

# A New Technique for the Mass Spectrometric Study of the Pyrolysis Products of Polystyrene

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Polystyrene was placed in a small tube furnace and the degradation products evaporated directly into the ionization chamber of a mass spectrometer. At about 330° C a fairly complicated mass spectrum was observed, extending to about mass 520. Major features of the spectrum are accounted for by a mixture of monomer, dimer, trimer, tetramer, and pentamer, with the first two by far the most abundant. The nonvolatile liquid fraction recovered from pyrolysis of polystyrene when heated to 80° C in the tube furnace gave a spectrum nearly identical to the above pyrolysis spectrum except that the styrene contribution is absent. The technique should be applicable to a wide range of polymers.

Studies of the structure of polymers by means of mass spectrometric analysis of degradation products have been described previously [1, 2, 3].<sup>1</sup> It has also been demonstrated [4] that small samples of a wide variety of complex materials could be identified by the same means. In previous studies, a small sample of the material was pyrolysed in an evacuated vessel outside the mass spectrometer. Consequently, when the vessel was opened to the mass spectrometer only stable products with appreciable vapor pressures at room temperature were observed. Although this often simplified the spectrum, it precluded information on larger fragments and molecules of possible importance in understanding the structure of the polymer and the process of degradation.

This paper is a preliminary report on a technique in which vacuum pyrolysis of high-molecular-weight compounds occurs inside the mass spectrometer envelope and the degradation products are evaporated directly into the ionization chamber after comparatively few collisions with walls and with each other.

The instrument used for the pyrolysis experiments was a Nier 60° mass spectrometer [5], using magnetic sweep and provided with a high-speed recorder. The connection from the sample inlet tube to the ion source was removed, and a small furnace was supported directly above the ion source inlet by a 6-mm outside diameter Pyrex tube, which also provided communication between the ionization chamber and the furnace interior. The upper end of this Pyrex tube was closed by a copper sample holder structure with its thermojunction leads. The sample holder proper was an upright cup of a few cubic millimeters capacity extending downward from this structure and opening directly to the Pyrex-tube interior. In the design care was taken to provide a short (approximately 1½ in.) open path from the sample to the ionization chamber. Toward this end a Pt gauze ion repeller was used in the ion source instead of the usual plate.

An essential precaution in analyses of this kind is the avoidance of lubricated or waxed joints that must be heated to remove or insert samples. In the structure used, the leads to the sample holder and furnace structure extended through a removable

4-contact Kovar seal, which closed a 1<sup>3</sup>/<sub>16</sub>-inch aperture in the metal spectrometer closure. The rigidity of these leads was sufficient to allow the tube furnace and sample holder to be removed and inserted as a unit. Air leakage at the edge of the seal was prevented by a screw-pressed Teflon ring.

In operation, the voltage applied to the furnace is controlled to keep the pressure in the spectrometer within its operating range. After the initial liberation of small quantities of occluded or dissolved volatile materials, the temperature is increased until decomposition begins (330° C). Repeated spectra run at this temperature are consistent. Finally, after the sample approaches exhaustion and the temperature is further raised, the character of the spectrum changes continually as the residue is driven off.

The pyrolysis products of polystyrene at 330° C give a rather complicated mass spectrum, with peaks appearing at almost every mass unit to beyond  $m/e=300$ . Scattered peaks appear to about  $m/e=520$ . After correcting for the contributions of ions containing C<sup>13</sup> and D atoms, the monoisotopic spectrum was calculated in the conventional manner relative to the most abundant ion peak ( $m/e=91$ ). Column 2 of table 1 gives these data, omitting, for the sake of brevity, ions with abundances less than 1 percent of the 91 peak. Also omitted as possible impurities were three peaks at  $m/e=18, 28, \text{ and } 44$ , approximately 1.1, 1.7, and 1.6 percent, respectively, of the maximum peak. Small peaks at  $m/e=416$  and about 520 were included because of particular interest. The mass number of the latter is somewhat uncertain and may be in error by several units.

In an extensive investigation of the vacuum pyrolysis of polystyrene, Staudinger and Steinhöfer [6] reported yields of monostyrene, dimer (2,4-diphenyl-1-butene), trimer, and tetramer. In addition, 1,3-diphenyl propane, 2,4,6-triphenyl-1-hexene, and 1,3,5-triphenyl pentane have been identified. Unfortunately, none of these compounds was immediately available for comparison. More recently Madorsky and Straus [1] have found that the pyrolysis products of polystyrene are about 40 percent by weight of monostyrene and 60 percent of nonvolatile liquid, with an average molecular weight of 264. A sample of the latter liquid was kindly supplied by S.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

Straus. This sample was evaporated without degradation (78° C) into the ion source. The mass spectrum of this dimer-trimer liquid is given in column 3 of table 1, with the 91 peak again taken as 100.

The contribution of monostyrene to the pyrolysis spectrum as given in column 4 was calculated from the published mass spectrum [7] and the abundance of the 104 peak remaining after subtracting the contribution of the dimer-trimer spectrum. The final residuals after subtracting the monomer and dimer-trimer contributions are given in column 5. Residuals of a few percent of the 91 peak are not considered significant except for peaks unaccounted for by either the dimer-trimer or the monomer spectra. The styrene spectrum in column 4 was obtained with a 180° Consolidated instrument and the comparison will not be as accurate as if it had been obtained from the instrument used in this work. The dimer-trimer

TABLE 1. Analysis of the monoisotopic spectrum of the pyrolysis products of polystyrene

Molecular weight	Relative abundance			
	Pyrolysis products	Dimer-trimer mixture	Styrene <sup>a</sup>	Residuals
27	1.70	-----	3.8	-2.1
39	4.77	-----	6.4	-1.63
50	5.40	-----	8.3	-2.90
51	12.8	1.00	16.	-4.2
52	3.74	-----	5.4	-1.66
62	1.10	-----	1.5	-0.40
63	3.68	-----	4.1	-0.42
65	6.45	4.04	1.0	1.41
74	2.20	-----	2.7	-0.50
75	1.78	-----	2.0	-0.22
76	2.74	-----	2.5	-.24
77	14.5	3.74	11.	-0.26
78	23.0	1.70	17.	4.3
79	1.62	0.72	-----	0.90
89	1.80	-----	1.0	.80
91	100.0	100.0	-----	-----
102	4.60	-----	4.4	.20
103	26.9	4.45	21.	1.45
104	57.9	2.85	55.	-----
105	1.90	1.64	-----	0.26
115	7.10	5.17	-----	1.93
116	1.62	2.07	-----	-0.45
117	23.5	22.0	-----	1.5
128	1.65	1.56	-----	0.09
129	3.53	3.74	-----	-.19
130	4.00	-----	-----	4.00
178	1.63	1.63	-----	0
179	1.47	1.43	-----	.04
193	5.77	4.71	-----	1.06
194	8.33	11.6	-----	-3.3
206	1.36	1.14	-----	0.22
207	11.4	14.4	-----	-3.0
208	5.80	2.50	-----	3.30
221	1.35	1.30	-----	0.05
312	1.73	1.14	-----	.59
416	0.02	-----	-----	.02
520 <sup>b</sup>	.02	-----	-----	.02

<sup>a</sup> Calculated from the spectrum of ref [7], corrected for ions containing C<sup>13</sup> and D atoms.

<sup>b</sup> Mass uncertain. Possibly in error by several units.

mixture may have been separated somewhat in evaporation and the ratio of dimer to trimer changed.

In spite of the qualitative nature of the monomer and the dimer-trimer spectra, the sum of their contributions account satisfactorily for nearly all the major peaks in the pyrolysis spectrum. The small peaks at  $m/e=416$  and about 520 very probably represent the molecule ions of the tetramer and the pentamer, respectively. The residual at  $m/e=130$  may indicate divinyl benzene, although at present no evidence other than ions corresponding to the molecular weights is available to support the presence of this and several other hydrocarbons, including triphenyl benzene. No conclusive evidence was obtained to indicate the presence of ethyl benzene, toluene, isopropyl benzene, or methyl styrene as previously reported for mass spectrometric analyses of the volatile products of pyrolysis [1, 2].

These spectra do not afford a quantitative basis for determining the molar ratios of monomer, dimer, trimer, and tetramer. Staudinger and Steinhofler [6] find these to be in the ratio 4:1:0.7:0.1, and the spectrum of table 1 is not inconsistent with this except that there is also a pentamer. They identify the dimer as 2,4-diphenyl-1-butene, and the large peaks at 91, 117, and 194 are consistent with such a structure. Two isomers of this compound, 1,3-diphenyl-1-butene and 1-methyl-3-phenylindan, were supplied by W. S. Thurber of the Dow Chemical Co. They give spectra very different from the spectra of table 1. Further efforts are being made to obtain samples of 2,4-diphenyl-1-butene and 2,4,6-triphenyl-1-hexene, for it should be possible to identify unambiguously the abundant chemical compounds in the pyrolysis products.

This new technique was first applied to polystyrene because there is rather extensive information on the pyrolysis products [8]. In general, the results are quite consistent with those obtained by other methods. Furthermore, the reproducibility of the pyrolysis spectra over a moderate temperature range indicates the absence of secondary reactions or free radicals that might be critical functions of the experimental conditions. It is planned to extend the technique to a variety of other synthetic and natural polymers.

## References

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