Effect of solvent on thermal degradation of poly(p-methylstyrene)

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The thermal degradation of poly(p-methylstyrene) (P-pMS) was studied in several solvents, such as 1-methylnaphthalene, tetralin and phenol, in the temperature range 300–400°C. No undesirable by-products, such as gels and cross-linked high molecular weight products, were formed, in contrast to the significant yield of these products with conventional polymer pyrolyses without solvents. The conversion of P-pMS to low molecular weight products, and the molecular weight of the residual polymer after pyrolysis, depended markedly on the kind of solvent used. Such degradation behaviour is explained well by a proposed mechanism including hydrogen transfer from solvents to intermediate polymer radicals.

INTRODUCTION

Pyrolysis in solution is considered to differ in behaviour from conventional pyrolysis, i.e. pyrolysis without a solvent. It has not been paid much attention so far while the latter has been studied by many workers[1–12]. Thus we have carried out the pyrolysis of polymers in solution using several kinds of solvent. Our previous report showed that polystyrene (PS) is degraded to low molecular weight products without formation of any undesirable by-products, such as high molecular weight products and cokes, which are often produced during conventional pyrolysis[13]. These results encouraged us to apply pyrolysis in solution to other polymers. The objective of the present paper is to examine the effectiveness of pyrolysis in solution for polymers which tend to produce undesirable by-products during conventional pyrolysis. Poly(p-methylstyrene) (P-pMS) was investigated as such a polymer. It is known to form gel-like materials and cross-linked high molecular weight products during conventional pyrolysis[14,15].

EXPERIMENTAL

Preparation of P-pMS

P-pMS was prepared by a similar procedure to PS in ref. 13, except that the reaction temperature was 70°C. The weight average molecular weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$) of the purified P-pMS computed from gel permeation chromatography (g.p.c.) were 33 000 and 22 000, respectively.

Pyrolysis procedure

The reaction temperature was varied from 300 to 400°C. For comparison, conventional pyrolysis was also carried out using 2 g of P-pMS without solvents under

conditions similar to those for the pyrolysis under study. This gave considerable amounts of gel-like by-products, as will be seen later, so the pyrolysis mixtures were extracted with tetrahydrofuran (THF) and the extract residues were weighed as gel-like compounds. The other experimental conditions and procedures, including the kinds of solvent used, were the same as in the previous work[13], unless otherwise stated.

Analysis of products

The liquid and volatile products of the pyrolyses were analysed by g.p.c. and gas chromatography (g.c.), respectively, as in the previous work. The conversion of polymer to low molecular weight products was calculated using the same procedure as in the pyrolysis of PS using g.p.c. curves of the polymer before and after the pyrolyses as follows:

$$\text{conversion} = \frac{\begin{array}{c}(\text{area of parent polymer} \\ - \text{area of parent polymer after pyrolysis})\end{array}}{\text{area of parent polymer}} \times 100$$

RESULTS

Comparison of by-product formation

The conventional pyrolysis of P-pMS has been reported to form by-products, which are believed to be responsible for intra- and intermolecular cross-linkage. First, conventional pyrolysis and that in solution were studied from the point of view of by-product formation. The pyrolysis in solution was run using tetralin under conditions typical of this work.

Figure 1 shows the dependence on pyrolysis temperature of the amount of gel produced by conventional pyrolysis. The gel yield varied with change in reaction temperature and had a maximum value of about 60 wt% at 340°C. *Figure 2* shows results of g.p.c. analyses for the
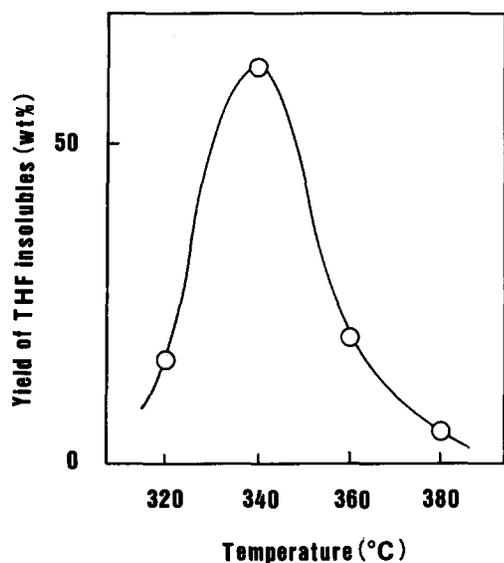
Figure 1 Variation of gel yield with reaction temperature in conventional pyrolysis

Figure 4 shows the plots of conversion in the presence of tetralin, 1-methylnaphthalene and phenol against reaction temperature. A marked increase in conversion occurred above 370°C with all the solvents. The temperatures at which degradation became significant were almost the same as those reported for conventional pyrolysis. However, the dependence of conversion upon reaction temperature varied considerably with the solvent: as the pyrolysis temperature increased, conversion increased gradually with tetralin but rapidly with phenol, and was intermediate in the case of 1-methylnaphthalene. At higher temperatures, at which conversion became significant, the effect of solvents was in the order: phenol > 1-methylnaphthalene > tetralin. At pyrolysis temperatures below 370°C, pyrolysis did not proceed significantly and the solvents showed different conversion levels from those at higher temperatures; there was even negative conversion with phenol. Such an irrational conversion resulted from the great change in molecular weight distribution between the residual polymer and the parent polymer and will be discussed in the next section.

Solvent effects were studied further using several other solvents at a reaction temperature of 380°C, at which the

Figure 2 G.p.c. curves of parent P-pMS (——) and P-pMS pyrolysed without solvent at 380°C (- - -)
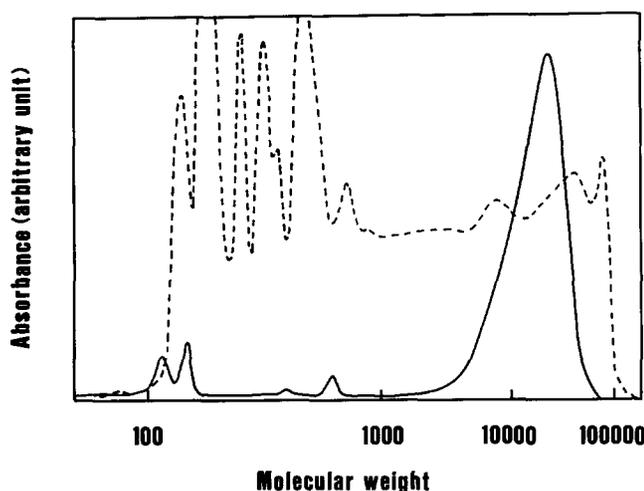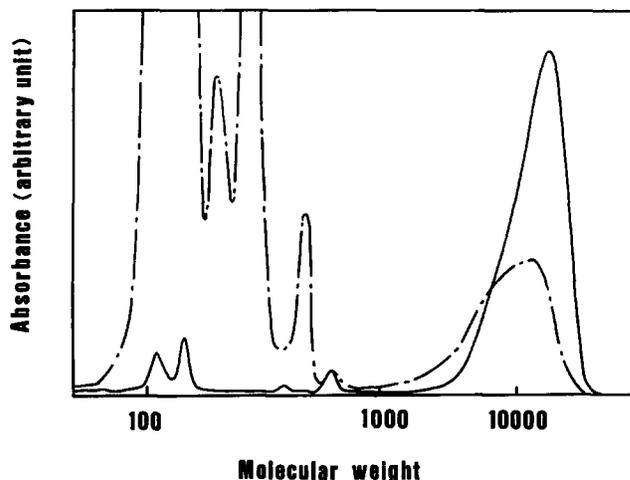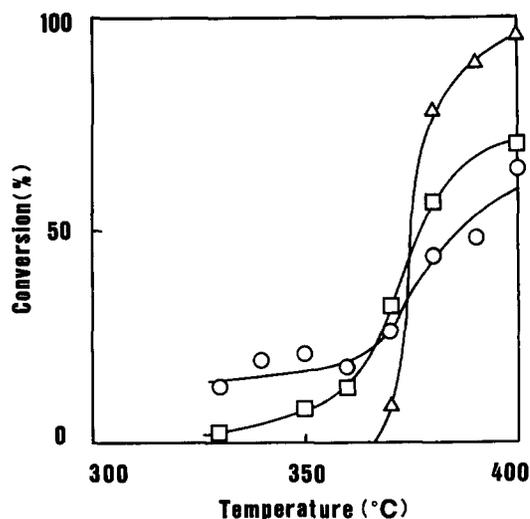

Molecular weight

Figure 3 G.p.c. curves of parent P-pMS (——) and P-pMS pyrolysed in tetralin at 380°C (—·—)

products, separated from gel-like components formed in conventional pyrolysis at 380°C, and for the parent polymer. The products were found to consist not only of low molecular weight compounds but of polymers which had higher molecular weights than the parent polymer.

The pyrolysis in solution, in contrast to conventional pyrolysis, did not form gel with all the solvents. *Figure 3* shows g.p.c. curves for products obtained by pyrolysis using tetralin at 380°C and for the parent polymer. The pyrolysis produced only low molecular weight products below 1000 indicating that this pyrolysis depressed the cross-linking reaction.

In conclusion, no by-products were formed in pyrolysis in solution, compared to a high yield in conventional pyrolysis.

Effects of solvent on conversion

The degradation behaviour of P-pMS in pyrolysis in solution was thought to be affected by the kind of solvent, as found for pyrolysis of PS[13]. Therefore, the effects of solvent on conversion were studied.

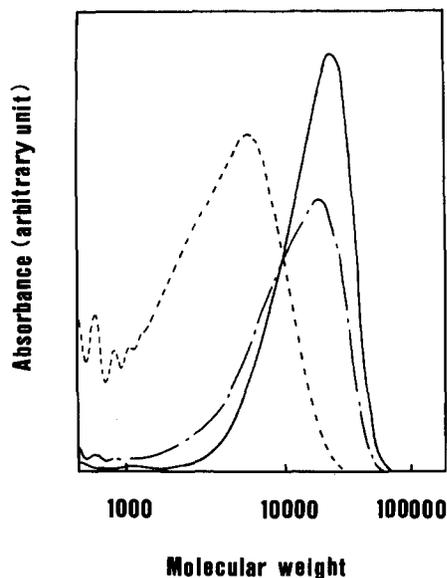**Figure 4** Temperature dependence of P-pMS conversion in various solvents: △, phenol; □, 1-methylnaphthalene; ○, tetralin

Table 1 Effects of solvent on P-pMS conversion

Solvent	Conversion (%)	B.p. (°C)[a]
2-Naphthol	78.8	286
Phenol	78.6	182
1-Methylnaphthalene	56.7	242
Decalin	58.0	187
Tetralin	44.2	207
9,10-Dihydroanthracene	23.8	312

[a] Boiling point under 1 atmosphere

Figure 5 Comparison of g.p.c. curves of parent P-pMS (——) with P-pMS pyrolysed at 360°C in phenol (———) and in tetralin (—·—)

irrational conversions mentioned above did not occur. *Table 1* shows the experimental results. They reveal that the phenols and the poor hydrogen-donating solvents, 1-methylnaphthalene and decalin, gave high conversions, while tetralin and 9,10-dihydroanthracene, which are good hydrogen-donating solvents, gave low conversions.

Effects of solvent on molecular weight distribution of residual polymer

Figures 5 and *6* show g.p.c. curves of the parent and the residual polymers for pyrolyses in solution carried out at low and high pyrolysis temperature, respectively. The solvents used were tetralin and phenol, which exhibited the two extreme characteristics among the solvents. When tetralin was used, the shape of the chromatogram of the residual polymer at both temperatures did not change greatly in comparison with that of the parent polymer, and only the peak height decreased. On the other hand, the use of phenol broadened and shifted the chromatogram of the residual polymer to the lower molecular weight side. This change was more significant at lower pyrolysis temperatures. Similar behaviour was observed for 2-naphthol, another phenol. As shown in both figures, the broadening and shift of the molecular weight distributions of the residual polymer were not marked at the higher temperatures. Such behaviour can be explained by the production of oligomers during polymer degradation, which then decomposed to lower molecular weight products.

For 1-methylnaphthalene, the chromatograms broadened slightly and also shifted to the lower molecular weight side. These properties suggested that the mode of polymer scission is dependent on the kind of solvent used.

The shift of the chromatograms was always accompanied by their broadening and, in spite of the expectation of considerable polymer degradation owing to the chromatogram shift, the conversions at low reaction temperatures were low or frequently negative. This was because the conversion calculations applied to the present work tended to overestimate the amount of residual polymer when the broadening and shift of chromatograms occurred.

To clarify the solvent effects, average molecular weights of the residual polymer were calculated from the molecular weight distributions, shown in *Figures 5* and *6*, and plotted against conversions. *Figure 7* shows the results. With tetralin, the molecular weight decreased
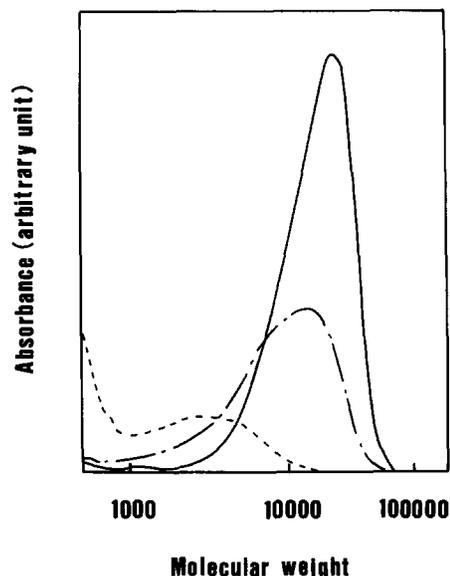
Figure 6 Comparison of g.p.c. curves of parent P-pMS (——) with P-pMS pyrolysed at 380°C in phenol (———) and in tetralin (—·—)
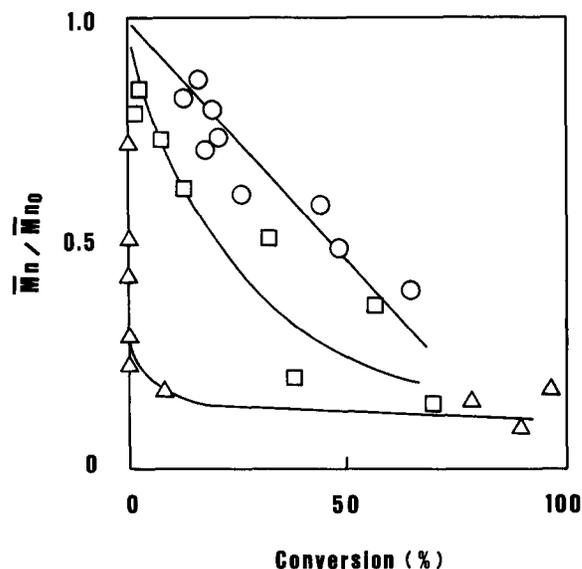
Figure 7 Relationship between conversion and normalized average molecular weight, $\bar{M}_n/\bar{M}_{n_0}$, where $\bar{M}_{n_0}$ and $\bar{M}_n$ represent the number average molecular weight of the polymer before and after pyrolysis, respectively: ○, tetralin; □, 1-methylnaphthalene; △, phenol

gradually with increase in conversion. For phenol, the molecular weight decreased significantly at the initial stage of degradation, i.e. at the low conversion stage, and the conversions at pyrolysis temperatures below 370°C became negative, for the reason given above. They are plotted on the vertical axis of the figure for convenience. For 1-methylnaphthalene, the result was intermediate between that for tetralin and phenol.

Other properties of pyrolysis in solution

Volatile components of the low molecular weight products were identified by g.c. to be *p*-xylene, 4-ethyltoluene and *p*-methylstyrene (monomer). Their yields were in the order of *p*-xylene > 4-ethyltoluene > *p*-methylstyrene in most cases. Other components of the low molecular weight products could not be identified due to the large peak representing the solvents on the chromatograms. The liquors produced after the pyrolyses were different colours depending on the solvents used: transparent and slightly yellow for good hydrogen-donating solvents such as tetralin or 9,10-dihydroanthracene, and dark for poor hydrogen-donating solvents such as 1-methylnaphthalene and phenol. The dark coloration is thought to be due to the formation of hydrogen-deficient molecules having conjugated double bonds. Thus these results suggest the presence of hydrogen transfer paths from solvent molecules to polymer radicals and/or other products.

DISCUSSION

Mechanism of conventional pyrolysis

The degradation of P-pMS must be initiated by thermal cracking of its polymer chain, forming polymer radicals. These radicals may then react through two paths: (1) depolymerization to produce low molecular weight compounds; (2) hydrogen abstraction from the methyl group at the *para* position on the aromatic groups to produce *para*-methyl radicals. The formation of gels and high molecular weight polymers can be explained in terms of intermolecular coupling between the *para*-methyl radicals: high cross-linkage accounts for the gel formation and low cross-linkage for the high molecular weight polymer formation. The depolymerization and the coupling are competitive, and either may predominate, depending on the reaction temperature. At lower temperatures, the coupling precedes the depolymerization to make gel and high molecular weight products. At higher temperatures, the depolymerization precedes the coupling, because the products of coupling, if it occurs, are so unstable at such temperatures that they are depolymerized rapidly and thus the pyrolysis is characteristic of depolymerization. These mechanisms may reflect the maximum gel yield at around 340°C of the relatively lower pyrolysis temperature.

Mechanism of pyrolysis in solution

In contrast to conventional pyrolysis, no gel or high molecular weight products were formed at any temperature for the pyrolysis in solution. Two explanations may be given for such properties. One relates to a dilution effect which decreases collision frequency in bimolecular reactions, such as coupling, and consequently depresses the formation of by-products. The other relates to the decrease in concentration of the *para*-methyl radicals

through hydrogen transfer from solvent molecules, as suggested from the coloration of the liquors produced. *Figure 8* illustrates pyrolysis mechanisms consisting of reaction schemes (a), (b) and (c). In the absence of a solvent (scheme (a)), the polymer radicals produced by thermal scission of polymer chains abstract hydrogens from *para*-methyl groups to form *para*-methyl radicals. In the presence of a solvent (schemes (b) and (c)), however, the *para*-methyl radical formation may be depressed, because the polymer radicals may prefer to abstract hydrogens from their neighbouring solvent molecules (scheme (b)) and a large portion of the methyl radicals, if formed, may also be quenched by directly abstracting hydrogens from solvent molecules prior to coupling (scheme (c)).

Mechanistic difference between solvents

The results shown in *Figure 7* clearly reflect the difference in degradation mechanism among the solvents. The pyrolysis with tetralin proceeded preferentially through depolymerization, because the average molecular weight $(\bar{M}_n)$ of the residual polymer decreased gradually with increase in conversion. With phenol, $\bar{M}_n$ decreased rapidly at the initial stage of degradation. Such behaviour is typical of a random scission mechanism. From the chemical structure, however, the polymer cannot be considered to degrade substantially without depolymerization. Thus, besides depolymerization, random scission contributed significantly when phenol was used as a solvent. In the case of 1-methylnaphthalene, the behaviour of conversion *versus* $\bar{M}_n$ was intermediate between that for phenol and tetralin, and therefore
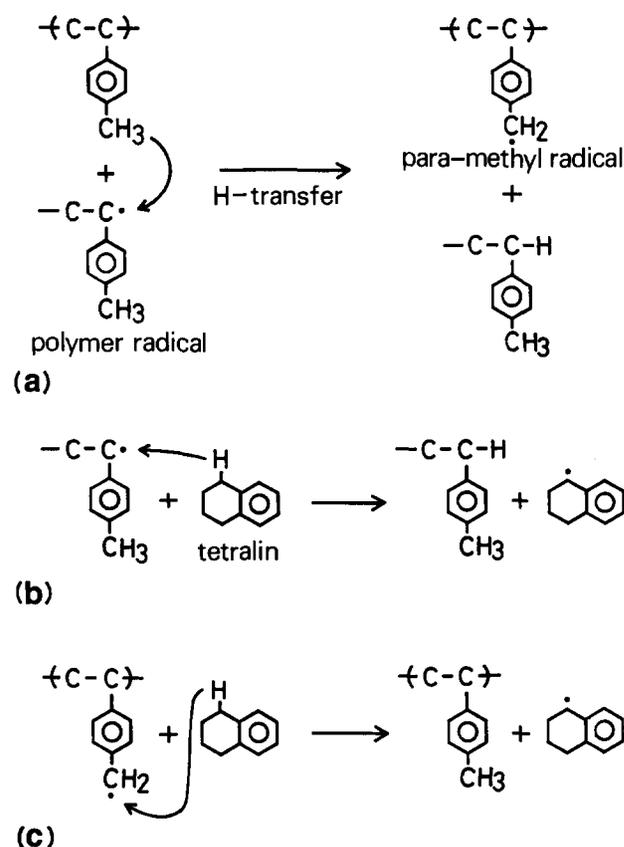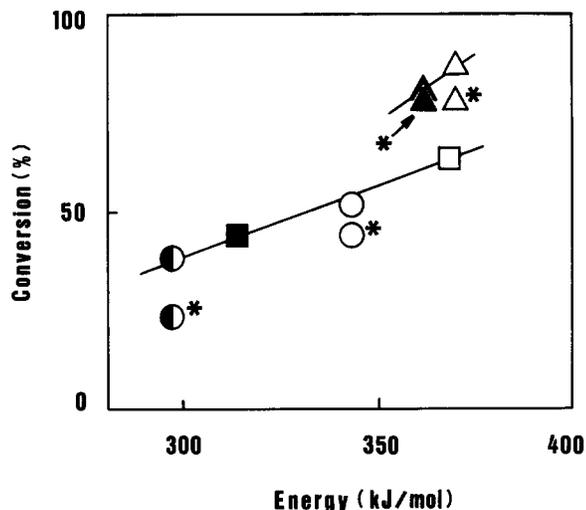

Figure 8 Reaction mechanisms for depression of *para*-methyl radical formation in pyrolysis with solvent

Figure 9 Relationship between conversion and bond dissociation energy of solvents: ◑, 9,10-dihydroanthracene; ■, triphenylmethane; ○, tetralin; □, diphenylamine; ▲, 2-naphthol; △, phenol. Symbols with asterisk represent P-pMS, and those without, PS

of the solvent[16], where the correlation for P-pMS was made for the degradation results obtained under the higher pyrolysis temperature, at which no irrational conversion occurred. *Figure 9* shows the results. For both polymers, the conversion and the bond dissociation energy give almost linear plots with positive slopes, although the plots in the case of phenols deviate from the straight line because of the effect of random scission. The above results prove that the proposed mechanism is rational.

CONCLUSION

P-pMS was pyrolysed in several different solvents. The pyrolysis suppressed cross-linking among para-methyl radicals which led to the formation of gel or high molecular weight products, owing to hydrogen transfer from solvents to the para-methyl radicals. The polymer conversion depended on the hydrogen-donating ability of the solvent used. The different effects of the solvents on depolymerization of the polymers was explained in terms of the bond dissociation energy of the solvents.

random scission also contributed, although the extent of its effect was considerably less than for phenol.

As shown in *Table 1*, solvents with low hydrogen-donating ability, such as 1-methylnaphthalene, gave high conversions and those with high hydrogen-donating ability, such as tetralin and 9,10-dihydronaphthalene, gave lower conversions. This degradation behaviour may be explained in terms of the mechanism previously proposed in our study on PS pyrolysis[13] as follows. Polymer radicals, produced thermally, degrade to low molecular weight compounds through depolymerization and/or intra- and intermolecular hydrogen transfer processes. This is a radical chain mechanism and therefore the extent of polymer degradation depends on the chain length. When a solvent is present, the chain length decreases owing to hydrogen donation by the solvent to intermediate polymer radicals. Thus the chain length is dependent upon the hydrogen donating ability of the solvent, namely C–H, O–H or N–H bonding strength of the solvent. This leads to the hypothesis that the conversion of polymers may be related to the bond dissociation energy of solvents. Therefore, the conversions for the pyrolyses of PS[13] at 400°C and P-pMS at 380°C were correlated with the bond dissociation energies

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