PYROLYSISIAS CHROMATOGRAPHIC BEHAVIOUR OF HEAD-TO-HEAD POLYSTYRENE AND HEAD-TO-HEAD POLY(-METHYLSTYRENE)

MINORU TANAKA, TATSUHISA SHIMONO, YOSHIKAZU YABUKI and TOSHIYUKI SHONO *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaha 565 (Japan)
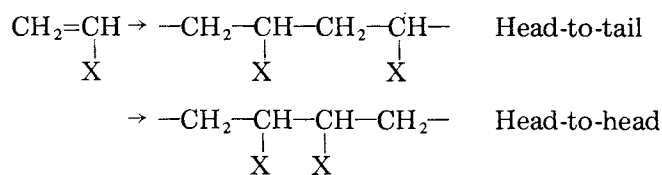
SUMMARY

Pyrolysis-gas Chromatographic investigations of head-to-head polymers of styrene and a-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 597o or 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 cationical1y polymerized poly(3-methy1-1-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 ct-methylstyrene were studied and the amounts of the H-H and the H-T linkages in polystyrenes were evaluated.

$$CH_2=CH \rightarrow -CH_2-CH-CH_2-CH- \quad \text{Head-to-tail}$$
$$| \quad \quad | \quad \quad |$$
$$X \quad \quad X \quad \quad X$$

$$\rightarrow -CH_2-CH-CH-CH_2- \quad \text{Head-to-head}$$
$$| \quad |$$
$$X \quad X$$

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(-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-ioniza-

TABLE 1

Polymerization conditions and H-H contents of polymers

Polymer	Monomer feed (g)		Reaction time (h)	H-H content (%)
	2,3-Diphenyl-butadiene	Styrene		
H-H Pst I	3.3	0	19	100
II	0	10.4	0.8	18.4 **
III	0.5	4.5	50	8.0
IV	1.0	4.0	72	21.3
V	1.5	3.5	92	36.5
VI	2.0	3.0	93	51.9
VII	3.0	2.0	114	73.5
VIII	4.0	1.0	62	88.4
H-H PMSt	0	12.0 *	1.5	100

* α-Methylstyrene was used.
** Estimated from the ^{1}H 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 with 10% silicone DC 550. The column temperatures were 80   or 200 for the former and 185   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 at a rate of 6   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 1,2diphenylethane) were prepared in our laboratory.

RESULTS AND DISCUSSION

Polystyrenes

When polystyrenes were prepared in the usual manner, the styrene monomer, the dimer (2,4-dipheny1-1-butene) and the trimer (2,4,6-triphenyl-1-he3tene) Were observed as the major pyrolysis products. In this work, the pyrolysis products of monomer and dimer regions from polystyrenes having
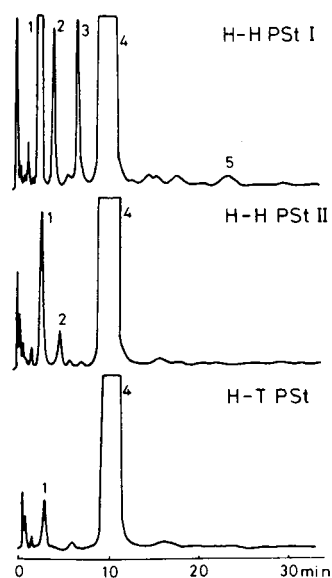

Fig. 1. Pyrograms of polystyrenes at 434°C (PEG 20M, at 80°C). Peaks: 1 = toluene; 2 = ethylbenzene; 3 = n-propylbenzene; 4 = styrene; 5 = β-methylstyrene.
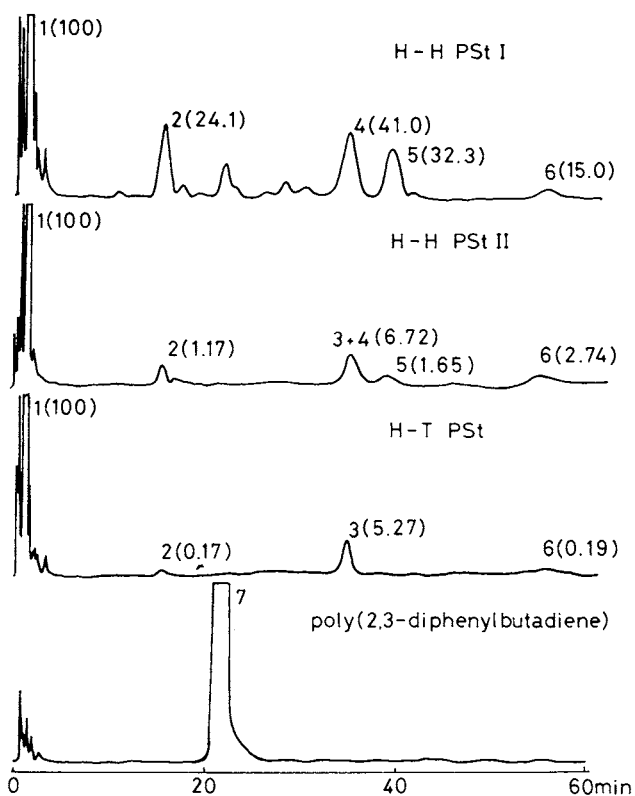
Fig. 2. Pyrograms of polystyrenes and poly(2,3-diphenylbutadiene) at 434°C (silicone DC 550, at 185°C). Peaks: 1 = styrene; 2 = 1,2-diphenylethane; 3 = 2,4-diphenyl-1-butene; 4 = unidentified H-H dimer; 5 = 1,4-diphenylbutane; 6 = 1,4-diphenyl-1-butene; 7 = 2,3-diphenylbutadiene. Values in parentheses are relative peak area ratios.

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 diner 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 1,4dipheny1-1-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 2,3diphenylbutadiene 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 pst

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 13c 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-diphenyl-butane, 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.
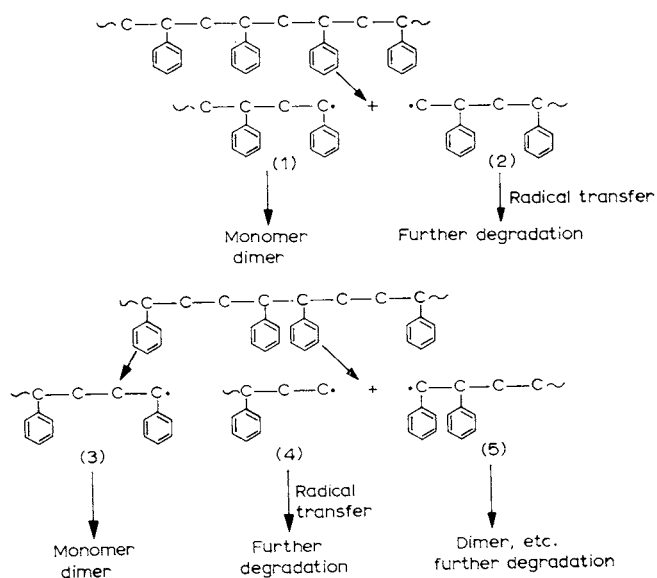
Polymers with various compositions of H-H and H-T linkages were prepared by hydrogenation of the copolymers of styrene and 2,3-diphenyi-butadiene. Their pyrograms are similar to that of H-H Pst II, although the relative amounts of the pyrolysis products differ according to the polymer.

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 capmary column at a pyrolysis temperature of 358 . The peaks of 2,4-dipheny11-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 I1 (closed circle in Fig. 4) shows
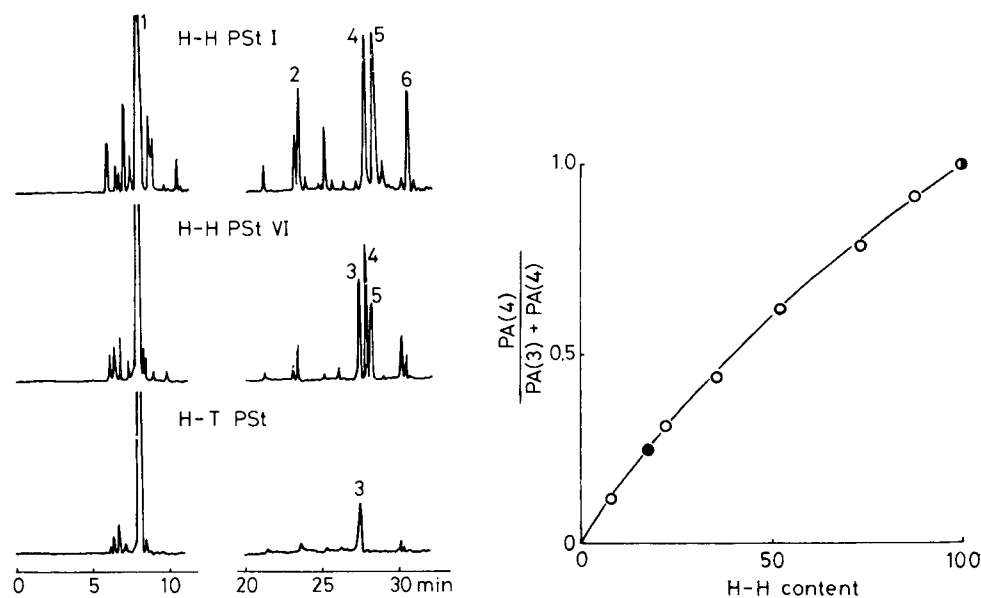

Fig. 3. Pyrograms of polystyrenes at 358°C (capillary column). Peaks: 1 = styrene; 2 = 1,2-diphenylethane; 3 = 2,4-diphenyl-1-butene; 4 = unidentified H-H dimer; 5 = 1,4-diphenylbutane; 6 = 1,4-diphenyl-1-butene.

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.

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 (-methylstyrene)

Fig. 5 shows the pyrograms of H-H and H-T poly(-methylstyrenes) obtained at a pyrolysis temperature of 434 . This H-H polymer is composed entirely of H-H linkages as judged by the comparison of its ^{13}C NMR spectrum with that of the H-T polymer, shown in Fig. 6. With poly(-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-2,4diphenyl-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
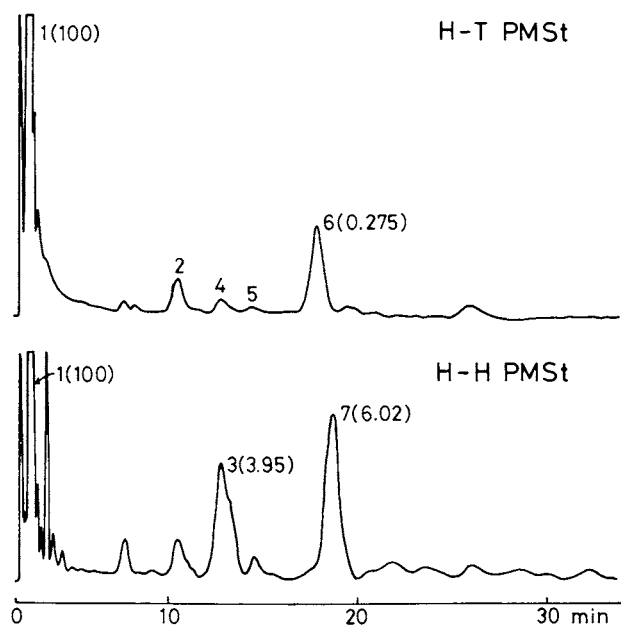

Fig. 5. Pyrograms of poly(α-methylstyrenes) at 434°C (PEG 20M, at 200°C). Peaks: 1 = α-methylstyrene; 2 = 4-methyl-2,4-diphenylpentane; 3 = 2,5-diphenylhexane; 4 = 2,4-diphenyl-1-pentene; 5 = 4-methyl-2,4-diphenyl-1-pentene; 6 = unidentified H-T dimer; 7 = 2,5-diphenyl-1-hexene. Values in parentheses are relative peak area ratios.
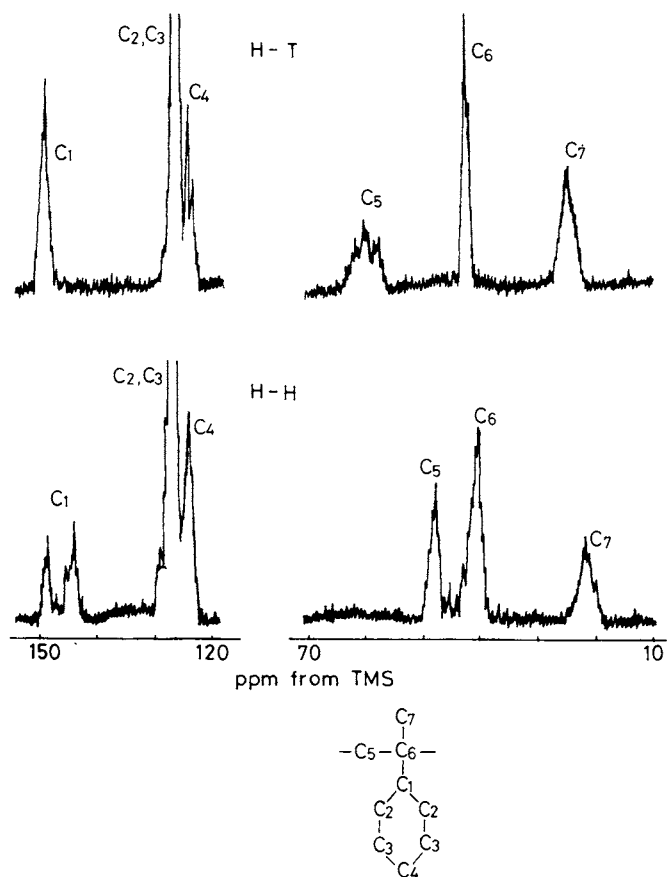
Fig. 6. ^{13}C NMR spectra of H-H and H-T poly(α-methylstyrenes) in CDCl$_3$.

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.

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