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## Mass Spectrometric Characterization of Polystyrene Cross-Linked with Pure m- and Pure p-Divinylbenzene

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### SUMMARY

Mass spectral data for polystyrene and its copolymers with 8% pure m- and 8% pure p-divinylbenzene show characteristic differences. Polystyrene is differentiated by the enhanced M/e 193 over 194, 207, and 208 peaks; the reverse relative intensities being observed for the copolymers. The para copolymer has characteristic peaks at 222, 235, and 236 m/e which do not appear in the spectra of either the meta copolymer or polystyrene. The last is tentatively assigned to the [3, 3]-paracyclophane structure formed in a  $\gamma$ -hydrogen rearrangement from adjacent p-DVB units fragmented from the copolymer network.

### INTRODUCTION

We wish to record our observations of the characteristics of the mass spectra for polystyrene and its 8% copolymers with pure m- and pure p-divinylbenzene. Previous mass spectral studies of polystyrene [1-3] and monomeric styrene [4] have established the characteristics of the systems involved. These have been confirmed and extended using slightly different techniques. When adapted to studies

of cross-linked copolymers prepared according to techniques developed in our laboratories [5], it appears that the meta and para cross-linkages can be distinguished and perhaps characterized. In this report, we wish to state briefly our techniques, the characteristics of the spectra, and the significance thereof.

## EXPERIMENTAL

### Materials

Bead copolymers of styrene (PS) cross-linked with 8 mole% pure (99.8+ % by GLC) p-divinylbenzene (8% p-DVB) or pure (99.9+ % by GLC) m-divinylbenzene (8% m-DVB) were prepared by a previously described technique [5] with initiator (dibenzoyl peroxide) concentration of 0.1% and carboxymethylcellulose (CMC) dispersant at 80°C. Beads of 20-30 mesh size, dried at 60°C for 48 hr under high vacuum (1 mm Hg) to remove any possible traces of residual monomer, were used. The non-cross-linked polystyrene and the pure divinylbenzene polymers were obtained under similar conditions (0.1% benzoyl peroxide, 80°C, CMC).

### Mass Spectrometer

A Varian M-66 mass spectrometer was used in these experiments. Mass spectrometric operating conditions were as follows: electron energy 70 eV, electron current 40  $\mu$ A, analyzer temperature 100°C, ionization chamber temperature 200°C (and above) and at  $7-13 \times 10^{-7}$  torr.

### Procedure

Two to four mg of bead polymer was loaded into a 35 mm  $\times$  1 mm i.d. (1.4 mm o.d.) melting-point capillary. The capillary was placed in the solid sample inlet probe and inserted into the ionization chamber. The probe was heated rapidly to 150°C and continued heating at 200°C at a rate of 10°C/min. Increasing the temperature further resulted in large increases in analyzer pressure. The temperature was increased further after the pressure stabilized. Spectra were recorded at 250, 275, 300, 325, and 350°C temperatures after stabilization of both pressure and temperature were obtained. The temperature of the sample introduction probe was regulated to  $\pm 0.25^\circ\text{C}$  and was resettable to  $\pm 5^\circ\text{C}$ . Analyzer temperature was regulated to  $\pm 5^\circ\text{C}$ . At higher probe temperatures (up to 450°C) fragments of  $m/e$  up to 815 have been observed from polystyrene. The homo-divinylbenzene polymers give  $m/e$  patterns not distinguishable by techniques used thus far.

## RESULTS

The mass spectral data from our experiments show that peaks of low molecular weight, i.e., below a mass of about  $m/e$  100, are probably unreliable as a means of distinguishing differences in the polymers, since some alternations were noted in peak intensities for the fragment ion peaks,  $m/e$  39, 51, 63, 77, 78, and 91, that could not be readily correlated with pyrolysis temperature and/or polymer type. Although there are some notable differences in relative intensities for the groups of peaks at  $m/e$  50-53; 77, 78, 91, 92; 165-167; 178-181, for both polymers and copolymers, we feel the more significant differences are at masses greater than  $m/e$  100 and particularly in the  $m/e$  190-250 region. In polystyrene, the  $m/e$  193 peak is more intense than  $m/e$  194, 207, and 208 peaks, whereas in the DVB copolymers  $m/e$  193 peak is less intense than the  $m/e$  194, 207, and 208 peaks. In the  $m/e$  129-134 range the  $m/e$  129 is the most intense peak of this group for polystyrene and the *m*-DVB copolymer, while in the *p*-DVB copolymer the  $m/e$  132 is the most intense. The relative intensities of  $m/e$  119 peak and the pair of peaks  $m/e$  235, 236 are much greater in the *p*-DVB copolymer than in the *m*-DVB copolymer or homopolymer. These characteristic intensity differences were observed throughout the temperature ranges at which the spectra were collected.

Figure 1 shows the actual 70-eV spectra of the above regions for the 300°C pyrolysis of the polymers. In this figure the higher gain portions of the spectra were run at the same electrometer settings, whereas the lower traces were run at various settings dictated by the amplitude of the most intense peak in the spectrum. The data in Table I are relative peak heights obtained by ratioing the individual peak intensities with the intensity of the dimer peak  $m/e$  208,  $M_2$ , for the 300°C pyrolysis. These data represent the average of two separate pyrolyses. The gross average deviation was 0.03 relative unit.

## DISCUSSION

The fragmentation patterns in the  $m/e$  51/77-78/91-92 ranges are typically those observed with aromatic systems. The  $m/e$  77/91/105/119/133 pattern is similar to that observed with phenyl-alkyl groupings. There are differences in these patterns for the three materials, as noted above, which it is believed may ultimately be related to structural characteristics.

The presence of the  $m/e$  104 peak as the most intense peak is presumably a result of the formation of the styrene monomer ion by depolymerization. It is recognized that the existence of an even-

mass fragment requires that such a fragment be derived by either a rearrangement, which is probably not involved here, or by a reversal of an addition reaction, such as a Diels-Alder reaction [6] or the addition polymerization. It is obviously not the "parent" peak in the usual sense.

The groups of peaks at  $m/e$  235-236 is characteristic of the p-DVB copolymer. This suggests that there is a structural feature in this material which is not present in the homopolymer or m-DVB copolymer. This structural feature may be an isolated single p-DVB unit itself. It is not however, immediately apparent how the para, but not the meta or monovinyl unit might be involved in the formation of a mass of this value (i.e.,  $C_{18}H_{20}$ ). There is also a possibility that adjacent para units, thought to be present in the para copolymer chain on the basis of copolymerization kinetic data [7], are the source of this 235-236  $m/e$  fragment. A [3, 3]-paracyclophane structure can conceivably be formed from such adjacent para units by rearrangement of (four)  $\gamma$ -hydrogen atoms to the benzylic odd electron ions in a paracyclophane precursor.

**Table 1.** Relative Peak Intensities from the Spectra of Fig. 1<sup>a</sup>

M	M/e	Polystyrene	8% p-DVB polystyrene	8% m-DVB polystyrene
$M_2 - 26$	182	0.31	0.24	0.24
$M_2 - 25$	183	0.33	0.19	0.20
$M_2 - 24$	184	0.29	0.13	0.14
$M_2 - 23$	185	0.42	0.08	0.07
$M_2 - 15$	193	1.92	0.76	0.72
$M_2 - 14$	194	1.44	1.50	1.45
$M_2 - 1$	207	1.42	1.32	1.22
$M_2$	208	1.00	1.00	1.00
$M_2 + 11$	219	0.14	0.08	0.07
$M_2 + 12$	220	0.15	0.12	0.08
$M_2 + 13$	221	0.18	0.26	0.14
$M_2 + 14$	222	—	0.22	—
$M_2 + 27$	235	—	0.23	—
$M_2 + 28$	236	—	0.15	—

<sup>a</sup>Actual average deviation  $\pm 0.03$  unit.

M-66 300 C PYROLYSIS AT 70 eV

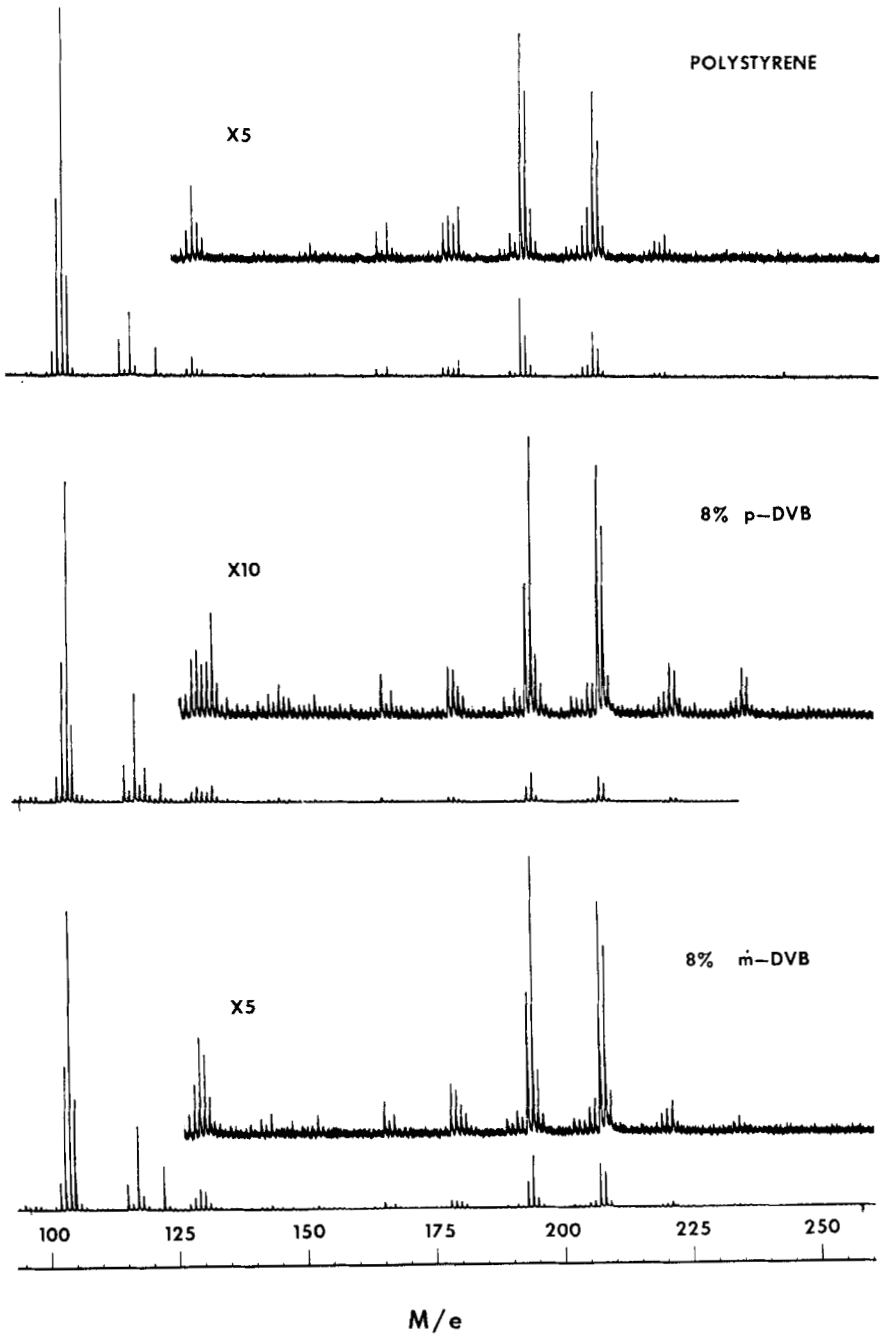


Fig. 1. Actual 70-eV mass spectrum of the 300°C pyrolysis of polystyrene and its 8% p-, and 8% m-divinylbenzene copolymers.

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