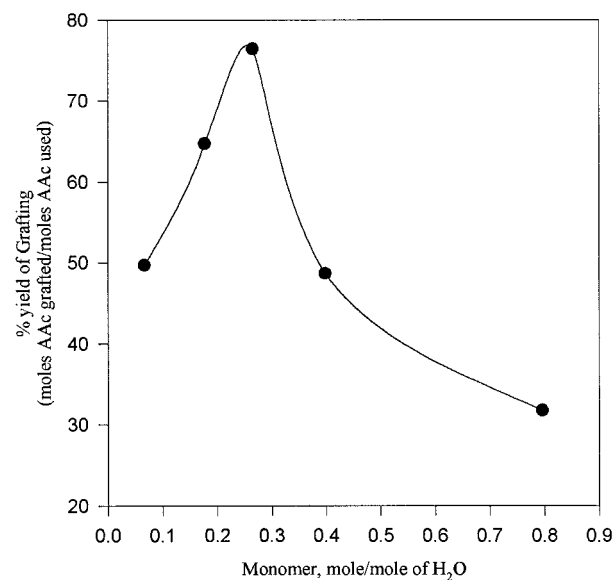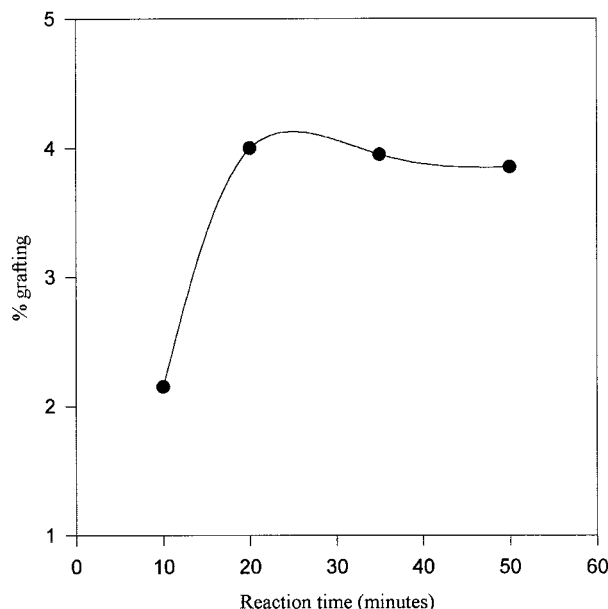
Effect of Monomer Concentration

The effect of monomer concentration on graft percentage was studied in the range 3.69×10^{-4}–1.1×10^{-3} mol/g PS (Fig. 7). A continuous increase in the graft level was observed on increasing the monomer concentration from 3.69×10^{-4} to 7.37×10^{-4} mol/g PS. On a further increase of the monomer concentration, the graft level dropped. This is because as the amount of monomer increases, there is an excess of monomer competing for the initiator, resulting in the homopolymerization of the monomer.

Effect of Monomer to Solvent Ratio

The AAc monomer is a highly reactive monomer and, generally, its aqueous solution is used for polymerization purposes. Figure 8 shows the ef-

Figure 8 Effect of the ratio AAc/H_2O on grafting. Reaction time = 20 min; temperature = 105°C; initiator concentration = 1.24×10^{-4} mol/g PS.

Figure 9   Effect of reaction time on the percent grafting. Monomer concentration = 7.37×10^{-4} mol/g PS; initiator concentration = 1.24×10^{-4} mol/g PS; monomer-to-solvent ratio = 0.265 mol AAc/mol H_2O; temperature = 105°C.

fect of the monomer-to-solvent ratio on the percentage yield of grafting, which is defined as the ratio of the amount of monomer grafted to the amount of monomer used in the reaction. The effect of monomer to solvent ratio was studied in the range 0.0663–1.061 mol AAc/mol H_2O. It can be seen from Figure 8 that 0.265 mol AAc/mol H_2O gives the maximum yield. As the concentration of the monomer solution increases up to about 0.265 mol AAc/mol H_2O, the amount of monomer in the reaction increases, resulting in an increase in the percentage yield of grafting. However, at very high concentrations of monomer solution, there is an excess of monomer competing for the initiator, facilitating the homopolymerization of the monomer. This leads to a lower level of grafting.

Effect of Reaction Time

The effect of reaction time on percentage grafting is shown in Figure 9. The reaction time was varied between 10 to 50 min. This study was carried out at 105°C. The weight percent of grafting increased with time and then decreased slightly after 20 min. This may indicate that within 20 min, all the active sites are exhausted, and a further increase in reaction time would preferentially lead to homopolymer formation.

CONCLUSIONS

1. Acrylic acid has been successfully grafted on polystyrene using the solid phase graft copolymerization technique. In previous studies and in the present one, it has been shown that the solid phase graft copolymerization technique is an easy and environmentally friendly (low solvent use) method to graft monomers onto polymers.
2. A maximum graft level of 4 wt % of acrylic acid has been obtained at the chosen reaction conditions. The effects of various reaction parameters have been investigated and quantified.
3. The graft copolymer has been characterized by Fourier transform infrared spectroscopy. The graft level has been determined by the IR absorbance ratio technique and verified by wet chemical analysis. There is good agreement between the graft values obtained by the 2 techniques.

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