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Pyrolysis–Gas Chromatographic Studies on Head-to-Head Polystyrene

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ABSTRACT: Pyrolysis–gas chromatography (PGC) with a high-resolution glass capillary column was used in an investigation of head-to-head polystyrene (H–H PS). The peaks on the resulting pyrograms were identified by combining PGC–mass spectrometric results, retention data of the products, and pyrolysis–hydrogenation gas chromatographic results. On the basis of the resulting characteristic pyrograms, the thermal degradation behavior of H–H PS is discussed and compared with that for head-to-tail PS (H–T PS).

Vinyl-type polymers synthesized through usual polymerization reactions mostly consist of a head-to-tail (H–T) arrangement of the associated monomer units along the polymer chain. Therefore, stereoregularities and sequence distributions for the polymers have been mainly discussed by assuming only H–T linkages. On the other hand, it has been pointed out that minor amounts of irregular head-to-head (H–H) or tail-to-tail (T–T) linkages should affect the physical properties of the polymer.

So far, studies on the monomer arrangement have been most extensively carried out by IR and NMR spectroscopy. In addition to these, pyrolysis methods combined with either gas chromatography (PGC)[1-5] or mass spectrometry (PMS)[6] have been also demonstrated to be powerful techniques for the structural investigation of the polymers. Recently, PGC was effectively applied to the elucidation of the irregular monomer linkages in various highly alternating copolymers[3] and the estimation of the chemical inversions in polypropylenes.[5]

Recently, Fujimoto et al.[7] synthesized a model polystyrene (PS) consisting almost entirely of H–H linkages by a radical polymerization of 2,3-diphenyl-1,3-butadiene followed by selective reduction of the double bonds along the main chain with aniline and potassium metal. They studied its ^{1}H NMR spectrum and physical properties by light scattering, stress relaxation, and dilatometric methods and suggested that H–H PS should have a stiffer backbone than H–T PS. Later Inoue et al.[8] studied H–H PS synthesized through basically the same route as that used by Fujimoto et al.[7] and reported that H–H PS exhibited essentially the same glass transition temperature, T_g, and degradation temperature as those for H–T PS. The dilute-solution properties[9] and the detailed high-resolution ^{1}H and ^{13}C NMR spectra of H–H PS were also compared with those for H–T PS.[10] More recently, Lüderwald[6] studied the detailed thermal degradation behavior of H–H PS by the direct pyrolysis in a mass spectrometer (PMS) and reported that H–H PS yielded characteristic products such as stilbene and bibenzyl, which reflect the H–H structures of the polymer chain.

In this work, PGC with a high-resolution glass capillary column was used to characterize H–H and H–T PS. The peak assignment of the associated pyrograms was mostly carried out by combining the PGC–MS data and the retention data of the anticipated degradation products. Pyrolysis–hydrogenation gas chromatography was also utilized for peak confirmation. On the basis of the observed characteristic pyrograms, the degradation mecha-

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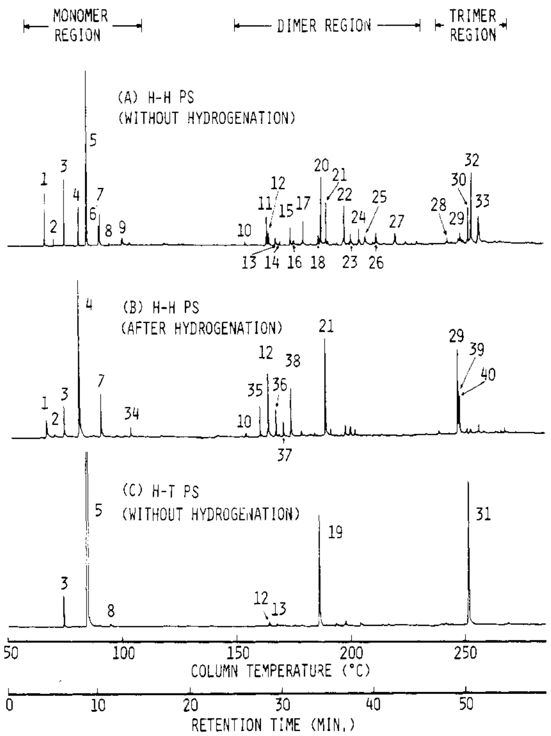

Figure 1. Pyrograms of H-H PS and H-T PS at 500 °C. Peak numbers correspond to those in Tables I and II.

nisms of H-H PS are discussed and compared with those for H-T PS.

Experimental Section

Samples. H-H PS, which was prepared by hydrogenation of fractionated poly(2,3-diphenylbutadiene) in the presence of aniline and potassium,[7] was kindly supplied by Dr. T. Fujimoto. The weight-average molecular weight, $\bar{M}_w = 4.5 \times 10^5$, was obtained by light scattering. A monodispersion H-T PS, which was synthesized by anionic polymerization and supplied by Waters Co. Ltd. ($\bar{M}_w = 8.6 \times 10^5$), was also used as a reference sample.

Pyrolysis-Gas Chromatographic Conditions. A vertical microfurnace-type pyrolyzer designed by the authors[11] was directly attached to a Shimadzu 7-AG gas chromatograph with a high-resolution glass capillary column (0.9-mm o.d. × 0.3-mm i.d. × 50-m long) suspension coated with OV-101 and Silanox (325 mesh) and deactivated by PEG 20M prior to the final dynamic coating with OV-101 solution. The column temperature was programmed from 50 to 250 °C at a rate of 4 °C/min. The 50 mL/min carrier gas flow at the pyrolyzer was reduced to 1.0 mL/min at the capillary column through a splitter (50:1). The dead volume of the splitter was packed with 5% OV-101 on Diasolid H (80-100 mesh) whose temperature was maintained at 250 °C. This packing prevents column contamination by less volatile degradation products. About 0.1 mg of the sample was pyrolyzed at 500 °C under a flow of the carrier gas. For conventional PGC, nitrogen was used as the carrier gas, while in pyrolysis-hydrogenation gas chromatography (PHGC) hydrogen was used instead. A precut column packed with 5 wt % OV-101 on Diasolid H (80-100 mesh) and a hydrogenation catalyst column[4] packed with 10 wt % Pt on Diasolid H (80-100 mesh) were inserted in series between the pyrolyzer and the splitter, whose temperatures were maintained at 300 °C.

The peak area of the resulting pyrograms was integrated by a Chromatopack E-1A integrator from Shimadzu, and the peak identification was mostly carried out by using a directly connected quadrupole mass spectrometer (QMS) (JMS-Q10A, JEOLCO) and the retention data of the degradation products according to their boiling points from Beilstein's "Handbuch der Organische Chemie".

Results and Discussion

Figure 1A-C illustrates the high-resolution pyrograms of H-H PS without hydrogenation, H-H PS after hydrogenation, and H-T PS, respectively. The pyrogram of H-T PS (Figure 1C) mainly consists of three peaks due to monomer (80.8%), dimer (5.8%), and trimer (9.4%). Early PGC work[12] established that H-T PS first degraded to a certain level L ($\bar{M}_w$ = 25 000 at 550 °C) by random chain scission in the polymer chain, provided that the initial $\bar{M}_w$ is above L, and then underwent depolymerization to yield mostly monomer. If only random scission were dominant throughout the thermal degradation of the sample, the associated peaks of monomer, dimer, and trimer would split at least into triplets in much the same way as for polypropylenes.[5] For example, the random scission of the H-T sequences must yield comparable amounts of the following monomers: $PhCH_3$, $PhCH{=}CH_2$, and $CH_3C(Ph){=}CH_2$. However, the fact that those peaks from H-T PS substantially consist of singlets implies that the formation of these products should be attributed mainly to a specific radical transfer along the macroradical rather than a simple random cleavage.

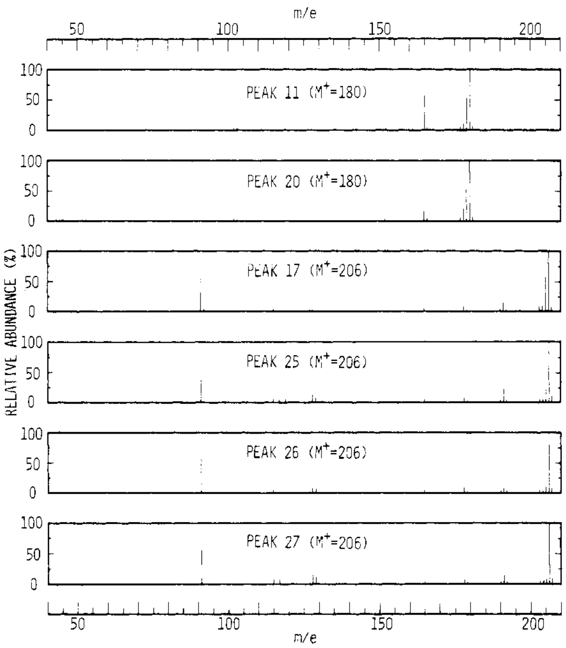

Figure 2. Mass spectra of some peaks on the pyrogram of H-H PS. Peak numbers correspond to those in Table I.

On the other hand, the associated peaks on the pyrogram of H-H PS (Figure 1A) are composed of many components. Thus, the number of identified peaks in the region of monomer, dimer, and trimer amounts to about nine (1-9), seventeen (10-27), and five (28-33), respectively. The identified or presumed peaks on the pyrograms of H-H PS and H-T PS are listed in Table I together with the relative yield. Here, the peak identification was mostly carried out by both PGC-QMS and the retention data of the peaks on the pyrograms. However, as shown in Figure 2, peaks 11 and 20 and peaks 17, 25, 26, and 27 give basically the same mass spectra with $M^+ = 180$ and $M^+ = 206$, respectively. Moreover, the separation column utilized (OV-101) retains solutes almost according to their boiling points under a given condition. Therefore, even a given pair of solutes with the same carbon skeleton sometimes have quite different retention times since given isomers with conjugate double bonds to an aromatic ring have fairly higher boiling points than those without the conjugate double bonds. For example, stilbene ($PhCH{=}CHPh$) and bibenzyl ($PhCH_2CH_2Ph$) have significantly different boiling points, 306 and 284 °C, respectively. Thus, the resulting pyrogram of H-H PS becomes too complicated,

Table I
Peak Assignment on the Pyrograms of H-H PS and H-T PS

peak no.	peak assignment	structure[a]	rel peak intensity,[b] % H-H PS	rel peak intensity,[b] % H-T PS
1	hydrocarbons (C_1-C_4)		2.2	
2	benzene		0.4	
3	toluene	Ph—C	3.3	0.9
4	ethylbenzene	Ph—C—C	2.0	
5	styrene	Ph—C=C	20.4	80.8
6	3-phenyl-1-propene	Ph—C—C=C	1.5	
7	1-phenylpropane	Ph—C—C—C	2.3	
8	α-methylstyrene	C—C(Ph)=C	0.3	0.2
9	1-phenylbutadiene	Ph—C=C—C=C	1.0	
10	diphenylmethane	Ph—C—Ph	0.3	
11	1,1-diphenylethylene	$(Ph)_2$—C=C	2.6	
12	1,2-diphenylethane (bibenzyl)	Ph—C—C—Ph	1.3	0.3
13	1,2-diphenylpropane	Ph—C—C(Ph)—C	0.7	0.1
14	1,2-diphenyl-1-propene	Ph—C=C(Ph)—C	0.5	
15	2,3-diphenyl-1-propene	Ph—C—C(Ph)=C	2.2	
16	3,4-diphenyl-1-butene	Ph—C—C(Ph)—C=C	0.5	
17	2,3-diphenylbutadiene	C=C(Ph)—C(Ph)=C	2.0	
18	1,1-diphenylpropene	$(Ph)_2$—C=C—C	1.0	
19	2,4-diphenyl-1-butene (styrene dimer)	C=C(Ph)—C—C—Ph		5.8
20	1,2-diphenylethylene (stilbene)	Ph—C=C—Ph	6.5	
21	1,4-diphenylbutane	Ph—C—C—C—C—Ph	3.5	
22	1,4-diphenyl-1-butene	Ph—C=C—C—C—Ph	3.8	
23	1,4-diphenyl-1-pentene	Ph—C=C—C—C(Ph)—C	1.3	
24	1,3-diphenylpropadiene	Ph—C=C=C—Ph	2.1	
25	1,2-diphenylbutadiene	Ph—C=C(Ph)—C=C	1.8	
26	1,4-diphenylbutadiene	Ph—C=C—C=C—Ph	1.9	
27	1,4-diphenylbutadiene	Ph—C=C—C=C—Ph	2.1	
28	1,3,4-triphenylbutene	Ph—C=C—C(Ph)—C—Ph	0.6	
29	1,2,5-triphenylpentane	Ph—C—C(Ph)—C—C—C—Ph	1.5	
30	1,2,5-triphenyl-1-pentene	Ph—C=C(Ph)—C—C—C—Ph	4.6	
31	2,4,6-triphenyl-1-hexene (styrene trimer)	C=C(Ph)—C—C(Ph)—C—C—Ph		9.4
32	2,3,6-triphenyl-1-hexene and 2,5,6-triphenyl-1-hexene	C=C(Ph)—C(Ph)—C—C—C—Ph C=C(Ph)—C—C—C(Ph)—C—Ph	8.9	
33	1,4,5-triphenyl-1-pentene	Ph—C=C—C—C(Ph)—C—Ph	4.4	
		total	87.8	97.5

[a] Ph designates a phenyl ring. [b] Relative peak area (%) among all peaks appearing on the pyrograms.

Table II
Peak Assignment on the Pyrogram of H-H PS after Hydrogenation

after hydrogenation[a]			without hydrogenation[a]	
peak no.	peak assignment	rel peak intensity, %	corresponding peak no. in Table I	rel peak intensity, %
1	hydrocarbons (C_1-C_4)	2.9	1	2.6
2	benzene	0.5	2	0.5
3	toluene	3.5	3	3.7
4	ethylbenzene	19.8	4 + 5	18.4
7	propylbenzene	5.2	6 + 7	3.6
34	butylbenzene	1.3	9	0.9
10	diphenylmethane	0.3	10	0.3
35	1,1-diphenylethane	3.1	11	3.0
12	1,2-diphenylethane	8.9	12 + 20	8.6
36	1,2-diphenylpropane	3.0	13 + 14 + 15	3.1
37	2,3-diphenylbutane	1.9	17	2.3
38	1,2-diphenylbutane	5.7	16 + 25	3.1
21	1,4-diphenylbutane	10.8	21 + 22 + 26 + 27	11.4
29	1,2,5-triphenylpentane	7.6	29 + 30 + 33	10.5
39 40	triphenylhexanes	6.8	32	8.5

[a] Hydrogen was used as carrier gas for both cases.

especially in the dimer region, for unequivocal peak identification.

Therefore, in order to simplify the pyrogram for thorough interpretation, the degradation products were hydrogenated in line and subsequently separated to give the pyrogram (Figure 1B) for H-H PS. Under the utilized hydrogenation condition at 300 °C, only olefinic double bonds were reduced while aromatic ring was free from the hydrogenation. Accordingly, all side chains for the resulting products on the pyrogram become saturated hydrocarbons. Thus, for example, peaks 21, 22, 26, and 27 on the pyrogram in Figure 1A, all of which have a Ph—C—C—C—C—Ph skeleton are combined into a single peak, peak 21, on the pyrogram in Figure 1B. The correlation between the peaks before and after hydrogenation is summarized in Table II together with the relative yield. Here, in order to attain the same thermal degradation of the polymer sample, hydrogen carrier gas was used for both

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conventional PGC and PHGC with catalytic hydrogenation.

The fact that there exists fairly good agreement between the relative yields before and after hydrogenation supports the validity of the presumption for the assignment of some peaks on the pyrogram in Figure 1A. Thus, the identified peaks in the monomer and the trimer regions on the pyrograms in Figures 1A and 1B mostly reflect the H–H and/or the T–T structures. Although the monomer is still most abundant among the products on the pyrogram, its yield only amounts to 20.4%. On the other hand, the formation of a comparable size for the multiplets of the monomer, dimer, and trimer regions suggests that random scission type thermal degradation might be predominant for H–H PS.

As was reported in the PMS work on H–H PS by Lüderwald,[6] we can also find on the pyrogram in Figure 1B a very minor $PhCH_2Ph$ peak (peak 10) and a fairly strong $PhCH(CH_3)Ph$ peak (peak 35). This suggests either that these structures were incorporated through minor byproducts at the stage of the monomer preparation or that thermal rearrangements took place during the pyrolysis. Furthermore, it is very interesting to note that, even though very minor, $PhCH_2CH_2Ph$ and $PhCH_2CHPhCH_3$ peaks can be observed on the pyrogram of H–T PS (Figure 1C). This fact, which was also pointed out by Alajbeg et al.,[13] could be indicative of the existence of H–H linkages even in H–T PS.

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Epimerization of Vinyl Polymers to Stereochemical Equilibrium. 1. Theory[1]

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ABSTRACT: Flory's theory of stereochemical equilibrium in vinyl polymers is generalized. Equilibrium frequencies for stereochemical sequences of any length (m-ads) in chains of any length x can be obtained with the new formulation; the calculated frequency is averaged over the entire length of the chains. Some numerical results for sequences up to $m = 5$ (pentads) are presented, and it is demonstrated that the dyad distribution in vinyl chains at equilibrium does not follow any type of unidirectional statistics, e.g., any order Markoff.

Introduction

Vinyl polymers exist in a potentially extraordinarily large number of diastereomers. We will consider chains of the general formula

$$CH_3\text{–}(CHRCH_2)_x\text{–}H \qquad (1)$$

Under conditions where the diastereomers are epimerized to stereochemical equilibrium, the different diastereomers occur in fractions that are proportional to their partition functions. Although the large number of diastereomers quickly precludes resolution of diastereomers as x exceeds all but the smallest values, the frequency of occurrence of diastereomeric substructures comprising m monomeric units, m-ads, can often still be analytically determined. These frequencies are proportional to the sum over all the appropriate partition functions of the chains that contain the specified substructure, taken as many times as the substructure occurs in the chain. When the basic assumptions of rotational isomeric state models are accepted, it can be shown that the only relevant terms in the partition functions are the ones pertaining to conformation.

In 1967 Flory[2] formulated the concept of the method and presented a formulation that yields the frequency of occurrence of dyads and triads in chains of any length at stereochemical equilibrium, averaged along the chains (and over all chains), the only parameters required being the statistical weight parameters that govern the conformational equilibria. His comparison with some of the data from the first experiments of this kind carried out by Clark[3] with derivatives of 2,4-dicarboxypentane and 2,4,6-tricarboxyheptane (as model compounds for the corresponding polyacrylates) gave satisfactory agreement. Since then, the method has been applied to equilibria in low molecular weight model compounds of vinyl polymers ($x = 2$ and 3, except for the polypropylene models, where $x = 4$ and 5) in a number of cases,[4–12] mostly in order to obtain information on conformational statistical weight parameters.

Polymers have resisted epimerization without side reactions until recently. Suter[13] and others[14] succeeded in transforming isotactic polypropylene to ether-soluble "atactic" products as early as 1970, but stereochemical equilibrium was not reached. The first apparently successful equilibrium epimerization was published in 1979 by Shepherd, Chen, and Harwood;[15,16] these authors reported on the epimerization of isotactic polystyrene to a product with the same ^1H NMR spectrum as atactic polystyrene (the triad frequencies were estimated, using their data, to be $f_{mm} \approx 0.2$, $f_{mr} \approx 0.5$, and $f_{rr} \approx 0.3$; $f_m \approx 0.45$).

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