

# Solvent Effect on Thermal Degradation of Polystyrene

SHIMIO SATO, TADAHIRO MURAKATA, SYUNJI BABA, YASUNOBU SAITO, and SINYA WATANABE, *Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Japan*

## Synopsis

The thermal degradation of polystyrene (PS) in various kinds of solvents was studied in the temperature range from 300 to 450°C. The conversion of PS to low molecular weight products was dependent on the hydrogen donating ability of the solvents used: Solvents with greater donating ability resulted in less conversion of PS. A different degradation behavior was evident when phenols or other kind of solvents were used. These reaction properties are explained with a proposed degradation mechanism that includes hydrogen transfer steps from solvents to intermediate PS radicals and from PS to the solvent radicals.

## INTRODUCTION

Thermal degradations of polymers have been investigated by many workers.<sup>1-3</sup> The thermal degradation of polystyrene (PS) in particular has been investigated quite often from both basic interests and industrial needs. Thus, extensive knowledge has been accumulated about its reaction mechanism and kinetics: A chain depolymerization mechanism with inter- and intramolecular hydrogen transfer has been considered reasonable.<sup>4-8</sup> Several kinetic simulations for the experimental results have been tried.<sup>9-12</sup> Polystyrene degradation also has been studied with pilot plants during exploration for industrial feasibility. The major problems interrupting the development of a commercial plant have been found to be caused from low heat transfer rate and high viscosity of melting polymer. Besides these problems, the thermal degradation behavior of polymers is known to be very complex. For instance, the degradation rate is dependent on pressure, reactor geometry, stirring rate, etc.<sup>13,14</sup> The volatile products obtained from the degradation also are affected by such a physical condition as pressure. The complexity of the degradation behavior results from the highly viscous state of melting polymer, where mass and heat transfers are slow. On the other hand, thermal degradation in solution cannot be affected by such physical conditions. Furthermore, heat transfer and viscosity, which sometimes cause problems in a plant, will be controlled easily. However, there are few studies on such thermal degradation of a polymer.

In this article, reaction properties of the thermal degradation of PS in solution are discussed using several solvents, and a mechanism for the reaction is proposed to explain these properties.

## EXPERIMENT

### Preparation of PS

PS used for the experiments was prepared in *o*-dichlorobenzene by the free radical polymerization at 60°C for 7 h with 2,2-azobisisobutyronitrile as a thermal initiator. The crude PS was purified by reprecipitation several times with methanol.  $\bar{M}_w$  (weight average molecular weight) and  $\bar{M}_n$  (number average molecular weight) of the purified PS, which were computed from gel permeation chromatogram, were 32,000 and 22,000, respectively.

### Pyrolysis Procedure

A 100-mL magnet-driven autoclave was used for the reaction. The PS (2 g) and a solvent (20 g) were placed into the autoclave. It was pressurized to 2 MPa with nitrogen and then heated at a rate of 7.5°C/min up to reaction temperatures, followed by holding 1 h. After that, it was cooled down to room temperature, followed by sampling the reaction mixture for analysis. The reaction temperature was varied from 300 to 450°C. Phenol, 2-naphthol, diphenylamine, 1-methylnaphthalene, tetralin, and 9,10-dihydroanthracene were used as solvents, which were all reagent grade. They were employed because of their good thermal properties, i.e., relatively low vapor pressure and high thermal stability at the reaction temperatures.

### Analysis of Products

The conversion of PS to low molecular weight products and the molecular weight of degraded polymer were determined by gel permeation chromatography (GPC) equipped with an UV detector. The identification and quantification of the low molecular weight products were done by gas chromatography (GC).

## RESULTS AND DISCUSSION

### Analysis of Low Molecular Weight Products

Usually, pyrolysis of a polymer has been studied with open semibatch systems where volatile products are removed for analysis with an inert carrier gas or vacuum distillation. In this study, a closed batch system was adopted because of its easy experimental procedure and no escape of a solvent outside the system.

Figure 1 shows results from GPC analysis of degraded reaction mixtures. On the chromatograms, peaks spread over 28–40 min of elution time are those for degraded PS, and peaks spread over 40–60 min are those for low molecular weight products and the solvent (tetralin). The solid line shows the peaks for feed PS and the solvent. The PS fraction decreases and the low molecular weight products increase with an increase of temperature. Complete degradation needed higher reaction temperature (> 400°C) with a reaction time of 1 h in all the solvents used. No THF insoluble products (crosslinked high molecular weight polymer or cokes) were detected.

The low molecular weight products (volatile products) obtained at 400°C were analyzed with GC. Toluene, ethylbenzene, and styrene were identified in

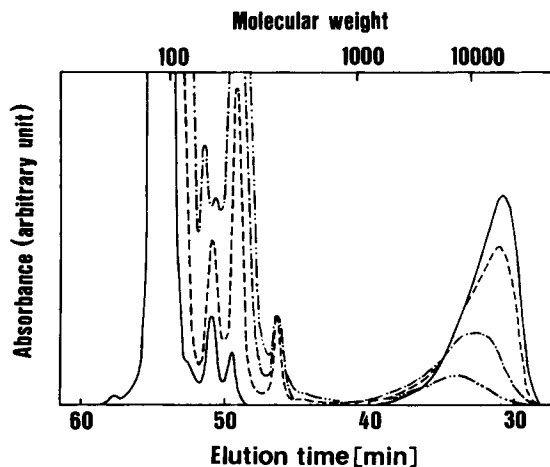


Fig. 1. Change in GPC curves for degradation products of PS in tetralin with temperature. — feed PS (peaks around  $M_w = 100$ , solvent peak); --- 350°C; — · — 400°C; - · · - 450°C.

all the solvents used. Volatile oligomers could not be identified by GC because of interference by large solvent peaks. However, on the GPC chart (Fig. 1), relatively larger molecular weight products (elution time: 48–50), which can be considered as oligomers, are found. The amounts of volatile products were found to decrease in the following order: ethylbenzene > toluene > styrene, in all the solvents used here. For pyrolysis of PS without solvent, it has been known that product distribution is affected by several factors, e.g., reaction temperature or pressure, which are related not only to reactivity but also to mass transfer of products in melting PS.<sup>14,15</sup> The primary products are considered to be styrene monomer and some oligomers. However, when the products are not removed immediately, they react to give secondary products, i.e., toluene, ethylbenzene, etc. For this pyrolysis, the primary products were dissolved in the solvent and could not be removed from the reaction system, so that the secondary reactions became significant. As a result, for pyrolysis of PS in solution, the low molecular weight products are toluene, ethylbenzene, styrene, and some oligomers. A lower yield of styrene monomer, as compared with other products, resulted from its secondary reaction.

### Solvent Effects on PS Conversion

The change in elution time of PS before and after the pyrolysis was small. Therefore, the conversion of PS to low molecular weight products was determined conveniently from the area of PS on the GPC charts: Conversion (%) =  $\{(\text{the area of feed PS} - \text{the area of PS after pyrolysis}) / \text{the area of feed PS}\} \times 100$ .

Figure 2 shows the plot of PS conversion against reaction temperature. Significant increase in conversion proved to occur above 360°C, independent of the kind of solvents. The thermal degradation of PS initiates by the cleavage of a C—C bond at a random position in its polymer chain, and then leads to a chain depolymerization. Thus, the result shows that the solvents do not par-

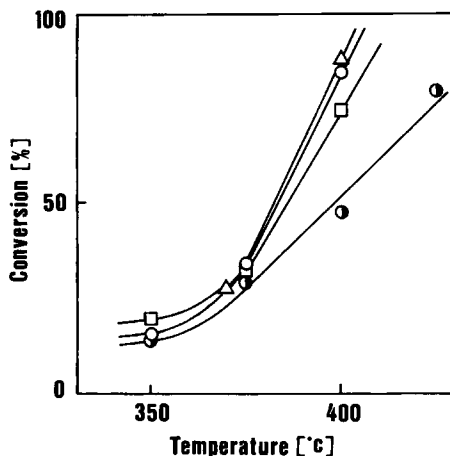


Fig. 2. Temperature dependence of PS conversion in various solvents:  $\Delta$  phenol;  $\circ$  1-methylnaphthalene;  $\square$  decalin;  $\bullet$  tetralin.

icipate in the initiation step (the cleavage of C—C bond in polymer chain). However, the conversions above 360°C were greatly dependent on the solvents. Table I shows the conversions at 400°C in various solvents. The phenols (phenol and 2-naphthol) give the highest conversion. 1-Methylnaphthalene allows PS to degrade at the highest conversion next to phenols. 9,10-Dihydroanthracene and tetralin give lowest conversion. Since the initiation step of PS degradation, as already stated, was not affected by the kind of solvent, the conversion differences among the solvents must arise from mechanism differences and/or rate differences in depropagation and termination steps in the chain depolymerization.

To discuss whether or not the degradation mechanism of PS differs with the solvent,  $\bar{M}_w$  of the unconverted PS for every PS degradation were plotted against the conversion. Figure 3 shows such results. Plots for the phenols are found to deviate extremely from those for the rest of the solvents, whereas the plots for the rest of solvents follow a straight line. From this result, the conversion differences among the solvents, except for the phenols, must arise from rate differences in depropagation or termination in the chain depolymerization. In the phenols, however, PS is considered to degrade through a different reaction mechanism from the other solvents.

TABLE I  
Effect of Solvent on Conversion of PS at 400°C

Solvent	Conversion (%)
2-Naphthol	100
Phenol	87.8
1-Methylnaphthalene	84.2
Decalin	73.8
Diphenylamine	70.6
Tetralin	50.6
9,10-Dihydroanthracene	43.3

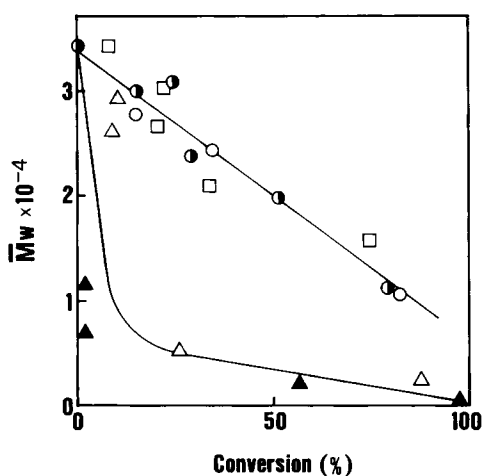


Fig. 3. Relationship between conversion and  $M_w$ : solvent  $\Delta$  phenol;  $\blacktriangle$  2-naphthol;  $\circ$  1-methylnaphthalene;  $\square$  decalin;  $\bullet$  tetralin.

The difference in degradation behavior between the phenolic and the other solvents is attributable to that of polymer chain scission. Figure 4 [(a) and (b)] shows changes in GPC curves of PS obtained under several reaction temperatures using both tetralin and phenol. In the case of tetralin, the decrease of molecular weight of PS was small and the polymer disappeared without providing oligomers. For phenol, the decrease of molecular weight was great and the polymer finally converted to oligomers. Similar results were also found between these two types of solvents.

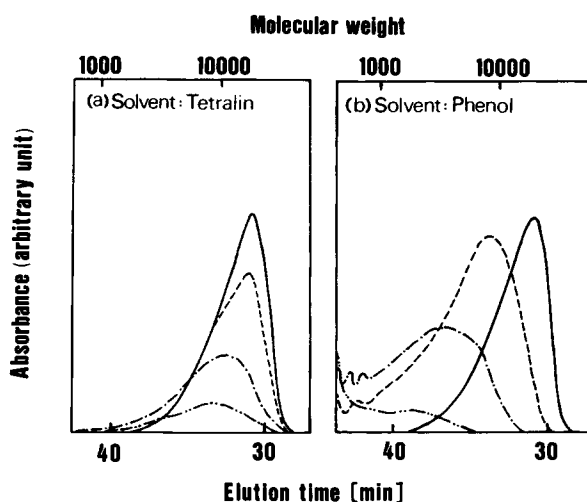
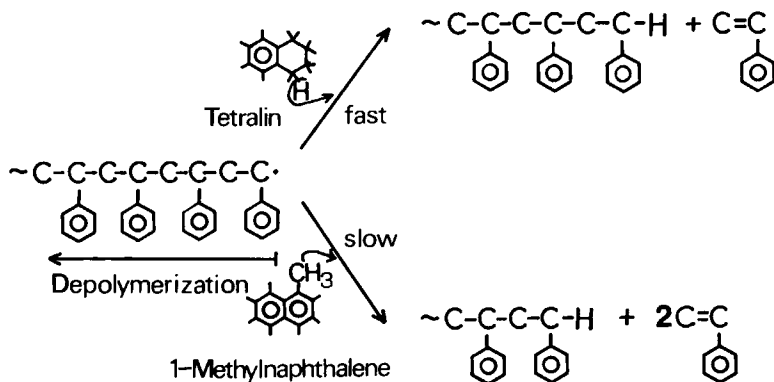


Fig. 4. Comparison of GPC curves for PS degraded in tetralin (a) and in phenol (b): (a) — feed PS; - - - 350°C; - · - 400°C; · · · 450°C; (b) — feed PS; - - - 350°C; - · - 375°C; · · · 400°C.

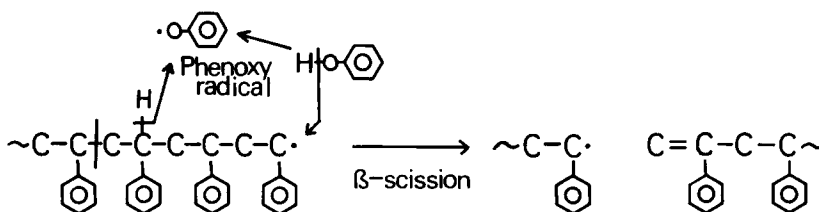
### Thermal Degradation Mechanisms of PS in Solution

The thermal degradation of PS in solution is considered to proceed essentially through a chain reaction mechanism similar to that without solvent. That is, the degradation is initiated by the thermal cleavage of polymer chains to produce polymer radicals. The polymer radicals then proceed to the chain reactions by following two paths: One is a depolymerization, which gives monomers; the other is intra- and intermolecular hydrogen transfers, which induce  $\beta$  scission of polymer chains to produce new polymer radicals. From experimental results shown in Table I, Scheme 1 is reasonable as a mechanism for the degradation of PS in the solvents other than the phenols. Tetralin and 9,10-dihydroanthracene are known to be good hydrogen donor solvents because of their high hydrogen donating ability.<sup>16,17</sup> This ability is related to their weak C—H bond. On the other hand, 1-methylnaphthalene is a poor solvent in terms of the hydrogen donating ability. The good hydrogen donor solvent must easily terminate the chain reactions because the polymer radical may abstract hydrogen from the solvent and convert to a stable molecule. Thus, good hydrogen donor solvents such as tetralin gave lower conversion, while solvents with poor hydrogen donating ability like 1-methylnaphthalene allowed PS to decompose with little retardation of the chain reactions, and gave higher conversion.

With the phenols, the degradation mechanism seemed to be somewhat different from that in the other solvents. The rapid decrease in molecular weight of PS during the degradation leading to oligomer formation, as shown in Figure 4, is typical for random scission mechanism. Thus, besides the chain mechanism stated previously, a mechanism for a random scission must play a role with phenols. It may be more reasonable to consider that the phenols break the polymer chain. Scheme 2 illustrates the additional mechanism. The phenoxy radical, produced by the hydrogen abstraction by the polymer radical, may also abstract hydrogen from the polymer chain at a random position. The polymer from which hydrogen has been abstracted then undergoes chain scission at the  $\beta$  position. Such a random scission-type mechanism must degrade PS to a higher degree than at 400°C. The catalytic action of phenols in this mechanism may be due to the relatively longer lifetime of the resonance stabilized phenoxy radicals.



Scheme 1. Termination mechanism for chain depolymerization of PS by hydrogen transfer from solvents to polymer radical.



Scheme 2. Random scission mechanism for PS induced by phenoxy radical.

## CONCLUSION

The volatile products obtained by thermal degradation of PS in solution contained large amounts of ethylbenzene and toluene, besides styrene monomer, which might be mainly secondary products from styrene and oligomer.

The thermal degradation properties of PS in solution were dependent on the kind of solvent used. The conversion of the polymer to low molecular weight products was considered to be affected by the hydrogen donating ability of a solvent. The degradation behavior mediated by solvents other than phenols were explained via chain depolymerization mechanism in which the polymer radicals abstract a hydrogen from the solvents. When phenols are used as solvents, the behavior appeared to result partly from a random scission mechanism. This may be interpreted as competition between a depolymerization and a random scission mechanism in which a phenoxy radical, produced from phenol, plays the role of a chain transfer agent.

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