

Graft Polymerization of Styrene on Soy Protein Isolate

Donglei Xi, Cheng Yang, Xiaoya Liu, Mingqing Chen, Chao Sun, Yulan Xu

School of Chemical and Material Engineering, Southern Yangtze University, 214036 Wuxi, China

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ABSTRACT: The grafting of styrene on soy protein isolate (SPI) in an 8 mol/L urea aqueous solution initiated by ammonium cerous nitrate and potassium persulfate was studied. The grafted copolymers were characterized by IR spectroscopy and DSC. The results indicated that styrene was grafted on the SPI. The influence of the reaction conditions on the grafting and efficiency percentages was investigated. The grafting and efficiency percentages initially in-

creased and then decreased with the increase of the initiator concentration, monomer concentration, and reaction temperature. With the increase of reaction time, the grafting and efficiency percentages increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1457–1461, 2005

Key words: soy protein isolate; graft polymerization; grafting; efficiency

INTRODUCTION

There is increased interest in using renewable, degradable, and compatible materials from natural polymers, including cellulose,^{1,2} starch,^{3,4} and protein.^{5,6} As one of the main renewable sources, protein, however, has only recently been studied as a polymer from a materials science perspective.^{7,8} Because plant protein is the main source of proteins on earth, a number of plant sources such as alfalfa leaf, cotton seed, winged bean, peanut, and soya have been investigated for possible application. Among plant protein sources, soy protein isolate (SPI) is abundant and has relatively low cost, so it has been attracting much attention.

The seed proteins of legumes, including soybeans, are albumins and globulins. Globulins, the dominant storage properties, account for about 50–90% of seed proteins. Storage globulins are grouped into two types according to their sedimentation coefficients: 7s globulins (vicilin, 7.1–8.7s) and 11s globulins (legumin, 10.1–14s). The ratio of 11s to 7s globulins varies among cultivars, and it is about 0.5–1.7 in soybeans.

A significant amount of literature refers to the graft copolymerization of monomers onto natural polymers, such as casein,^{9,10} corn protein,¹¹ wool,^{12,13} silk,^{14–23} and so forth. However, there are only a few reports about the graft copolymerization of SPI.²⁴ Styrene (St) is a hydrophobic monomer, so grafting St on SPI will change the balance of hydrophobicity and

hydrophilicity of SPI. The grafted SPI could undergo micellization in a selective solvent. Thus, they could be applied in drug delivery.

This study investigated the graft copolymerization of St on SPI, which was initiated by ammonium cerous nitrate and potassium persulfate in a 32 wt % urea solution. The influence of the reaction conditions on the grafting and efficiency percentages was discussed. The graft copolymers were characterized by IR spectroscopy and DSC.

EXPERIMENTAL

Materials

SPI was supplied by Heilongjiang Sanjiang Company. All of the reagents were analytical grade. Ammonium cerous nitrate, potassium persulfate, and THF were used as supplied. St was washed twice with 5 wt % aqueous sodium hydroxide solution and dried over anhydrous calcium chloride. The monomer was stored under refrigerated conditions. Distilled water was used in all copolymerization reactions.

Graft copolymerization

One gram of SPI was dissolved in 40 mL of 32 wt % urea aqueous solution at room temperature under constant stirring for 30 min. The mixture was then preheated at 50°C for 40 min. The graft copolymerization reaction was conducted in a 100-mL three-necked flask under a nitrogen atmosphere. Then, 1.5 g of St was added into the mixing reactor. After 10 min, under the protection of the nitrogen atmosphere, 16 mL of composite initiator $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6/\text{K}_2\text{S}_2\text{O}_8 = 1:15, \text{v/v}]$ was added to the flask. The concentration of

Correspondence to: C. Yang (cyang@sytu.edu.cn).

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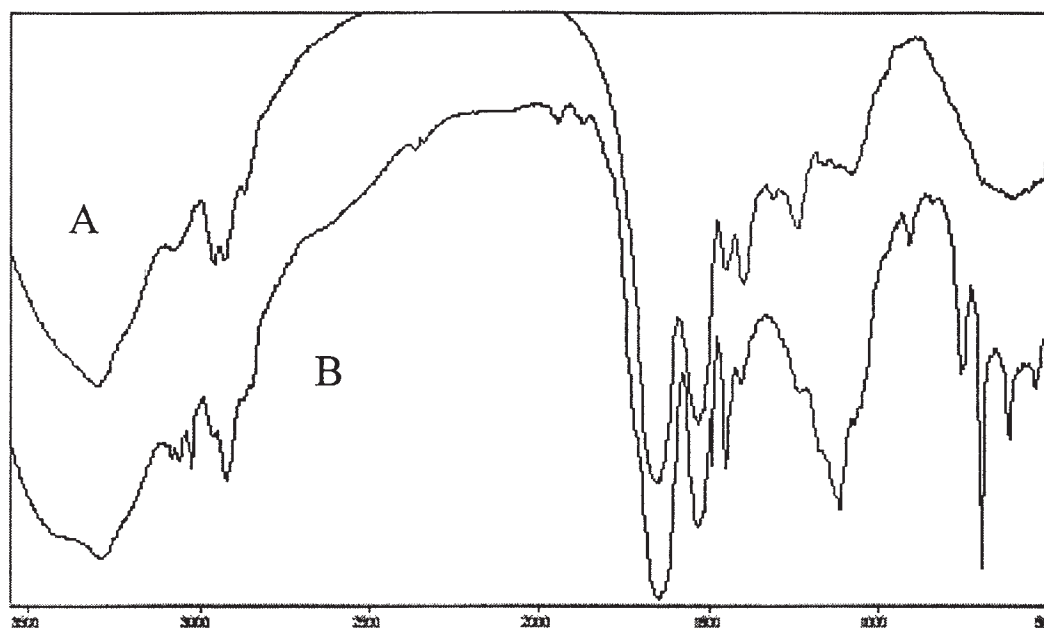


Figure 1 FTIR spectra in the range of 600–2500 cm^{-1} for ungrafted SPI (curve A) and SPI-g-St (curve B).

both ammonium cerous nitrate and potassium persulfate is 0.1 mol/L. The reactants were maintained at 50°C for 28 h. The resulting solution was then precipitated with acetone and collected by centrifugation. The resulting precipitate was extracted with THF for 30 h to remove the unreacted monomer and polystyrene (PS) homopolymer.

Measurements

The percentages of grafting and efficiency were calculated from the following relations:

$$\text{grafting (\%)} = (W_3 - W_1)/W_1 \quad (1)$$

$$\text{efficiency (\%)} = (W_3 - W_1)/W_2 \quad (2)$$

where W_1 and W_2 are the weights of the original SPI and St added to the reaction system, respectively, and W_3 is the weight of the products after extraction with THF.

The IR spectra of grafted and ungrafted SPI were run in the form of KBr disks on a Shimadzu FTIR 4200 spectrophotometer in the frequency range of 4000–500 cm^{-1} .

A Mettler Toledo DSC 822e was used to investigate the thermal behavior of ungrafted and grafted SPI. Under the nitrogen environment (N flow rate = 200 mL/min), the specimen was scanned at a scanning rate of 20°C/min from 20 to 200°C.

RESULTS AND DISCUSSION

FTIR spectra

The IR spectra of ungrafted SPI and SPI-g-St shown in Figure 1 indicate that both ungrafted SPI and SPI-g-St

have a broad absorption band characteristic of the —CONH_2 group of SPI between 3500 and 3200 and 1700 and 1500 cm^{-1} , respectively. Moreover, there is an increment in the intensity of this band in the case of the SPI-g-St sample, because of the phenyl group.

There was a remarkable difference in the wavenumber range of 1120–620 cm^{-1} , where strong absorption peaks are present at 1113, 696, and 618 cm^{-1} , which are characteristic absorptions of PS.

DSC curve

Compared to the ungrafted SPI, the grafted SPI shows a glass-transition temperature (T_g) at 114°C, which is consistent with the T_g of PS (Fig. 2). Note that the PS homopolymer was removed by extraction. The FTIR spectra and DSC curve indicate that PS was grafted on the SPI.

Effect of initiator concentration

The effects of varying the concentration of the composite initiator on the percentage graft yield and percentage efficiency are presented in Figure 3. As the concentration of the composite initiator increases from 5 to 20 mmol/L, a large number of SPI macroradicals are formed through the interaction of free radicals with the groups present in the SPI main chain, which initiate grafting, thereby increasing the graft yield and graft efficiency. However, there is a decline in the percentage of grafting and grafting efficiency at concentrations above 20 mmol/L.

The reason for this may be rationalized as follows: abundant free radicals and homopolymer macroradi-

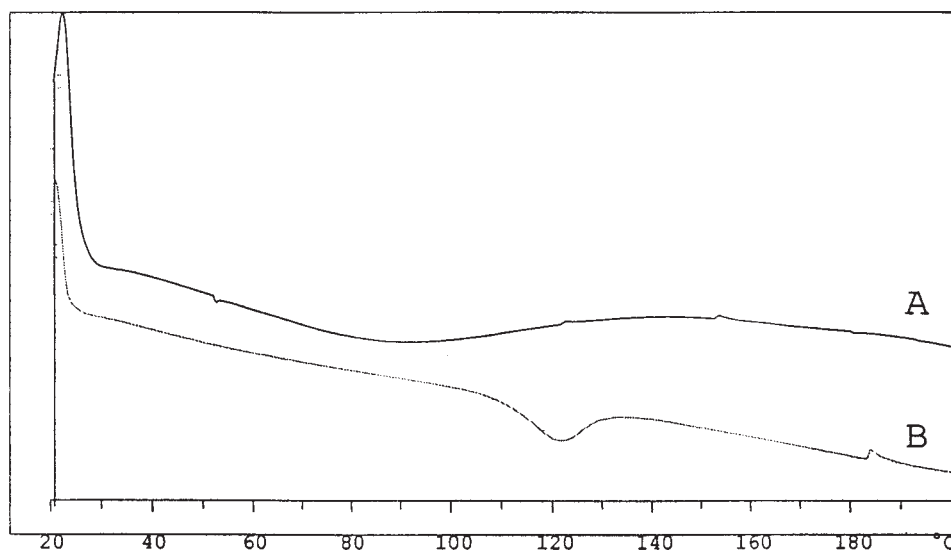


Figure 2 DSC curves of ungrafted SPI (curve A) and SPI-g-St (curve B).

cals are formed in the solution, which might terminate the growing chain; the free radicals formed on the main chain of SPI might be oxidized and thus terminate the reaction site; and the graft copolymerization and homopolymerization in such a system is a matter of competition, which depends on the direct attack of free radicals on SPI or on St monomer. When the concentration of the composite initiator was above a certain value, there were more free radicals attacking the St monomer than the SPI; thus, more PS homopolymer formed.

Effect of monomer concentration

Figure 4 shows the effects of the concentration of St on the percentage of grafting and efficiency. A perusal of the results show that the influence of the monomer concentration on the graft copolymerization can be divided into two stages. In the initial stage, both the

graft ratio and graft efficiency increase with the increase of the concentration of St. Although the St concentration is above 0.4 mol/L, the graft ratio and graft efficiency gradually decrease when increasing the St concentration.

The initial increase in the grafting and efficiency percentages was obviously due to the greater availability of monomer in the proximity of the SPI macroradicals. However, the decrease in grafting yield at a higher St concentration was probably attributable to the waste of St molecules in the formation of a large amount of homopolymer. Moreover, the large molecular weight PS homopolymer increased the viscosity of the reaction medium. The diffusion coefficient of the monomer molecules to the SPI macroradicals was reduced because of the increase of the viscosity of the reaction system, resulting in the gradual decrease in the percentage of grafting, as well as the percentage of efficiency.

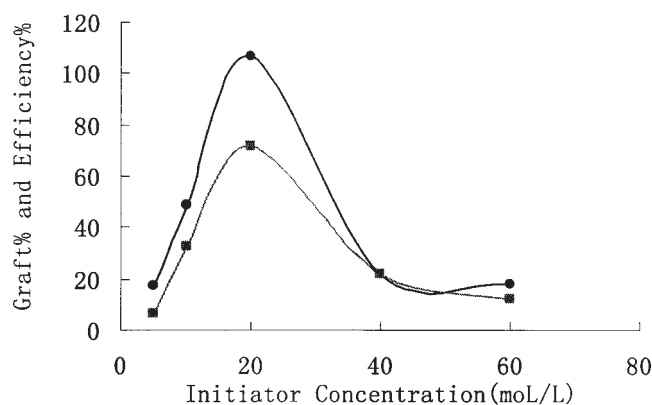


Figure 3 The effect of the composite initiator concentration on the (●) grafting and (■) efficiency.

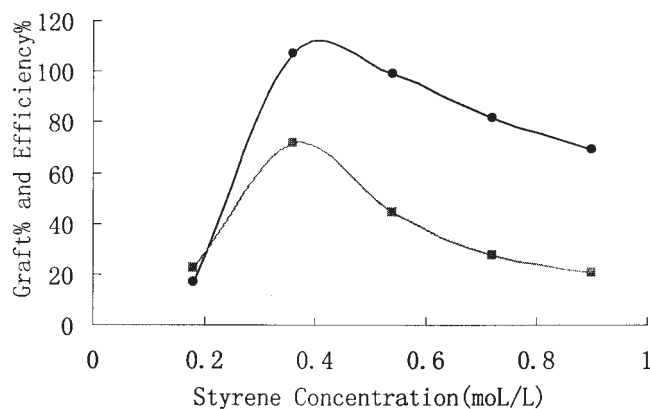


Figure 4 The effect of the monomer concentration on the (●) grafting and (■) efficiency.

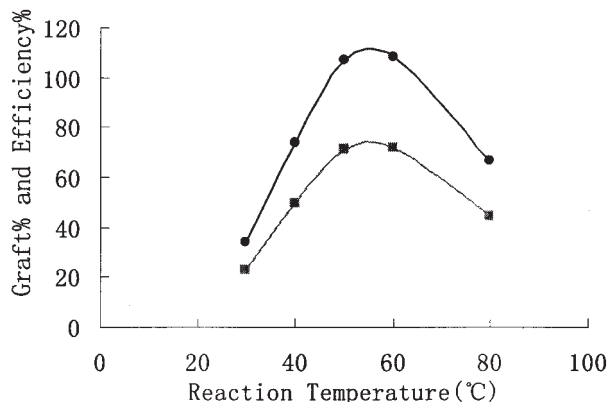


Figure 5 The effect of the reaction temperature on the (●) grafting and (■) efficiency.

Effect of reaction temperature

The effect of the temperature on the graft copolymerization was investigated over the range of 20–60°C. The results are presented in Figure 5. It indicates that the grafting and efficiency percentages increase with the increase of the temperature up to 60°C, then they decrease with the increase of the temperature.

When increasing the temperature, the reaction active and diffusion coefficients of the monomer increase; thus, the grafting and efficiency percentages increase. However, with the increase of the temperature, more PS homopolymer forms; but above 60°C, the grafting and efficiency percentages decrease due to the increase of the homopolymerization ratio.

Effect of reaction time

Figure 6 shows the influence of the reaction time on the graft copolymerization. Note that with the increase of the reaction time up to 28 h, the percentages of grafting and efficiency increase and then become relatively constant with a further increase in the reaction

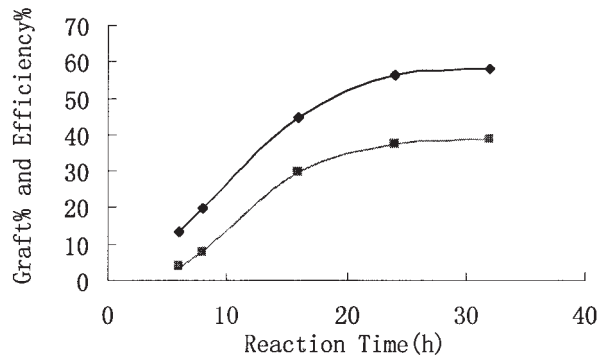


Figure 6 The effect of the reaction time on the (●) grafting and (■) efficiency.

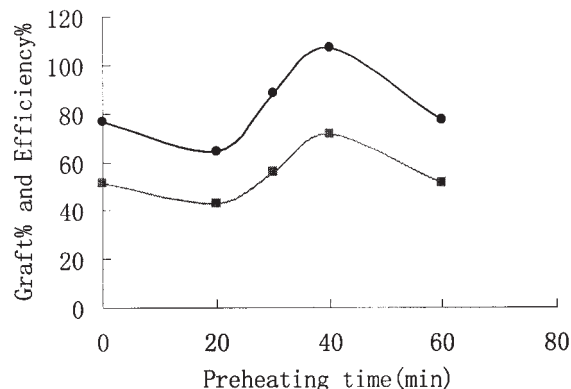


Figure 7 The effect of the preheating time on the (●) grafting and (■) efficiency.

time. Thus, the graft copolymerization is almost complete for 28 h.

Effect of preheating time

Figure 7 shows that, with the increase of the preheating time, the grafting and efficiency percentages increase from 64 to 106 and 43 to 71, respectively, and then decrease.

The native globular SPI is an oblate cylindrical structure. Heating the folding SPI causes it to unfold. With the increase of preheating time, the unfolding structure of SPI increased. These unfolded structures of SPI have exposed active groups, such as —OH, —NH, and so forth, and can easily react with PS.

However, if the preheating time was long enough, more SPI main chains assembled or self-assembled because of hydrogen bonding interactions. We noted that with the unfolding of SPI, —OH groups and —NH groups of globulins such as 2s, 7s, 11s, and 15s formed strong intermolecular hydrogen bonding during the preheating process. Therefore, these globulins will assemble or self-assemble. Thus, less active radicals were created, which led to the lower percentage of grafting and efficiency.

Effect of pH value

Figure 8 shows the effect of the pH value on the percentages of grafting and efficiency.

SPI is composed of acidic and basic subunits. Varying the pH value changes the structure of SPI. At the isoelectric point of SPI, the electric screening effects make the SPI fold. When the pH value is removed from the isoelectric point of SPI, the SPI will unfold because of small electric screening effects.

Generally, the grafting and efficiency percentages increase with the increase of the pH value. When the pH value was 5.1, the percentage of grafting slightly

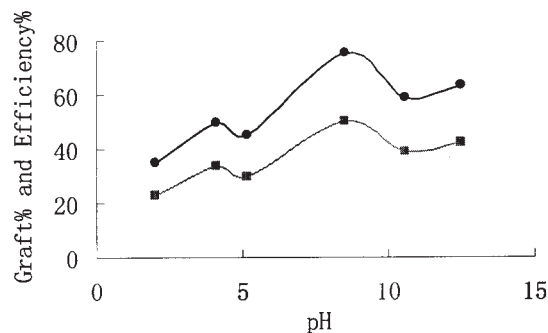


Figure 8 The effect of the pH value on the (●) grafting and (■) efficiency.

decreased. This result may be attributed to the fact that the isoelectric point of SPI is 5.1.

CONCLUSION

PS can be grafted on SPI by using ammonium cerous nitrate and potassium persulfate as the initiator. The highest grafting and efficiency are 110 and 61%, respectively. The graft copolymerization was almost finished at 28 h. Further studies will be focused on the effect of the reaction medium on graft polymerization of St on SPI.

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