A Study on New Polymerization Technology of Styrene

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ABSTRACT: The classic polymerization technology of polystyrene is a high-cost and nonfriendly environmental technology. Furthermore, the weight-average molecular weight of polystyrene is hard to enhance up to 400,000 in the classic polymerization technology. The disadvantages limit the growth rate of polystyrene. The solution for increasing the growth rate of polystyrene lies in new technology. The reactive extrusion process of polystyrene was studied in detail and the whole reactive extrusion process of polystyrene was obtained. By means of controlling the flow rate of styrene and the initiator and the screw rotational speed, samples of polystyrene with different molecular weights were synthesized by the twin-screw extruder. The properties of synthesized polystyrene with different molecular weights were studied; the mechanic properties of polystyrene will increase with an increase of the weight average molecular weight of polystyrene. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2130–2135, 2002

Key words: reactive extrusion; polystyrene; twin-screw extruder; polymerization technology

INTRODUCTION

Polystyrene (PS) is a kind of thermoplastic resin with wide applications. Due to its low cost, good processibility, transparency, and good electrical property, PS products are found almost everywhere, including as picnic utensils, food containers, and novelties. Typical molded products include refrigerator parts, appliance housings, furniture, automobile interior parts, plastic optical pieces, bottles, and imbedded electrical parts. At present, output of PS has a tendency to rise and is a little less than that of polyethylene (PE) and poly(vinyl chloride) (PVC). However, the growth trend for PS has lagged behind that of other plastics, despite its many advantages; for example, PS grew 33% between 1992 and 1997, a growth rate all the more imposing because it came on top of a massive volume base. In the same period, PVC grew 55%, engineering resins grew 60%, and polypropylene grew 70%. Even with the smallest volume base, PS grew only 20%.[1] The solution for increasing the growth rate of PS lies in new technology and new product development.

The polymerization process of styrene has undergone four stages, namely, solution polymerization, suspension polymerization, emulsion polymerization, and bulk polymerization, because Dow Corp. applied the polymerization process of styrene to the industrial field. The follow-up procedures of solution, suspension, and emulsion polymerization of styrene are very complex, especially in the course of deprivation of solution and

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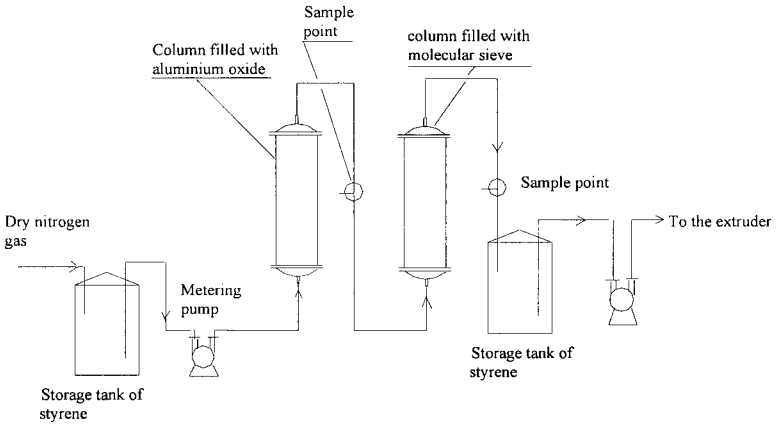

Figure 1 The flow chart on purification of styrene.

will cause serious environmental pollution. At present, the continuous bulk polymerization of styrene has been widely applied in the industrial field, because BASF Corp. took the lead in applying the continuous bulk polymerization to the industrial field.[2] However, the continuous bulk polymerization of styrene has difficulties in controlling the heat transfer and enhancing the molecular weight of PS; for example, if the weight-average molecular weight of PS is enhanced from 200,000 to 400,000, the productivity will be decreased by 50%.

We successfully synthesized PS with the weight-average molecular weight between 100,000 and 800,000 in a corotating closely intermeshing twin-screw extruder in our research lab, by way of controlling the transfer of heat and mass and the mean residence time in twin-screw extruder. We researched the mechanism for scale-up of the process. The new reactive extrusion process of PS is low-cost and pollution-free. We may freely adjust the output and molecular weight of PS according to market demand and push the development of PS.

EXPERIMENTAL

Materials

The reactive extrusion process of PS was performed by using the following starting materials:

- Aluminum oxide: sphere diameter, 3–5 mm; bulk density, 0.6–0.9 kg/m^3
- Molecular sieve: sphere diameter, 3–5 mm; bulk density, 0.7–0.9 kg/m^3
- Styrene, industrial grade
- Dry nitrogen, high purity

Apparatuses

The reactive extrusion process of PS was performed by using the following experimental apparatuses:

- Stainless steel column: diameter, 40 mm; height, 1500 mm; thickness, 4 mm
- Model GS-2 pressure vessel: maximal appli-

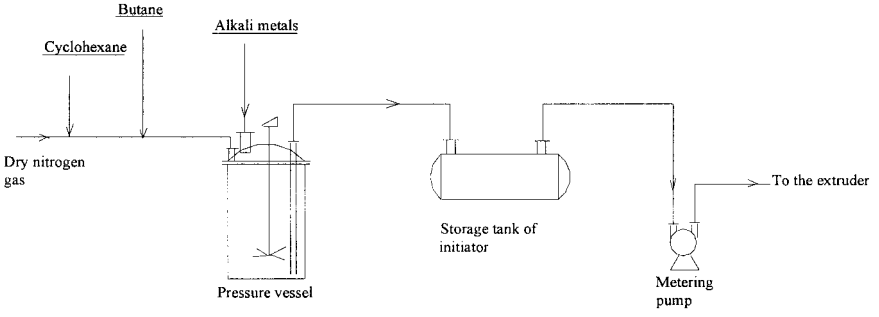

Figure 2 The flow chart on synthesis of the initiator.

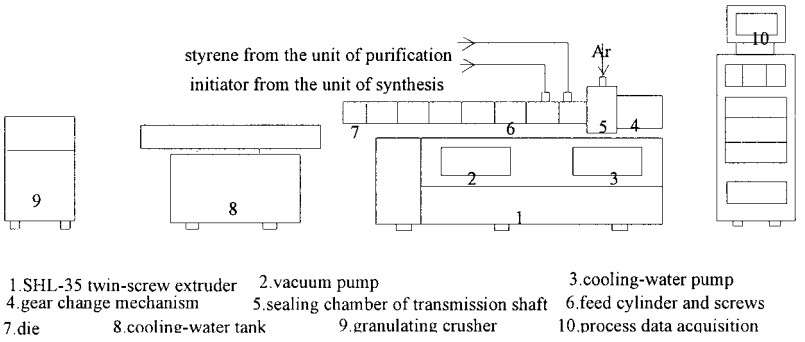

Figure 3 The flow chart on reactive extrusion of PS.

cation pressure, 30 atm; maximal application temperature, 250°C
- Model J-W plunger metering pump
- Model WGP-6 metering pump
- Model SHL-35 closely intermeshing corotating twin-screw extruder: screw diameter: 35 mm; L/D: 29; cylinder temperature: 150/160/170/180/200°C.

Analysis

The reactive extrusion processing of PS was analyzed with the following analytical methods:

- Trace amount of water analysis: analysis system: Model WS-1 trace water measuring meter; measurement range: 0–9999 ppm (wt %)
- Gel permeation chromatography (GPC): column, (2)*AM GEL5um LIN; solvent: THF; polymer concentration: 2 mg/mL; flow rate: 0.982 mL/min; system: T60+External RI; concentration detection: external RI
- Thermal gravimetry analysis (TGA): analysis system: PE Company Thermal Analyzer PC Series TGA7; sample mass: 8–10 mg; temperature range: 160–450°C; heating-up rate: 20°C/min; air flow rate: 30 mL/min
- Infrared spectroscopic analysis: analysis system: Nicolet 2DSX FTIR
- Dynamic mechanical analysis (DMA): analysis system: AG-2000A; testing machine of strength of material; testing rate: 50 mm/min; testing temperature: 23°C

Experimental Setup

The reactive extrusion process of PS consists of the following units:

- Unit for purification of styrene
- Unit for synthesis of initiator
- Unit for reactive extrusion process of PS

During the reactive extrusion of PS, styrene is first metered into stainless steel columns filled with either aluminum oxide or molecular sieve. The aluminum oxide and molecular sieve were pretreated at 280°C in an oven for 3 h. The unit for purification of styrene is shown in Figure 1. Second, the initiator was synthesized in the pressure vessel (Fig. 2). Third, the purified styrene and initiator were metered directly into the closely intermeshing corotating twin-screw extruder (Fig. 3). By means of controlling the flow rate of styrene and the initiator and the screw rotational speed, PS with different molecular weights were synthesized by the twin-screw extruder.

RESULTS AND DISCUSSION

Effect of the Solid Adsorbents

In the process of anionic polymerization, water content in the monomer should not exceed 10 ppm

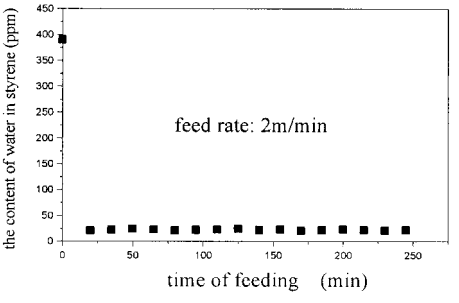

Figure 4 The adsorption curve of aluminum oxide.

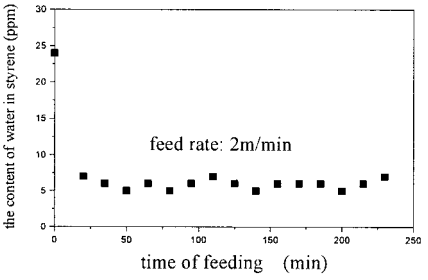

Figure 5 The adsorption curve of molecular sieve.

(wt %). For the classic distillation, it is very difficult to meet the request for water content. In our unit for purification of styrene, it is easy to meet the request for water content. In Figure 1, most of the water in styrene is adsorbed by aluminum oxide, and the trace water in styrene is adsorbed by molecular sieve. The results of solid adsorbent are shown in Figures 4 and 5.

Figures 4 and 5 illustrate that the water content in styrene was reduced to about 24 ppm (wt %) after styrene flows through the column filled with aluminum oxide and the water content was reduced to about 6 ppm (wt %) after styrene flows through the column filled with molecular sieve. In our experiment, we find that the feed rate has a great effect on adsorbing water in monomer. On the same experimental conditions, we change the feed rate and study its effect on adsorptive capacity of the aluminum oxide and molecular sieve (Fig. 6):

$$\text{adsorptive capacity} = \frac{\text{weight of adsorbed water}}{\text{weight of adsorbent}} \times 100\% \quad (1)$$

Figure 6 illustrates that by increasing the feed rate the adsorptive capacity will decrease. In general, when the aluminum oxide and molecular sieve are applied in adsorbing water in monomer, the maximal feed rate cannot exceed 3 m/min.[3]

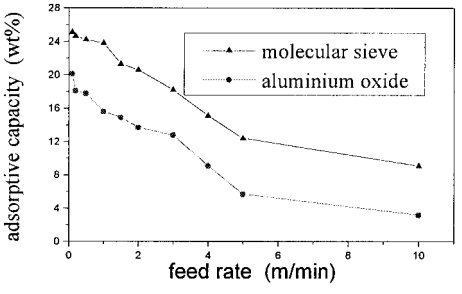

Figure 6 The relation curve of adsorption capacity and feed rate.

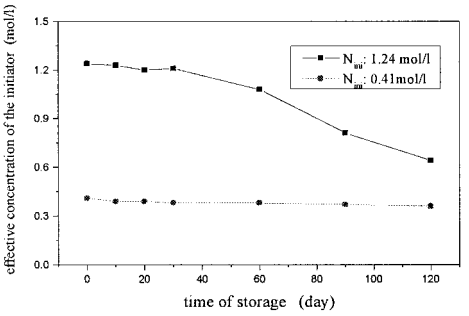

Figure 7 The effect of storage time on effective concentration of the initiator.

Effective Concentration of the Initiator

In this article, the double titration of Gilman and Haubein is adopted to measure the effective concentration of the initiator.[4] The method is as follows.

First, benzyl chloride is added to the known quantity of the initiator (V_{ini}). Then to hydrolyze the system, the standard concentration of hydrochloric acid (N_{HCl2}) is used to titrate the system; the quantity of the standard concentration of hydrochloric acid is V_{HCl1}.

Second, to hydrolyze directly the known quantity of the initiator (V_{ini}), the standard concentration of hydrochloric acid (N_{HCl2}) is used to titrate the system. The quantity of the standard concentration of hydrochloric acid is V_{HCl2}. The effective concentration of the initiator is calculated as:
The effective concentration of the initiator is affected by the storage conditions; the effective concentration is lower and is more favorable to storage (Fig. 7). In an atmosphere of argon gas and below zero 5°C, the effective concentration of the

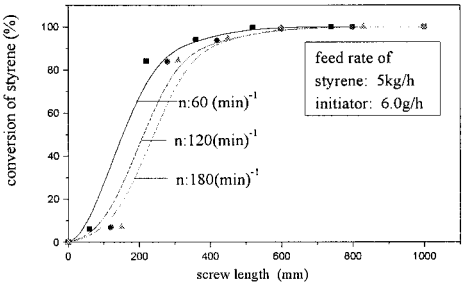

Figure 8 The curve of conversion of styrene along screw in the different screw rotational speed (n).

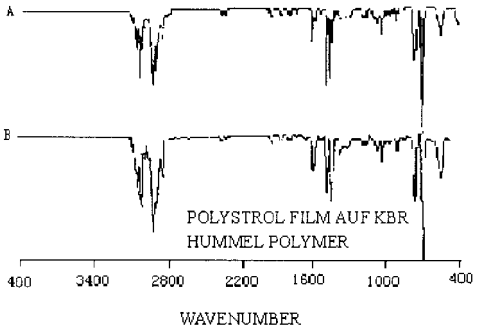

Figure 9 The infrared spectrogram of polystyrene (M_w = 520,000) of reactive extrusion. (A) Polystyrene of reactive extrusion; (B) general purpose polystyrene.

initiator will be basically changeless in 30 days. But after 120 days, the effective concentration of the initiator will sharply decrease. In the industrial field, it is useless that the effective concentration of the initiator is too low; it is necessary to choose the appropriate effective concentration of the initiator. In our reactive extrusion of PS, the appropriate effective concentration of the initiator is 1.25 mol/l.

$$N_{\text{ini}} = \frac{(V_{HC12} - V_{HCl1}}{V_{ini}} \quad (2)$$

Conversion of Styrene in Reactive Extrusion of PS

In the reactive extrusion of PS, styrene and the initiator are separately fed (Fig. 3). By controlling the transfer of heat and mass and the mean residence time in twin-screw extruder, PS with a weight-average molecular weight between 100,000 and 800,000 is synthesized. The sample points are set along the barrel of the twin-screw extruder. At steady state, the samples of PS are quickly taken out from the sample points and are

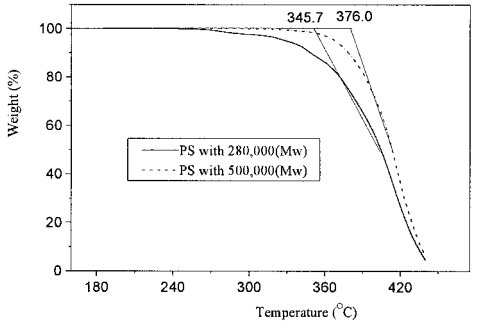

Figure 10 The curves of the loss weight rate of polystyrene.

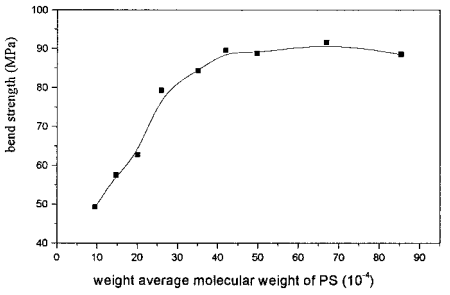

Figure 11 The effect of M_w on bend strength of PS.

quickly put into the mixture solution of toluene and methanol. The polymerization of styrene is quickly terminated, and then the remaining polymer is precipitated. The conversion of styrene is calculated in eq. 3 (Fig. 8)[5]:

$$\text{conversion} = \frac{\text{weight of remaining polymer}}{\text{weight of sample}} \times 100\% \quad (3)$$

Figure 8 illustrates that the polymerization of styrene in the twin-screw extruder is a very fast reaction; with the screw rotational speed increasing, the polymerization process will be deferred backward along the screw length.

The Infrared Spectrogram of PS of Reactive Extrusion

The infrared spectrogram of PS (M_w = 520,000) of reactive extrusion and the standard infrared spectrogram of general-purpose PS film in HUMMEL POLYMER are compared in Figure 9. They are almost completely the same; only three absorption peaks are different. At 696.2 cm^{-1}, the absorption peak of PS of reactive extrusion is higher than that of general-purpose PS. At 730.4 cm^{-1}, there is an absorption peak in the spectrogram of PS of reactive extrusion, but there is no

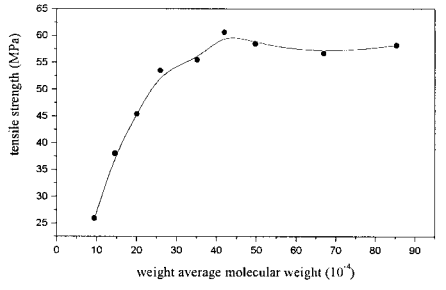

Figure 12 The effect of M_w on tensile strength of PS.

absorption peak in the spectrogram of general PS. At 673.4 cm^{-1}, it is the other way around, and the reason of that is not clear now.

Thermal Stability of PS of Reactive Extrusion

By way of TGA, we gain the curves of the loss weight rate of PS of reactive extrusion in the air (Fig. 10).

Connecting the point of 20% loss weight rate and point of 50% loss weight rate with the baseline of the curves, we obtained the decomposition temperature of PS. The decomposition of PS with 500,000 (M_w) is 376°C; the decomposition of PS with 280,000 (M_w) is 346°C. It is clear that with the molecular weight of PS increasing, the thermal stability of PS will increase. It is well known that the terminal group of polymer has a great effect on the degradation of polymer. With the molecular weight increasing, the amount of the terminal group will decrease, so that the thermal stability will be improved.

The Mechanic Properties of PS of Reactive Extrusion

By means of controlling the flow rate of styrene and the initiator and the screw rotational speed, PS with different molecular weights will be synthesized by the twin-screw extruder. It is found that with weight-average molecular weight (M_w) between 50,000 and 500,000 of PS increasing, the bend strength (Fig. 11), the tensile strength (Fig. 12), the impact strength (Fig. 13), and extension at break (Fig. 14) will increase. So it is our best choice to synthesize PS with about 500,000 (M_w) in the twin-screw extruder in the industrial scale.

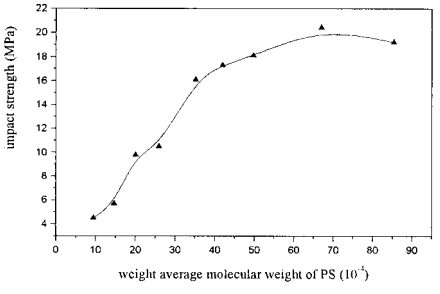

Figure 13 The effect of M_w on impact strength of PS.

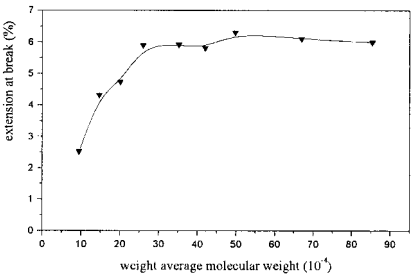

Figure 14 The effect of M_w on extension of PS at break.

Summary and Conclusions

In this article, the whole reactive extrusion process of PS in the industrial field was presented. The parameters of the new process of PS were obtained. PS with different molecular weights was synthesized in intermeshing corotating twin-screw extruder. With the weight-average molecular weight (M_w) between 50,000 and 500,000 of PS increasing, the mechanic properties will improve.

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