

## Collision-induced Decomposition of Cationic Radical Polystyrene Chains

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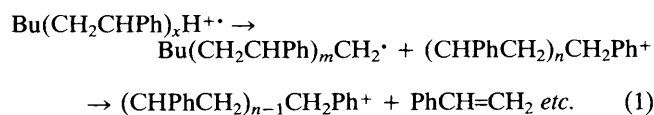
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Polystyrene radical cations undergo rapid depolymerisation following collisional activation.

We report collision-induced decomposition (c.i.d.) spectra<sup>1</sup> of radical ions ( $M$ )<sup>+</sup> of a synthetic organic polymer, namely polystyrene with the formula  $\text{Bu}(\text{CH}_2\text{CHPh})_x\text{H}$  ( $x$  is an integer). A distinctive feature is that the peaks in the spectra occur predominantly at low masses ( $m/z$  100–200), and this feature is most pronounced in the spectra of the ions of highest masses investigated (about  $m/z$  2000). The peaks can be related directly to the structures of the end-groups of polystyrene. We have investigated the c.i.d. of a number of other radical ions and also pseudo-radical ions of polyols and polyenes,<sup>2</sup> and their c.i.d. spectra exhibit this same distinctive feature. We suggest that the presence of peaks only at low masses is the result of more or less random initial cleavage of the polymer chain, followed by a series of consecutive depolymerisation reactions.

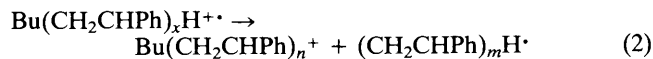
Polystyrene radical ions ( $M$ )<sup>+</sup> were formed by field desorption (f.d.),<sup>3,4</sup> and their collision-induced decomposition (c.i.d.) was studied using a double-focussing mass spectrometer of reverse geometry with a collision cell situated between the sectors.<sup>5</sup> C.i.d. spectra were measured with a number of collision gases (He, Ar, SF<sub>6</sub>) at various pressures, and using different emitter heating currents (e.h.c.s)<sup>6,7</sup> in forming the radical ions. The potential difference between emitter and counter electrode was 8 kV. C.i.d. spectra for the  $m/z$  682.5 and  $m/z$  1620.0 radical ions are shown in Figure 1. All peaks in the spectrum of the  $m/z$  682.5 ion and those below  $m/z$  500 in that of the  $m/z$  1620.0 ion disappeared if the collision gas was removed. The relative intensities of these peaks in the two spectra were not dependent upon e.h.c. The peaks above  $m/z$  700 (Figure 1a) were present in the absence of collision gas, and their intensities were strongly dependent upon e.h.c. The peaks above  $m/z$  700 (Figure 1a) are attributed to fragment ions formed by low-energy unimolecular processes involving hydrogen rearrangement.<sup>8</sup> The peaks below  $m/z$  500 in the spectrum of the 1620.0 ion and all peaks in that of the  $m/z$  682.5 ion (Figure 1b) are attributed to fragment ions formed by c.i.d.

Under the conditions of c.i.d., we expect initial fragmentation of a polystyrene chain to be randomly distributed among equivalent bonds, because the internal energy of the ions (*vide infra*) will be high and hence fragmentation will not be sensitive to slight differences in bond energy. It is, however, clear from Figure 1 that, while fragmentation of the lighter ion  $m/z$  682.5 in a sense may be considered to be close to random, fragmentation of the heavier ion  $m/z$  1620.0 appears to be distinctly non-random. The explanation in the case of the heavier ion is, we suggest, that initial random bond cleavages are followed by rapid depolymerisation, resulting ultimately in relatively small fragment ions containing one of the end-groups. Equation (1) for formation of the fragment ion



$m/z$  91, and other fragment ions in the B-series (Figure 1) whose masses are given by the formula  $n_B = (n104 + 91)$  ( $n$  is zero or an integer; masses are nominal), exemplifies the

general proposal. The fragment ions in the A-series (Figure 1) have masses given by  $m_A = (n104 + 57)$ , and the initial cleavage in the sequence of reactions in their formation is proposed to be as shown in equation (2). The fragment ions in



the C-series (Figure 1) have masses given by  $m_C = (n104 + 117)$ ; loss of benzene from fragment ions in the B-series would explain the C-fragment ions. The peak at  $m/z$  104 could be due to opposite charge retention during depolymerisation.

On the basis of the proposals advanced, the larger radical ions undergo depolymerisation to a greater extent than the smaller radical ions (consider Figure 1). This, we suggest, is a consequence of two factors. First, the internal energy uptake as a result of collision is greater in the case of the larger ions, according to recent measurements<sup>9</sup> and calculations.<sup>10</sup> Secondly, the depolymerisation once initiated is likely to proceed to completion, since each individual step will be approximately thermoneutral, and at each consecutive step the number of internal degrees of freedom of the reactant ion is that much less. Thus the greater internal energy of larger ions (perhaps 20 eV for  $m/z$  1620.0)<sup>9,10</sup> compensates for the greater original number of degrees of freedom, permits the initial simple bond cleavage within the backbone, and leaves sufficient internal energy thereafter to induce the rapid depolymerisation. With the smaller ion, a significant proportion of the available internal energy (perhaps 10 eV for  $m/z$

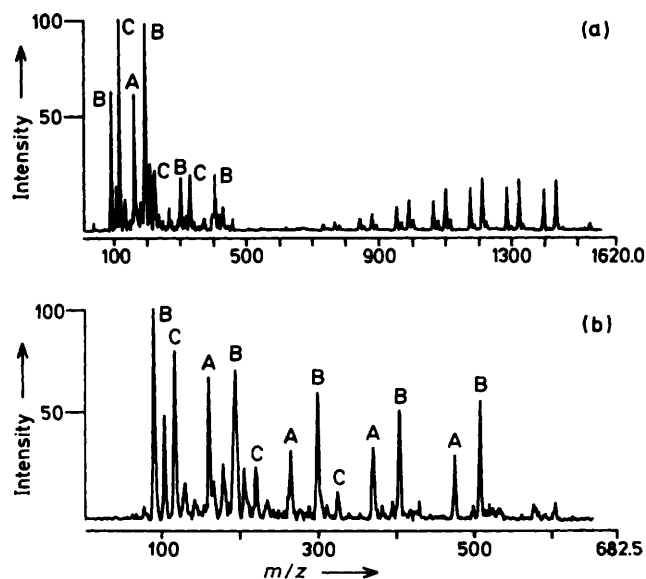


Figure 1. Collision-induced decomposition spectra of (a) the  $m/z$  1620.0 and (b) the  $m/z$  682.5 radical ions ( $M$ )<sup>+</sup> of polystyrene. Emitter heating currents 15 mA for (a) and 11 mA for (b). Argon collision gas at pressures at which fragment ion intensities were most intense.

682.5) is consumed in the initial bond cleavage, and subsequent depolymerisation is retarded.

In conclusion, we draw attention to the contrast between the behaviour of the polymer ions reported here and that of other ions, for example peptide ions, of comparable masses under identical conditions.<sup>9</sup> Peptide ions tend not to undergo consecutive decompositions in c.i.d. and tend, in the case of parent ions above  $m/z$  1500, to form fragment ions of high masses.<sup>9</sup> The difference is not associated with the peptide ions being even-electron ( $M + H$ )<sup>+</sup> species, since polypropylene glycol ( $M + H$ )<sup>+</sup> ions behave in the same way as the polystyrene ( $M$ )<sup>+</sup> ion.<sup>2</sup> Rather, we suggest the extensive fragmentation with the polymer ions is indicative of an intrinsic instability of cationic polymer chains with respect to depolymerisation, once a backbone bond has been cleaved. Finally, we point out that the fragment ions observed in the c.i.d. spectra (Figure 1) allow the masses of the end-groups of the polymer chains to be determined exactly.

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