Selective Pyrolysis of Polystyrene to That with a Desired Low Polymeric Degree

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Received 11 December 1997; accepted 1 June 1998

ABSTRACT: To obtain low polymeric polystyrene (PS), pyrolysis of high polymeric PS in solution was studied in the temperature range from 290 to 400°C by using additives or acid catalysts. The low polymeric PS targeted here was that with average molecular weight of 10⁴. When the feed PS was pyrolyzed in tetralin by adding sulfur or diphenyl disulfide, the molecular weight of PS decreased greatly, even at lower temperatures, and the desired low polymeric PS was formed in a relatively large amount at the temperatures below 350°C. The degradation behavior was able to be explained in terms of a random polymer chain scission mechanism initiated by sulfur radicals formed from the additives. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2299–2305, 1998

Key words: polystyrene; pyrolysis in solution; recovery of low-molecular-weight polymer; random polymer chain scission; sulfur radicals

INTRODUCTION

Low polymeric polymers are frequently needed in various industries. They can be prepared with two methods. One is a controlled polymerization in which a propagation step is restricted to a low extent so as to yield the needed polymer. The other is a pyrolysis in which high polymeric feed polymers are degraded into the needed polymers. The latter looks advantageous because of the facility for the application and the possibility of the utilization of polymers, which are currently manufactured as raw materials. Further, it may be capable of recycling waste polymers as the feed polymers. However, it has rarely been studied from the viewpoint of whether it is efficient for production of the needed polymers or not, though it has been studied from basic mechanistic interests^{1–10} and for social demands of treating waste polymers^{11,12} by many workers.

To carry out the pyrolysis in question so efficiently as to convert the feed polymer into the desired low polymeric polymer (hereafter, described as the desired polymer), some problems to be solved remain, as follows: how to inhibit side reactions bringing by-products, such as crosslinking polymers and carbonaceous materials^{13,14} from occurring; and how to suppress depolymerization producing predominantly volatile products like monomers² and, therefore, how to promote the degradation through random scission. We have reported the properties of the pyrolysis carried out in solvents (pyrolysis-in-solvent) using polystyrene (PS) or its derivatives as feed polymers.^{15–17} The reports indicate that the pyrolysis-in-solvent was able to inhibit the undesired reactions from occurring and to suppress the depolymerization if solvents used furnish suitable physicochemical properties like relatively low vapor pressures, even at higher temperature, great thermal stability, and hydrogen donating ability. Of the experiments having been made, the pyrolvsis-in-solvent using tetralin especially was able to degrade the raw polymer without forming the by-products. Using phenol made the pyrolysis-in-

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Journal of Applied Polymer Science, Vol. 70, 2299-2305 (1998)

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Figure 1 Additives and catalysts used for pyrolysis.

solvent proceed through random scission together with only restricted occurrence of depolymerization to yield low polymeric polymers greatly.

In this context, we are stimulated to apply the pyrolysis-in-solvent to obtain a low polymeric polymer. For the basic analysis, PS was mentioned as a typical feed polymer to be investigated. The targeted polymerization degrees of the desired polymer is about 100, which is equivalent to 10^4 in molecular weight of PS. Tetralin and phenol were mentioned as solvents furnishing suitable physicochemical properties. In association with the solvents, a few catalysts and several additives were inspected so as to degrade PS more selectively to the targeted polymer.

EXPERIMENTAL

Materials

A feed PS was purchased from Wako Pure Chemical Industries, Ltd. Its weight-average molecular weight (\bar{M}_w) was 1.75×10^5 . Tetralin and phenol were used as pyrolysis solvents. Figure 1 shows the additives and catalysts used for the pyrolysis. Sulfur, diphenyl disulfide (DPS), diphenyl (DP), and diphenyl ether (DPE) as additives and silica-alumina (SiO₂-Al₂O₃) and *p*-toluenesulfonic acid (*p*-TSA) as acid catalysts were used. The acid catalysts were employed from an expectation of their ability to promote catalytically the random scission of the polymer chain through an ionic mechanism. The SiO₂-Al₂O₃ was given courtesy of Nikki Chemical Co., Ltd. (N631-HN). It was calcined at 500°C for 2 h and pulverized to pass

through a 100-mesh screen. The additives and the p-TSA of catalysts were of reagent grade and were used as received.

Procedure of Pyrolysis and Analysis

A 100-mL magneto-driven autoclave was used as a reactor. The PS (2 g), the solvents (20 g), and the additives or catalysts (0.2 g) were placed into the autoclave. It was pressurized to 2 MPa with nitrogen gas and heated at a rate of 6.7°C per min⁻¹ up to reaction temperatures and then held for 1 h while the reaction mixture was stirred at 750 rpm by a magnetically driven stirrer. After that, it was cooled rapidly to room temperature, followed by taking out the reaction mixture. Its 0.2 mL was sampled, diluted with 4 mL of tetrahydrofuran (THF), and analyzed by a gel permeation chromatography (GPC) equipped with an ultraviolet (UV) detector. Concentration of components in the mixtures was measured by absorbance at 254 nm assigned to the phenyl group. Preliminary experiments showed that the mixture contained products having various molecular weights. Therefore, different peaks attributable to the lowmolecular-weight components, such as the pyrolysis solvent and the monomer of PS, were shown in the chromatograms besides high-molecularweight products. Since degraded products with molecular weights around 10^4 , the desired polymer's molecular weight, were the interest of this work, the low-molecular-weight products were ruled out for comprehensible understanding of the pyrolysis property. On the basis of the above consideration, the chromatograms obtained were converted to molecular weight distributions (MWDs), and only MWDs corresponding to pyrolyzed products having molecular weights of more than 10^3 were paid attention to. From the MWDs, weight-averaged molecular weight (M_w) of the degraded products was also calculated as a measure representing the degradation property of the pyrolysis-in-solvent.

To know the yield of the desired polymer, it was precipitated using *n*-hexane as a precipitant from the degradation mixtures which were regarded as being rich in the desired polymer and then vacuum-dried and weighed. To discuss whether or not sulfur was bound to the recovered polymer when the additives containing sulfur were used, it was analyzed with a LINK Q200J X-ray analyzer mounted on a JEOL JSM-T330 scanning electron microscope.



Figure 2 GPC curves of feed PS $(-\cdot -)$ and PS degraded in phenol (--) and in tetralin (--).

RESULTS

Investigation of Which Solvent Should Be Used

Figure 2 shows MWDs of feed PS and those of the degradation mixtures obtained using each solvent. The pyrolyses were made without both the additive and the catalyst to obtain the information of basic degradation properties of PS in solvents and to investigate which solvent was suitable. From the figure, it is found that, according to kinds of solvents used, the MWD varied in a respective manner against an increase in the pyrolysis temperature. When the pyrolysis temperature increased, the mode molecular weight, that is, the molecular weight of the most frequently occurring components, tends to decrease in proportion to the temperature for the tetralin use and then to decrease rapidly at lower temperatures for the phenol use. Further, from areas under the MWD curves, the degraded products that are interesting in this work are found to be greater for the phenol use and to be less for the other solvent use. These properties suggest that the feed PS degraded mainly through depolymerization into products uninterestingly in this work like the monomer for the tetralin use, while it did through random scission into the products interestingly in this work for the phenol use. Thus, for the purpose of the present project, phenol seems to be appropriate as a solvent. The products obtained in the presence of the phenol, however, were severely colored against colorless products obtained in the presence of tetralin. Since the coloration is considered to be responsible for degraded products having conjugated double bonds,



Figure 3 Comparison of GPC curves of PS degraded in tetralin between use of sulfur (---) and no use of it (---).

the severely colored products may lack in stability. Further phenol may corrode reactors owing to its acidity. To accomplish the purpose of this project, the alternative method is to use tetralin while its property progressing the depolymerization is improved to promote random scission. The improvement may be attained with support of additives and/or catalysts.

Effect of Additives and Catalysts on MWD Change of PS

Figures 3–6 show MWDs of the PS degraded in the presence or absence of additives. When sulfur or DPS was added (Fig. 3 and 4), MWD of the polymer shifted greatly to a low-molecular-weight



Figure 4 Comparison of GPC curves of PS degraded in tetralin between use of DPS (\longrightarrow) and no use of it (--).



Figure 5 Comparison of GPC curves of PS degraded in tetralin between use of DP (\longrightarrow) and no use of it (--).

side with an increase in the reaction temperature. From the areas under the MWD curves, the decrease in the amount of the PS degraded was found to be less for the pyrolysis using the additives than for that not using the additives. The behavior resembled that for the case using phenol, shown in Figure 2. Further, the temperature at which MWD began to shift depended on the kinds of additives, as follows: DPS gave a lower temperature at which MWD shifted. In contrast, when DP and DPE were used (Figs. 5 and 6), a little difference was found in MWD between the presence and absence of the additives. Since no consistent change was observed for the difference with an increase in the pyrolysis temperature, the



Figure 7 Comparison of GPC curves of PS degraded in tetralin between use of p-TSA (——) and no use of it (– – –).

difference probably arose from an experimental error. Thus, DP and DPE had no effect on the degradation of PS.

Figures 7 and 8 show MWDs of PS degraded under the presence and absence of the acid catalysts, respectively. In case of the *p*-TSA presence (Fig. 7), MWD shifted significantly, not at 350°C, but at 360°C, when compared with that under the absence of the catalyst, although an extent of the shift and amounts of the desired polymer formed were not so great as that for the use of sulfur and DPS. Under the influence of SiO₂-Al₂O₃ of catalyst (Fig. 8), quite different properties were found versus the above cases, as follows: At a lower temperature of 365°C, no marked change was



Figure 6 Comparison of GPC curves of PS degraded in tetralin between use of DPE (\longrightarrow) and no use of it (--).



Figure 8 Comparison of GPC curves of PS degraded in tetralin between use of SiO_2 -Al₂O₃ (-----) and no use of it (---).



Figure 9 Effect of pyrolysis temperature on weight average molecular weight (M_w) of PS degraded in (\Box) phenol and in tetralin in the (\bigcirc) absence and $(\triangle, \blacktriangle, \blacktriangledown, \diamondsuit, \diamondsuit, \clubsuit)$ presence of additives or catalysts. Additive or catalyst: (\triangle) sulfur; (\blacktriangle) DPS; (\blacktriangledown) *p*-TSA; (\diamondsuit) DPE; (\blacklozenge) DP; (\clubsuit) SiO₂-Al₂O₃.

found in MWDs from those obtained in the absence of the catalyst; at a higher temperature of 380°C, however, the amount of polymer decreased greatly while the MWD shifted a little.

Figure 9 shows that the M_w of PS degraded for all the runs. The figure indicates that the degradation property can be classified roughly into two types. One is a type at which M_{m} decreased greatly at low temperatures and the desired polymer was formed to a great extent relatively. That is the case for the pyrolysis in phenol and in tetralin with addition of sulfur or DPS. The other is a type at which M_{m} decreased at a higher temperature and the amount of the desired polymer formed was little. The former and the latter type of degradation property can be explained in terms of the random scission mechanism and the depolymerization one, respectively; although, at higher temperatures, the depolymerization mechanism is regarded as being predominant, even in the former type. Aside from the above 2 types of degradation properties, a different behavior was seen for use of *p*-TSA, as follows: the MWD shift was not significant at 330 and 350°C but was significant at 360°C. This is considered to correspond to a case in which the random scission occurs at higher temperatures.

Obtained Amount of the Desired Low Polymeric PS

The PS pyrolysis in the presence of sulfur or DPS gave the desired polymers in the large amount

Table IYield of Low-Molecular-WeightPolymers

Additives	Temperature (°C)	Yield (%)
Sulfur	340	29.7
Sulfur	350	18.5
DPS	320	56.5
DPS	330	40.4

when the pyrolysis temperature was controlled properly. Table I shows their yields. The yield became higher as the pyrolysis temperatures were lower. Specifically, when DPS was used, the yield went up to 56.5% at 320°C. The desired polymers recovered were white or slightly gray powders. Since both polymer and the sulfur radicals should coexist during the pyrolysis, we supposed that sulfur was incorporated more or less into the recovered polymer by coupling between polymer and the sulfur radicals. However, no sulfur was determined in the recovered polymers.

DISCUSSION

Thermal Degradation Mechanism in the Presence of Additives

In the previous article,¹⁵ we explained the thermal degradation behavior of PS in phenol with a random scission mechanism as follows. During the pyrolysis, phenoxy radicals are formed from phenol molecules and abstract hydrogens from PS at random positions of its chain to form carbon radicals, and then the polymers having carbon radicals rupture through β -scission. This random scission mechanism suggests that if any radical having enough reactivity to abstract hydrogen from PS is formed during the pyrolysis, the radical can induce the random scission of PS. The degradation behavior in the presence of sulfur or DPS is thought to correspond to that proceeded through the above mechanism. From comparison of the molecular structure of DP and DPE, not affecting the degradation behavior of PS, with that of DPS, the radicals that can abstract hydrogen from PS was considered sulfuric ones, which are thive radical $(RS \bullet)$ and $\bullet Sx \bullet$. The sulfuric radicals are regarded as being formed from additives' -SS- bonds by their thermal rupture and/or by radical chain transfer to them from carbon radicals formed in PS through thermal



Figure 10 Random scission mechanism of PS induced by sulfur radicals.

decomposition of polymer chains. At low temperatures below 350°C, the radical chain transfer may be negligible because PS degradation in the absence of the additives was found to be insignificant at the temperatures; thus, the sulfur radicals are formed by the thermal rupture of -SSbond of the additives. The rupture of -SSbonds of the additives begin to occur at their inherent temperatures; and, therefore, the temperature at which PS degraded through the random scission mechanism depended on the additives. Of the degradation mixtures recovered, those obtained in the presence of sulfur or DPS had odors characteristic of H_2S and thiophenol (RSH), respectively. The presence of H_2S and thiophenol may be a piece of evidence of the hydrogen abstraction by the sulfur radicals. Figure 10 shows a possible mechanism of PS degradation under the influence of additives of sulfur or DPS. The sulfur radicals are formed from the additives [Fig. 10. (1)]. The radicals abstract hydrogens from PS to form a carbon radical at a random position of the chain of PS [Fig. 10 (2)]. The PS then degraded to low polymeric PS through the β -scission mechanism [Fig. (3)].

If PS degraded at a random position of PS chain, the desired low polymeric PS formed greatly while it did a little when depolymerized. The difference in their amount between random and depolymerized degradation can be explained as follows. In general, the amount of a polymer remaining after pyrolysis can be considered to depend on the conversion of the polymer to volatile products. If depolymerization occurs, the polymer degrades to volatile products, such as its monomer. Thus, the decrease in M_w is accompanied by a great decrease in the

amount of the desired low polymeric polymer. In the present experiments, PS depolymerized considerably above 350°C (from GPC measurement and analysis of the amount of volatile products¹⁵). On the other hand, when PS was pyrolyzed in the presence of sulfur or DPS, the polymer degraded below 350°C through the random scission mechanism, as stated above. At the lower temperatures, the rate of depolymerization is less, and, thus, PS was converted less to volatile products. Therefore, relatively large amounts of low polymeric PS are produced.

Thermal Degradation Mechanism in the Presence of Acid Catalysts

When p-TSA was used, a relatively large decrease in M_w appeared at 360°C, which is being considered due to the random scission of polymer chain. At this temperature, a odor characteristic of sulfur compounds could be smelled at the degradation mixtures. This implies that p-TSA was decomposed thermally and acted as a source of a sulfur radical rather than an acid catalyst. The radicals are considered to have promoted random scission of the polymer chain. However, a pyrolytic temperature of 360°C was high enough for the depolymerization to proceed at a great rate. Thus, the amount of the desired polymer was smaller than that obtained by addition of sulfur or DPS.

For the pyrolysis in the presence of SiO₂- Al_2O_3 , the amount of PS was observed to decrease greatly at 380°C, though the mode molecular weight did not change so much from that of the feed PS. This behavior can be explained in terms of being neither depolymerization nor random scission mechanism. The conventional pyrolysis, pyrolysis not using a solvent, of PS in the presence of SiO_2 -Al₂O₃ has already been studied by several workers.^{18,19} The catalyst was found to induce β -scission of the polymer chain and dephenylation of the polymer through mechanisms including carbonium ion formation on the polymer chain. As for the β -scission, contrary to our expectation, the experimental results did not indicate that the scission occurs under the present condition so frequently as to bring a large MWD shift. The great decrease in the amount of PS with a little MWD shift, found at 380°C, may be explained in terms of the dephenylation as follows. Since GPC curves of PS were obtained by measuring absorbance of its phenyl group, the intensity of GPC curve was considered to be proportional to the amount of PS as far as the structure of the polymer was unchangeable. However, if dephenylation occurs, the intensity of GPC curve is no longer proportional to the amount of the polymer and lower than that expected from the amount of the polymer. Further, by the dephenylation, ethylene, or vinyl units may have been formed in the polymer chain. The units are thought to have retarded the depolymerization of PS. Thus, the amount of the polymer appeared to decrease in spite of a little MWD shift.

Practical Aspect of the Pyrolysis-in-Solvent

As stated above, the desired low polymeric PS was obtained successfully when PS was pyrolyzed in tetralin using sulfur-containing additives. From a practical point of view, however, we should take into account recycling tetralin because the solvent is needed to be used in relatively large amounts for the pyrolysis in solvent. During the pyrolysis, a part of the solvent is considered as donating hydrogen to polymer radicals and being converted into naphthalene. Naphthalene is poor in hydrogen-donating ability, and, therefore, the hydrogen-donating ability of the solvent mixture will lower as the number of uses increase. From the results of gas chromatography analysis, however, the amount of the solvent converted into naphthalene is considered to be little for several times of recyclic use, though it will depend on the ratio of the polymer to the solvent. Even if the above problem arises, it will be solved by the following treatment. Since both tetralin and naphthalene have high boiling points, they may easily be separated from the volatile products by distillation. The solvent recovered can be refined by hydrogenation in such a way that naphthalene is hydrogenated to tetralin by using a proper catalyst in the presence of hydrogen.²⁰

CONCLUSION

PS was pyrolyzed in tetralin by adding several additives or catalysts to recover low polymeric PS. When sulfur or DPS was used as additives, the yield of desired low polymeric PS increased greatly. The thermal degradation behavior was explained in terms of random scission of the polymer chain caused by sulfur radicals formed from the additives. The pyrolysis described here may be an alternative for obtaining a low polymeric polymer to controlled polymerization.

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