SUMMARY

Pyrolysis-gas chromatographic investigations of head-to-head polymers of styrene and α-methylstyrene were carried out. The monomer yields of the head-to-head polymers are lower than those of the head-to-tail polymers. The pyrolysis products that directly reflect the head-to-head linkages are produced on pyrolysis of head-to-head polymers. By the use of these pyrolysis products, the content of the head-to-head linkages was evaluated for polystyrene, and the difference in the degradation mechanisms between the head-to-head and the head-to-tail polymers is discussed.

INTRODUCTION

In the conventional free-radical polymerization of asymmetric vinyl monomers, head-to-tail (H-T) linkages normally predominate. It has been reported that a substantial amount of the alternative head-to-head (H-H) linkages (and also tail-to-tail (T-T) linkages) exist in certain polymers, such as poly(vinyl fluoride) and poly(vinylidene fluoride) [1-3], although a more usual level is about 59 to 10 less in other polymers. The importance of the influence of such structural variations on polymer properties is well established. A number of methods have been suggested that lead to chains with predominantly H-H linkages and the properties often differ significantly from those of normal H-T polymers (i.e., glass transition temperature, stability characteristic, flexibility, etc.) [4-11].

It is therefore important to evaluate the structural variations. Pyrolysis-gas chromatography (Py-GC) is a useful method for the analysis of polymer microstructures. In our previous work, the amounts of two units (1,2- and 1,3-) existing in cationically polymerized poly(3-methyl-1-alkenes) were evaluated by Py-GC [12]. In this work, the differences in the Py-GC behaviour of the H-H and the H-T polymers of both styrene and α-methylstyrene were studied and the amounts of the H-H and the H-T linkages in polystyrenes were evaluated.
EXPERIMENTAL

Samples

Head-to-head polystyrenes (H-H PSt I and H-H PSt II) were synthesized according to the methods reported by Inoue et al. [10] and Richards and Scilly [13], respectively. H-H PSt III-VIII were obtained by hydrogenation of styrene-2,3-diphenylbutadiene copolymers with various compositions. The contents of the H-H linkages of H-H PSt III-VIII were evaluated from the UV spectra (absorbance at 250 nm) of the copolymers before hydrogenation. H-T polystyrenes were prepared by the usual polymerization techniques.

H-H poly(β-methylstyrene) (H-H PMSt) was synthesized by the method used for H-H PSt II [10], and H-T PMSt was obtained by anionic polymerization with potassium metal.

The H-H contents of the polymers and the polymerization conditions are given in Table 1.

Apparatus

A Curie-point pyrolyzer (Japan Analytical Industry JHP-2) was coupled directly to a gas chromatograph (Yanaco GC-180) with dual flame-ionization detection.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer feed (g)</th>
<th>Reaction time (h)</th>
<th>H-H content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2,3-Diphenyl-butadiene</td>
<td>Styrene</td>
<td></td>
</tr>
<tr>
<td>H-H PSt I</td>
<td>3.3</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>II</td>
<td>0</td>
<td>10.4</td>
<td>0.8</td>
</tr>
<tr>
<td>III</td>
<td>0.5</td>
<td>4.5</td>
<td>50</td>
</tr>
<tr>
<td>IV</td>
<td>1.0</td>
<td>4.0</td>
<td>72</td>
</tr>
<tr>
<td>V</td>
<td>1.5</td>
<td>3.5</td>
<td>92</td>
</tr>
<tr>
<td>VI</td>
<td>2.0</td>
<td>3.0</td>
<td>93</td>
</tr>
<tr>
<td>VII</td>
<td>3.0</td>
<td>2.0</td>
<td>114</td>
</tr>
<tr>
<td>VIII</td>
<td>4.0</td>
<td>1.0</td>
<td>62</td>
</tr>
<tr>
<td>H-H PMSt</td>
<td>0</td>
<td>12.0 *</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* α-Methylstyrene was used.
** Estimated from the 1H NMR spectrum.
tion detectors. The packed column used was a 2 m X 3 mm I.D. stainless-steel tube containing 60-80 mesh Celite 545 coated with 10% PEG 20M or 10% silicone DC 550. The column temperatures were 80 ° or 200 °C for the former and 185 °C for the latter. The flow-rate of the carrier gas (nitrogen) was 40 ml min⁻¹.

A Shimadzu GC-6AM gas chromatograph was used for the analysis, equipped with a 40 m X 0.3 mm I.D. support-coated open-tubular (SCOT) column with OV-17 as the stationary phase purchased from Shimadzu (Kyoto, Japan). The column temperature was increased from 50 ° to 200 °C at a rate of 6 °C min⁻¹. The nitrogen flow-rate was 0.2 ml min⁻¹.

The peak areas were integrated by a Shimadzu Chromatopac E-1A integrator. Identification of the peaks on the pyrograms was carried out by comparison of their retention data with those of known substances and/or by Py-GC-mass spectrometry (Shimadzu PYR-10A and GC-MS-7000). The dimers (except for 1,2-diphenylethane) were prepared in our laboratory.

RESULTS AND DISCUSSION

Polystyrenes

When polystyrenes were prepared in the usual manner, the styrene monomer, the dimer (2,4-diphenyl-1-butene) and the trimer (2,4,6-triphenyl-1-pentene) were observed as the major pyrolysis products. In this work, the pyrolysis products of monomer and dimer regions from polystyrenes having

![Fig. 1. Pyrograms of polystyrenes at 434°C (PEG 20M, at 80°C). Peaks: 1 = toluene; 2 = ethylbenzene; 3 = n-propylbenzene; 4 = styrene; 5 = β-methylstyrene.](image)
H-H and H-T linkages were considered but trimers were not.

Figs. 1 and 2 show the pyrograms of H-H and H-T polystyrenes. The pyrograms in Fig. 1 show the pyrolysis products with one benzene ring and those in Fig. 2 show the pyrolysis products having two benzene rings which correspond to the dimers. The difference between the H-H and the H-T polymers appeared on their pyrograms in both the monomer and the dimer regions. The H-H polymers produce compounds other than the styrene monomer (i.e., toluene, ethylbenzene, n-propylbenzene, etc.) in relatively large amounts, compared with the H-T polymer. The pyrolysis products corresponding to the dimers (i.e., 1,2-diphenylethane, 1,4-diphenylbutane and 1,4-diphenyl-1-butene) which reflect directly the H-H structures are identified as shown in Fig. 2. The pyrogram of poly(2,3-diphenylbutadiene) is also shown in Fig. 2. For this polymer, the 2,3-diphenylbutadiene monomer is the major pyrolysis product. H-H polystyrenes prepared by hydrogenation of the 2,3-diphenylbutadiene units have hardly any double bonds in their main chains, because very little 2,3-diphenylbutadiene is observed in the pyrolysis products.

From the relative peak area ratios of the dimers, the pyrogram of H-H polystyrenes and poly(2,3-diphenylbutadiene) at 434°C (silicone DC 550, at 185°C). Peaks: 1 = styrene; 2 = 1,2-diphenylethane; 3 = 2,4-diphenyl-1-butene; 4 = unidentified H-H dimer; 5 = 1,4-diphenylbutane; 6 = 1,4-diphenyl-1-butene; 7 = 2,3-diphenylbutadiene. Values in parentheses are relative peak area ratios.
II is considered to be intermediate between those of H-H Pst I and H-T Pst. This is illustrated in Fig. 1. It is assumed that H-H Pst II is not entirely composed of the H-H linkages, as Inoue et al. [10] reported. This result was supported by the lH and l3c NMR spectra of these three polymers (not shown).

All H-T polystyrenes prepared by various polymerization techniques show similar pyrograms and the relative amounts of the pyrolysis products are nearly identical. Even with H-T Pst obtained by radical polymerization only small amounts of the H-H dimers are produced. This fact suggests the existence of small amounts of H-H linkages in H-T Pst.

The lower monomer yield of H-H Pst I than that of H-T Pst results from the difference in their degradation mechanisms. By random main-chain scissions, the two radicals of (1) and (2) are produced from pure H-T Pst and the three radicals of (3), (4) and (5) from completely H-H structured Pst. The depolymerization of (1) to the monomer may be smoother and more continuous than that of (3), which is predominantly produced from the H-H linkages, because the secondary radical of (3) may "unzip" one monomer unit, with the resulting production of a relatively unstable primary radical. In addition, because of reproducing a relatively stable secondary radical, it is energetically favourable for (3) to give the dimers such as 1,4-diphenylbutane, 1,4diphenyl-1-butene, etc.; the H-H polymer produces a large amount of dimers. From the results obtained from differential thermogravimetry and thermal gravimetric analysis, Helbig et al. [14] have stated that there is no significant difference in thermal stability between the H-H and the H-T polymers owing to the lack of the fourth substituent on the carbon atom of the H-H linkages in Pst. However, differences in the distribution of the pyrolysis products on the pyrograms between H-H Pst and H-T Pst can apparently be observed and be qualitatively interpreted as mentioned above. The relative peak area ratios for H-H Pst II are closer to those for H-T Pst than to those for H-H Pst I. This Py-GC result agreed well with the NMR results.
Polymers with various compositions of H-H and H-T linkages were prepared by hydrogenation of the copolymers of styrene and 2,3-diphenylbutadiene. Their pyrograms are similar to that of H-H PSt II, although the relative amounts of the pyrolysis products differ according to the polymer.

There is a serious problem to be solved. In Fig. 2, the H-T dimer of 2,4-diphenyl-1-butene (3) and the H-H dimer with M⁺ = 208 which cannot be identified (4) have identical retention times measured on packed columns of silicone DC 550 and other commonly used stationary phases. It is impossible for completely H-H structured Pst I to produce 2,4-diphenyl-1-butene on pyrolysis.

In order to separate the peaks of 2,4-diphenyl-1-butene and the unidentified H-H dimer, the glass capillary column was used. Fig. 3 shows typical pyrograms of H-H Pst I, H-H Pst VI which has ca. 50% of H-H and H-T linkages, and radically polymerized H-T Pst obtained by the use of the capillary column at a pyrolysis temperature of 358°C. The peaks of 2,4-diphenyl1-butene (3) and the unidentified H-H dimer (4) are separated well.

The fraction of the peak area of unidentified H-H dimer in the total peak areas of these two pyrolysis products is plotted against the H-H content of each Pst in Fig. 4. The content of H-H linkage means the value of the fraction of H-H and T-T linkages in all linkages, that is, (H-H + T-T)/(H-H + T-T + H-T). This peak area ratio of H-H Pst I (closed circle in Fig. 4) shows

![Fig. 3. Pyrograms of polystyrenes at 358°C (capillary column). Peaks: 1 = styrene; 2 = 1,2-diphenylethane; 3 = 2,4-diphenyl-1-butene; 4 = unidentified H-H dimer; 5 = 1,4-diphenylbutane; 6 = 1,4-diphenyl-1-butene.](image1)

![Fig. 4. Fraction of unidentified H-H dimer peak area. ⊙, H-H PSt I; ●, H-H PSt II; ○, H-H PSt III—VIII. PA(3) = peak area of 2,4-diphenyl-1-butene; PA(4) = peak area of unidentified H-H dimer.](image2)
that the content of H-H linkages in this polymer is ca. 18%. This is a value comparable to that estimated from the 'H NMR spectrum. The peak area ratios for all H-T polystyrenes were nearly zero. On the pyrograms, however, the H-H dimers are clearly observed although their amounts are very small. It is concluded that these H-T polystyrenes do not consist of perfect H-T linkages but that the H-H contents of these H-T polymers are below 1%

Poly (α-methylstyrene)

Fig. 5 shows the pyrograms of H-H and H-T poly(α-methylstyrenes) obtained at a pyrolysis temperature of 434°C. This H-H polymer is composed entirely of H-H linkages as judged by the comparison of its 13C NMR spectrum with that of the H-T polymer, shown in Fig. 6. With poly(α-methylstyrenes), the monomer yields are higher than those of polystyrenes and other compounds are produced in only small amounts. The monomer yield of H-H PMSt is smaller than that of H-T PMSt and the characteristic pyrolysis products which reflect the H-H linkages, 2,5-diphenylhexane and 2,5-diphenyl-1-hexene, are observed in the dimer region on the pyrogram. The major dimer from the H-T polymer is unidentified (M+ = 236, not 4-methyl-2,4-diphenyl-1-pentene). The difference in monomer yields may result from the ease of scission of the H-H linkage to produce a tertiary radical and the difficulty in the continuous depolymerization to the monomer after the

Fig. 5. Pyrograms of poly(α-methylstyrenes) at 434°C (PEG 20M, at 200°C). Peaks: 1 = α-methylstyrene; 2 = 4-methyl-2,4-diphenylpentane; 3 = 2,5-diphenylhexane; 4 = 2,4-diphenyl-1-pentene; 5 = 4-methyl-2,4-diphenyl-1-pentene; 6 = unidentified H-T dimer; 7 = 2,5-diphenyl-1-hexene. Values in parentheses are relative peak area ratios.
random chain scission in the case of the H-H polymer, as described in the
degradation mechanisms of polystyrenes.

The apparent difference in the pyrograms between the H-H and the H-T
polymers is due to the following structural factor. The H-H linkages in PMSt
are weakened by steric hindrance between the substituents of two
quaternary carbon atoms and the H-T polymer, having quaternary carbon
atoms in its main chain like PMSt, has a very high monomer yield. With
PMSt, polymers with different compositions of H-H and H-T linkages cannot
be prepared. Therefore, it is not possible to draw quantitative conclusions.

REFERENCES

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