Solvent effect on thermal degradation of polystyrene and poly-α-methylstyrene

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Polystyrene (PS) and poly-α-methylstyrene (PMS) in various kinds of solvents such as 1-methylnaphthalene, tetralin and phenol were thermally degraded in the temperature range from 250 to 450°C. The conversion of PS to low molecular weight products depended on the kinds of solvents and the polymer concentration, whereas the conversion of PMS was independent of both of these. The difference in degradation behaviour between the polymers was explained in terms of a mechanism which involves hydrogen transfer steps from solvents to intermediate polymer radicals.

INTRODUCTION

Thermal degradations of polymers including vinyl polymers have been investigated by many workers[1-3]. Thus, extensive knowledge has been accumulated about the reaction mechanism and kinetics — the random scission mechanism is reasonable for some polymers, the chain depolymerization mechanism for others, while intermolecular chain transfer steps is an additional mechanism for several polymers[4-13]. Besides such basic interests, practical interests have also demanded the study of the thermal degradation of polymers: for example, for the recovery as useful products, waste polymers have been thermally degraded with pilot plants. The major problems affecting the scale-up to a commercial plant have been found to be caused from the severe heat transfer resistance due to the high viscosity of the melting polymer. In addition to these troubles, the behaviour of polymer degradation is rather complex because high viscosity is responsible for lowering the heat and mass transfer rates. For instance, the degradation rate is dependent on pressure, reactor geometry, stirring rate, etc[14-16].

In contrast to the characteristics of the conventional degradation stated above, the thermal degradation in solution may not be affected by such physical conditions because heat and mass transfer resistances may not be as severe as those in the conventional degradation. This is because of easier control of the reaction mixture viscosity. However, there have been few studies on such thermal degradations of a polymer.

Our previous paper mentioned the benefit of the pyrolysis in solution against conventional pyrolysis, reported experimental results about the thermal degradation of polystyrene (PS) in several kinds of solvents and discussed the degradation mechanism[17].

This paper presents the thermal degradation behaviour of poly-α-methylstyrene (PMS), a typical vinyl polymer having been considered to degrade through a different mechanism from that of PS, and further results for PS. On the basis of the experimental findings, the mechanism of degradation of both polymers in solution is discussed.

EXPERIMENTAL

Preparation of PS and PMS

PS was prepared in o-dichlorobenzene by the free radical polymerization at 60°C with 2,2-azobisisobutyronitrile as a thermal initiator. PMS was made in carbon disulfide by the cationic polymerization at −50°C with aluminium chloride dissolved in ethyl chloride as an initiator. The crude PS and PMS were purified respectively by reprecipitation several times with methanol and hexane. M_w (weight average molecular weight) and M_n (number average molecular weight) of the purified PS were computed respectively from its gel permeation chromatogram to be 32 000 and 22 000. The counterparts of the purified PMS were 50 000 and 26 000.

Pyrolysis procedure

A 100 ml magnet-driven autoclave was used for the reaction. In a typical experiment, each polymer (2 g) and a solvent (20 g) were placed into the autoclave. It was pressurized to 2 MPa with nitrogen and then heated at about 7.5°C min⁻¹ up to reaction temperatures, and then held there for 1 h. After that, it was cooled to room temperature, followed by a sampling of the reaction mixture for analysis. When the effect of solvent concentration on the conversion was examined, 1 g of a polymer and a corresponding amount of a solvent were charged in the autoclave. The reaction temperature was varied from 350 to 450°C for PS and from 250 to 350°C for PMS. Phenol, 2-naphthol, diphenylamine,

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1-methylnaphthalene, tetralin, triphenylmethane and 9,10-dihydroanthracene were used as solvents, being all reagent grade. They were employed because of their good thermal properties, i.e. relatively low vapour pressure and high thermal stability at the reaction temperatures.

Analyses of products

The conversion of polymer to low molecular weight products was determined by gel permeation chromatography (g.p.c.) equipped with a u.v. detector (254 nm). The low molecular weight products (volatile products) were identified and determined by gas chromatography (g.c.)

RESULTS AND DISCUSSION

Solvent effects on conversion

In the chromatograms of reaction mixtures from any polymer, peaks attributing unreacted polymer and low molecular weight products were clearly separated. The change in elution time of the unreacted polymers was a little before and after the pyrolysis. Therefore, the conversion of the polymers to low molecular weight products was determined from the area of the unreacted polymer on the g.p.c. chart: conversion (%) = {(the area of feed polymer − the area of unreacted polymer after pyrolysis)/the area of feed polymer} × 100.

Figure 1 shows the plot of the conversion of both polymers in several kinds of solvents against the reaction temperature. It is found that conversion significantly increased above 360°C for PS and above 250°C for PMS.
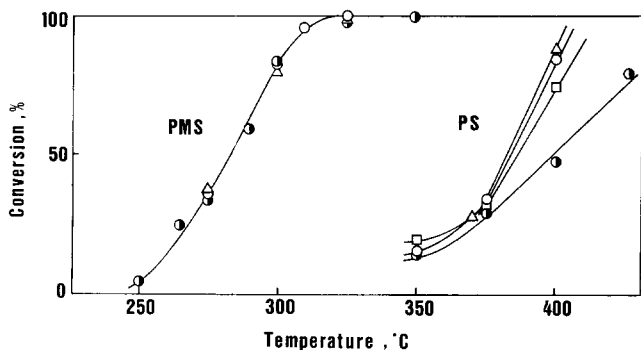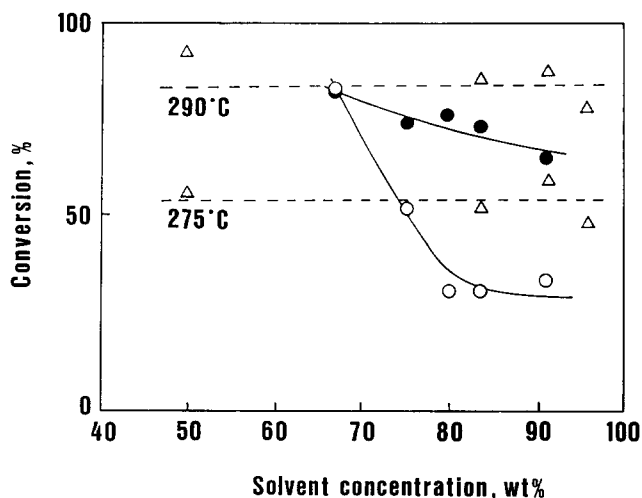

Figure 2 Plots of PS conversion (O, ●) and PMS conversion (△) against solvent concentration. Solvent O, △: tetralin, ●: 1-methylnaphthalene

These temperatures agreed with those for the pyrolysis without a solvent. These properties indicate no effect of solvents on the initiation step of the thermal degradation (the cleavage of the C–C bond in the polymer chain) of both polymers.

The conversion of PMS was found to lie on the same curve, independent of the kind of solvents, while that of PS was distinct. The effects of the kinds of solvents on the conversion, were studied for both polymers using eight solvents. *Table 1* shows the results. The PMS conversion was almost constant and independent of the kind of solvents, while that for PS varied with the solvents.

Effect of solvent concentration on conversion

The effect of the solvent was analysed in more detail as the solvent concentration was varied. In the case of PMS, tetralin was used as a representative solvent because the conversion was independent of the kind of solvent. It was pyrolysed at two different temperatures. For PS, tetralin and 1-methylnaphthalene were used as solvents because it was considered that PS would degrade differently with the respective hydrogen donating ability of the two solvents. *Figure 2* shows plots of the conversion against the solvent concentration. For PMS, the conversion did not vary with the solvent concentration, although it was different at different temperatures. On the other hand, PS conversion decreased with an increase in solvent concentration and the behaviour was significant in tetralin of a higher hydrogen donating ability. At experiments below 50 wt% of solvent concentration, the conversion could not be determined because it was so high that the degraded polymer showed gel permeation chromatograms quite different from that of the parent polymer.

Figure 1 Temperature dependence of PS and PMS conversions in various solvents; ◑: tetralin, □: decalin, O: 1-methylnaphthalene, △: phenol

Table 1 Effect of solvent on conversion of PS and PMS

| | Conversion (%) | | |
Solvent	PS[a]	PMS[b]	b.p.(°C)[c]
2-Naphthol	100	33.1	286
Phenol	87.8	41.9	182
1-Methylnaphthalene	84.2	35.7	242
Decalin	73.8	23.9	187
Diphenylamine	76.0	30.2	302
Tetralin	50.6	33.8	207
Triphenylmethane	44.1	–	360
9,10-Dihydroanthracene	43.3	30.3	312

[a] Reaction temperature: 400°C
[b] Reaction temperature: 275°C
[c] Boiling point under 1 atmosphere

Analysis of low molecular weight products

Low molecular weight products from PS. Toluene, ethylbenzene, styrene monomer and cuneme were identified as well as a small amount of other compounds. Oligomers were observed but could not be detected by g.c. because of the interference by a large solvent peak. Toluene, ethylbenzene and styrene were principal among the products. *Figure 3* shows the dependence of their
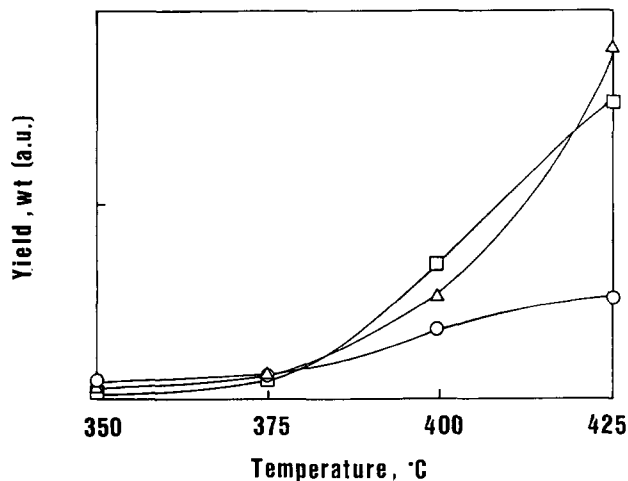
Figure 3   Effect of reaction temperature on amounts of volatile products from PS in tetralin; O: styrene, □: ethylbenzene, △: toluene
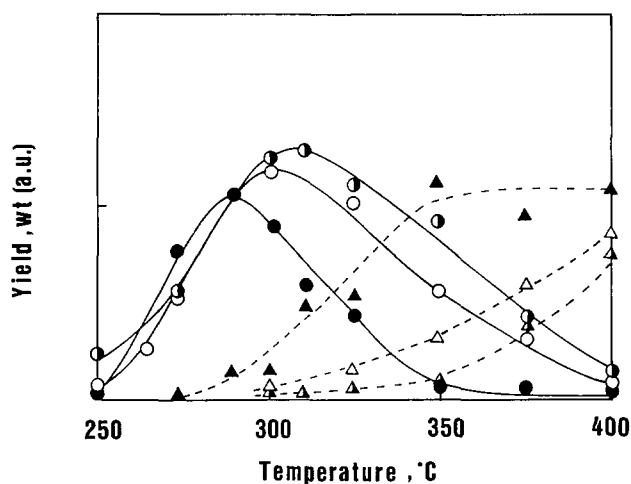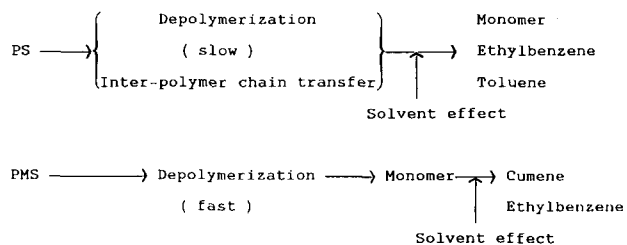
Figure 4   Effect of reaction temperature on amounts of volatile products from PMS in phenol (●, ▲), tetralin (O, △) and 1-methylnaphthalene (◐, ▲): product O, ◐, ●: α-methylstyrene △, ▲, ▲: cumene

Scheme 1   Solvent effects on the thermal degradation of PS and PMS

yield on the reaction temperature when tetralin was used as a solvent. The yield was expressed as component weight relative to the sampled reaction mixture, because the total amount could not be determined. The amount of the volatile products increased with a rise in reaction temperature. However, the yield of styrene seemed to be low when compared with that of the conventional pyrolysis methods, and this tendency became significant at higher temperatures. Similar results were obtained in the other solvents. Styrene may convert into further volatile products (toluene, ethylbenzene and others) owing to its high reactivity coming from the double bond.

Low molecular weight products from PMS. The volatile products converted from PMS were α-methyl-styrene, cumene, ethylbenzene and toluene, and other products were observed in small amounts. Oligomers could not be detected for the same reason as for PS degradation. Among the volatile products, the main products were α-methylstyrene, cumene and ethylbenzene.

Figure 4 shows the relative yields of α-methylstyrene and cumene. At low reaction temperatures below 280°C, only α-methylstyrene was formed. The yield was almost the same amongst the three kinds of solvent, which was consistent with the results that the conversion was independent of the kind of solvents. As the reaction temperature was higher, the yield increased and passed through a maximum and then decreased, while cumene was formed with monotonous increases or with such an increase followed by a plateau. Ethylbenzene also increased with a decrease of the yield of α-methylstyrene, although this is not plotted in the figure. Thus, the conclusions are: (1) the primary product from PMS degradation is α-methylstyrene monomer, which reacts to give cumene, ethylbenzene and other products at higher temperatures; (2) the rate of reactions, starting from the monomer, was greatly dependent on a kind of solvent at higher reaction temperatures.

Thermal degradation mechanism of PS and PMS in solution

The comparison of the behaviour of the thermal degradation in solution between PMS and PS is worthy of discussion, because for conventional pyrolysis the behaviour has been observed to be remarkably different. The behaviour of conventional pyrolysis is stated as follows: PS degrades via a competitive mechanism of depolymerization with an average zip length below 10 (see ref. 18) and inter-molecular chain transfer; PMS degrades via a single mechanism of depolymerization with a larger average zip length of 1300 (see ref. 19). With respect to the present pyrolysis, for PS degradation, the previous and present papers show that since some of the polymer radicals abstracted hydrogen from solvent molecules in order to be quenched, the degradation rate was dependent not only on the presence of solvents but on their hydrogen donating ability. For PMS degradation, the present paper indicates that PMS decomposed in a manner independent of both the presence of solvents and the kinds of solvents. Consequently, PMS must have degraded without abstraction of hydrogen from the solvents. As to the effect of solvent concentration variations, two effects are mentioned. The first is a change in the hydrogen donating ability of the solution because of the change in relative concentration of solvent. The second effect is in the rate of inter-molecular chain transfer, because of the change in inter-molecular distance. When the concentration decreases, both the effects promote degradation. In the case of PS, this promotion was found, particularly for the use of tetralin with a high donating ability. In the

case of PMS, the first effect can be excluded, because the polymer radicals were unlikely to abstract hydrogen from the solvents as mentioned. These differences in solvent effect between PS and PMS, may be responsible for those differences in their monomer configuration. The PS monomer has a hydrogen at the α-position and it is subject to abstraction by polymer radicals. The inter-molecular hydrogen abstraction (chain transfer) results in depolymerization of other polymer molecules and/or formation of products other than the monomer. In contrast, the α-position of PMS is blocked by the methyl group and therefore depolymerization proceeds exclusively. However, the hydrogen on the primary or secondary carbon may transfer, and may initiate depolymerization and affect the conversion. The PMS conversion, however, was found to be almost independent of solvent concentration. Therefore, the inter-molecular chain transfer process is not considered to affect the conversion and the degradation of PMS can be taken as a unimolecular reaction.

Volatile product distributions were considerably different from those with conventional pyrolysis. In the case of PS, the monomer was formed at low yields, particularly under higher reaction temperatures when compared with conventional pyrolysis. Usually, conventional pyrolysis has been studied with open semi-batch systems where the volatile products are removed immediately from the reaction systems by inert carrier gas or evaporation. In a closed batch process, as used in this work, they remain in the system and may react to become further products. Thus, styrene is supposed to have converted into ethylbenzene, toluene and other compounds. This speculation was confirmed from the experimental result that ethylbenzene and toluene were obtained when styrene was subjected to the same reaction condition as PS.

In the case of PMS, the monomer was predominantly produced at low temperatures and the yield of cumene and ethylbenzene increased with reaction temperature. The degradation of PMS in solution is a typical consecutive reaction which consists of the degradation of PMS to the monomer, followed by conversion of the monomer to cumene, ethylbenzene or others. Only the latter reaction was affected by the solvent (*Scheme 1*). The fact that the reaction of vinyl compounds, such as α-methylstyrene, depended on the kinds of solvents is particularly interesting. Detailed discussion about this property requires further experimental information and it was beyond the objective of this paper.

CONCLUSIONS

Different solvent effects were found on the thermal degradation properties between PS and PMS. The conversion of PS to low molecular weight products was dependent upon both the kind of solvent used and the solvent concentration. The conversion was low at good hydrogen donor solvents. The decrease in solvent concentration brought a rise in the conversion and the tendency was significant in good hydrogen donor solvents. These results were explained through hydrogen abstraction processes from the solvents by the polymer radicals.

In contrast, the conversion of PMS was independent of both the kind of solvent used and the concentration. These results indicated that the polymer radicals may not abstract hydrogen from both the solvent and the parent polymer.

The distributions of volatile products from both PS and PMS were different from those obtained by conventional pyrolysis, i.e. pyrolysis without solvents. These results were explained in terms of the secondary reaction from the monomers to the other products.

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