6970 *Macromolecules* 1992, *25*, 6970–6976

High-Resolution TOF-SIMS Studies of Substituted Polystyrenes

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Received February 18, 1992; Revised Manuscript Received July 22, 1992

ABSTRACT: High-resolution ($M/\Delta M = 7000$) time-of-flight secondary-ion mass spectrometry (TOF-SIMS) was used to study the mechanism of fragment-ion formation for several polystyrenes. Ions are formed from neutral fragments resulting from chain cleavage and are cationized with a silver ion. Spectra of the polystyrenes consist of repeating patterns of clusters of invidual peaks extending to $m/z > 3000$. Fragmentation of the polymer backbone can be explained by limited chain fragmentation, consistent with mechanisms proposed for other methods. Most polystyrenes show five clusters in their repeat pattern except for poly(α-methylstyrene) which differs considerably. This difference is discussed. Cluster structure can be explained by the contributing species having zero, one, or two rings and/or double bonds. The results of this study support the idea that chain fragmentation proceeds through a cyclic intermediate.

Introduction

Mechanisms of polymer degradation have been of interest for years.[1] Polystyrenes are used widely as packaging and insulating materials, and understanding how thermal and radiation-induced changes affect them is important. Radiolysis[2] and thermal degradation methods (such as pyrolysis)[3,4] have been the two major methods used for mechanistic investigations of polystyrene degradation. In most radiolytic studies, dilute solutions of the polymer were irradiated by a pulsed megaelectronvolt electron beam[5,6] and the decay of transient intermediates (radicals, ions) was followed by ESR or UV–vis spectrometry. Thermal degradation studies have been useful for determining activation energies of polymer decomposition[7,8] and obtaining kinetic information by analyzing volatile products as they escape the bulk polymer during rapid heating.[9,10]

The purpose of the present investigation was to characterize decomposition and fragment-ion formation for substituted polystyrenes, induced by argon kiloelectronvolt ion bombardment and measured by time-of-flight secondary-ion mass spectrometry (TOF-SIMS). A variety of mass spectrometric methods have been employed for characterization of styrene polymers. Field desorption[11] and laser desorption mass spectrometry[12–14] have successfully obtained fingerprint information (monomer and end-group masses) in the low-mass region and oligomer intensity distributions for low molecular weight polymers. Pyrolysis GC–MS[15] and quadrupole SIMS studies[16] have been limited to the fingerprint region by the cutoff of the mass analyzers used. Preliminary TOF-SIMS studies have reported oligomer and fragment ions for a variety of polymers as large as 10 000 amu.[17]

Studies of polymer ion formation and fragmentation have been few in number. Mass-analyzed kinetic energy spectra (MIKES) of field-desorbed polystyrene cations showed that end-group cleavage is favored over fragmentation toward the center of the chain.[18] This effect is predicted by a RRKM-based unimolecular decomposition model that describes fragmentation as a function of the number of monomer units.[19] TOF-SIMS studies of silver-cationized fragment-ion formation from polystyrene investigated ion formation as a function of surface thickness and the polymer molecular weight.[20] The relative abundances of silver-cationized fragments were found to be independent of the molecular weight of the polystyrene.

The present investigation represents the first high-resolution study of polystyrene fragment ions in the range m/z 600–3000; better than unit mass resolution is achieved. The focus here is on the effect of molecular structure on the overall spectral pattern and detailed analysis of the structures contributing to the mass spectrum of a given polymer fragment. Analysis of the spectra provides insight into the initial events of chain scission when a pulse of energy is provided to the polymer chain. The importance for decomposition studies of polymer chains is discussed.

Experimental Section

Mass spectra of the polystyrenes were obtained with a time-of-flight mass spectrometer specifically designed for SIMS applications.[21,22] Primary argon ions are formed in a conventional EI source and accelerated to 10 keV. The ion beam passes a 90° electrostatic reflector which chops the beam into ion packets having widths of ca. 20 ns. These pulses are time-focused onto the target by a second pulsed capacitor giving a final pulse width less than 1 ns. The primary-ion pulse frequency was 5 kHz with about 500 ions per pulse, and the sample was bombarded for typically 300 s, corresponding to a current of 1 pA. The total ion dose is in the static SIMS region. Secondary ions emitted from the target are accelerated to 4 keV prior to entering the drift tube. The TOF uses a reflectron to reduce line widths and has a total flight path of 2 m. Secondary-ion transmission is about 10%. Ions leaving the drift tube are postaccelerated to a total energy of 10 keV and are detected by a channel-plate, scintillator, photomultiplier tube combination. Data are recorded by a 100-MHz signal averager.

Polystyrene and seven substituted polymers were studied. The substituted polymers were α-methyl-, 4-methyl-, 4-methoxy-, 2-methyl-4-*tert*-butyl-, 2,4-dimethyl-, 2,5-dimethyl-, and 2,6-dimethyl-4-*tert*-butylstyrene. They were obtained from Polymer Products of Ontario, NY. The molecular weights of all polymers were approximately 70 000. Polymers were dissolved (1 mg/mL) in toluene, and 10 μL of the solution was deposited onto ca. 30 mm^2 of a silver target that had been etched in 20% nitric acid and rinsed thoroughly with distilled water. All targets were scratched with a knife prior to analysis to improve the yield of cationized secondary ions.[17]

Results and Discussion

Formation of large fragment ions from polymers involves chain-breaking events to produce neutral fragment mol-

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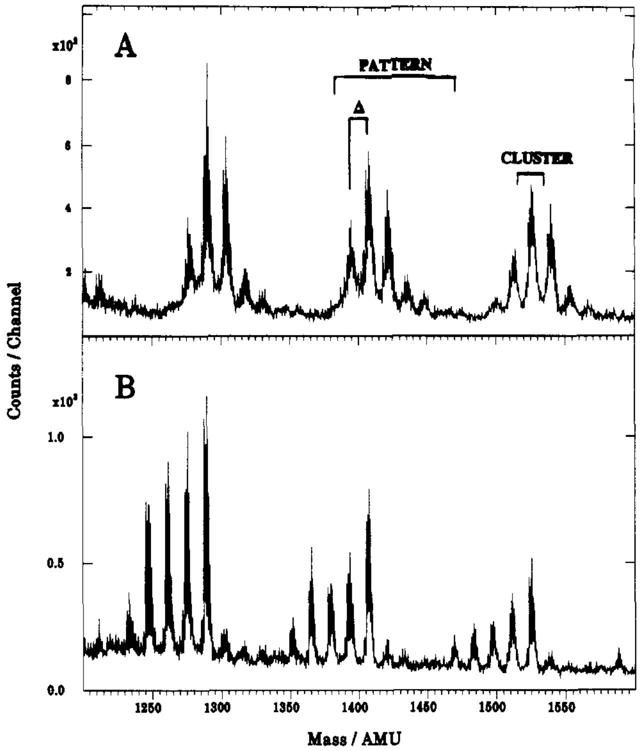


Figure 1. TOF-SIMS spectra of substituted polystyrenes (mass range 1200–1600 amu): (A) poly(4-methylstyrene); (B) poly(α-methylstyrene).

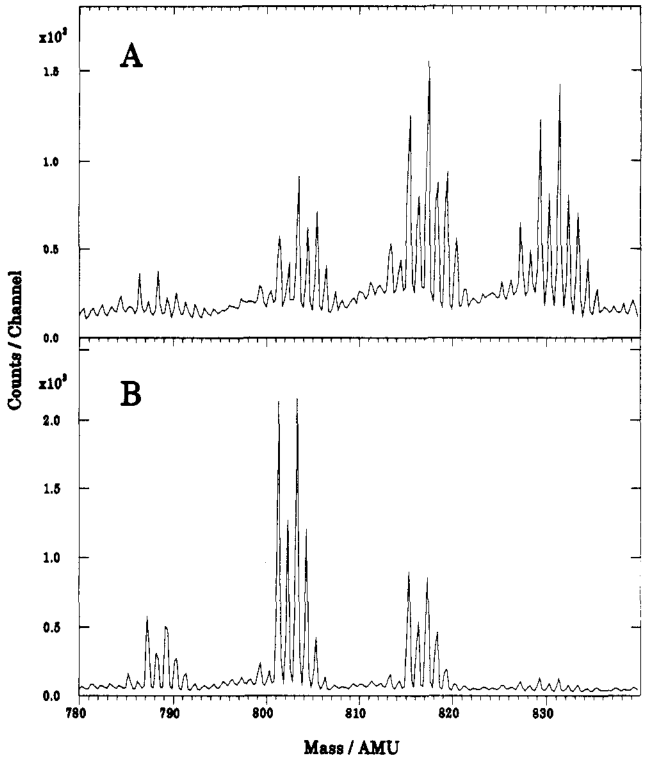


Figure 2. Detailed cluster structure for substituted polystyrenes (mass range 780–840 amu): (A) poly(4-methylstyrene); (B) poly(α-methylstyrene).

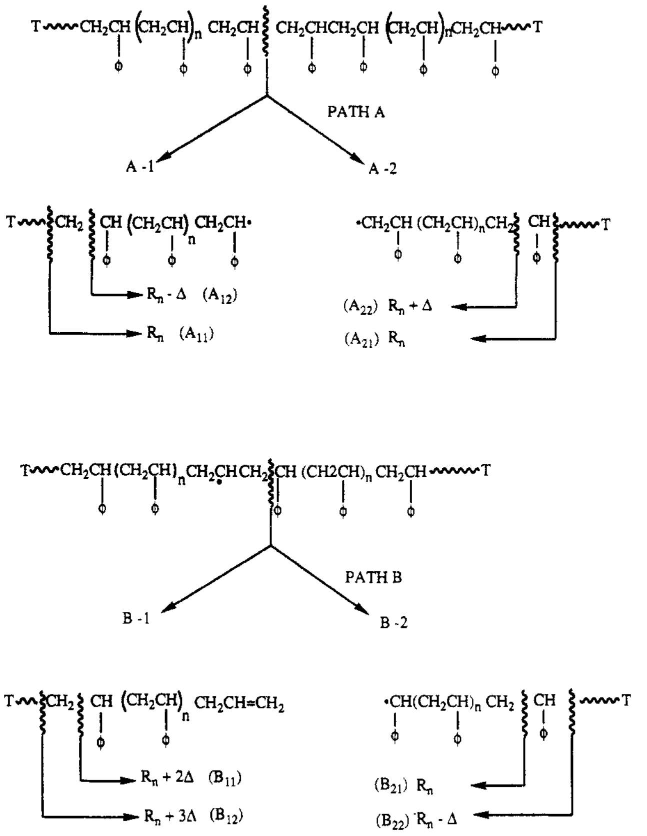
ecules which are then cationized by silver. Interpreting such fragment-ion spectra requires two separate considerations. First, it is necessary to explain the overall structural features of the mass spectrum. In the case of the polystyrenes, this constitutes a repeating pattern of peaks, separated by the mass of the polymer repeat unit. A typical example is shown in Figure 1A for poly(4-methylstyrene) (poly-4-MS). The repeating sequence will be referred to as a *pattern*, so noted in the figure. Second, each pattern consists of groups of peaks spaced approximately 14 amu apart. Each of these contains a number of individual lines and will be referred to as a *cluster*. This is also noted in the figure. The spacing between clusters will be noted by "Δ" (so noted in Figure 1) rather than by a numerical value, because species having varying degrees of unsaturation contribute to each cluster (loc. cit.). The pattern for poly-4-MS centered at m/z 1407 is derived from fragments consisting of 11 monomer units, plus or minus additional CH_n units (Δ). The detailed structure of the clusters having six repeat units is shown in Figure 2A for poly-4-MS. We will discuss pattern and cluster structure separately.

Pattern Structure. The spectrum for poly-4-MS in Figure 1 shows three repeat patterns, each consisting of three major clusters corresponding to R_n, $R_n + \Delta$, and $R_n - \Delta$ where R_n is some multiple (n) of the mass of the repeat unit. Two smaller peaks are observed at $R_n + 2\Delta$ and $R_n + 3\Delta$ for each pattern. All of the polystyrenes studied showed this general type of pattern except for poly(α-methylstyrene) (poly-α-MS) which was quite different, as can be seen from Figure 1B. None of the polystyrenes studied showed any evidence for fragmentation involving the phenyl group or functionalities on it. No polystyrene showed any ions having characteristic end groups (all had MW ≥ 70 000), and no uncationized radical ions were observed for species larger than one or two monomer units. All ions to be discussed here are derived from cationized neutral fragments.

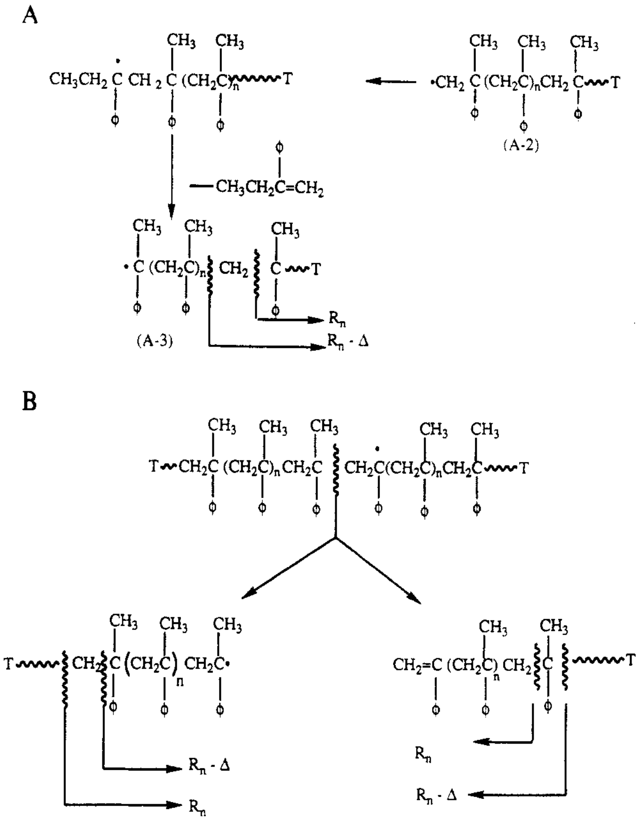
Poly-4-MS. We will make several assumptions for out discussion of polymer fragmentation. *First*, each event observed is initiated by only one primary ion and the initiation process does *not* involve the ion hitting the polymer chain directly. Chain fracture is initiated by the collision cascade resulting from impact of the primary ion with the silver surface. This assumption is reasonable because we work at very low primary ion doses (static mode) and the probability of the same spot as the surface being struck by two ions is below 10^{-3}. *Second*, each events involves an isolated polymer molecule. This is a reasonable assumption because the gross surface coverage is calculated to be a monolayer or less, minimizing intermolecular interactions. *Third*, two fragments are formed per event, in the mass range measured. The polymer chain is fractured initially, and two subsequent fractures occur, each of which produces a neutral fragment. *Fourth*, the cationization probabilities of all neutral fragments produced are equal. *Fifth*, the probabilities of breaking all carbon–carbon bonds involving the polymer backbone are the same; this assumption is reasonable given that the C–C bond energies vary by only a few kilocalories per mole.

The formalism for the interpretation is given in Scheme I for a generic polystyrene. We consider two possible fragmentation pathways for the polymer: initial fracture of the backbone chain (path A) and initial loss of a phenyl group with subsequent chain fracture (path B). The two pieces produced initially in path A can subsequently fracture, giving only two possible structures each: A-1 yields only $R_n - \Delta$ or R_n; A-2 gives only $R_n + \Delta$ or R_n. Either fragment from path A can lose styrene monomers (chain unzipping), but doing so merely generates the same type of radical having n reduced. Adding up the intensities, if this were the only fragmentation mechanism operative, the mass spectrum would consist of a series of triplets, centered about R_n and having relative intensities of 1:2:1. This is equivalent to what one would expect from simple statistical chain fracture, and this will be referenced as the "simple statistical model". To a large degree, this

Scheme I



Scheme II



model accounts for the spectra of the polystyrenes. We assume in all models that radicals will gain or lose hydrogen to form neutral molecules; more will be said about that in the discussion of cluster structure.

Path B differs qualitatively in that one piece generated by chain fracture has a neutral end (B-1) and other is a radical (B-2). Subsequent scission of the neutral fragment (path B-1) will produce peaks at $R_n + 2\Delta$ or $R_n + 3\Delta$; B-2 is equivalent to A-1 and as such produces R_n or $R_n - \Delta$. Thus the two pathways account qualitatively for the five peaks seen in the spectrum of poly-4 MS and are typical of polystyrene itself and most of the other polystyrenes studied.

We have ignored the loss of hydrogen as a possible initial event. This was done for two reasons. First, C–H bonds are generally stronger than C–C bonds, and second, the results of hydrogen loss are redundant with the above two mechanisms. For example, the most likely hydrogen to lose is the benzylic hydrogen. Loss of this hydrogen and subsequent chain fracture would be the equivalent of path A, except that the A-2 fragment would be neutral. This might explain why the $R_n + \Delta$ peak is somewhat higher than predicted by the mechanism in Scheme I, but one must be careful not to overinterpret the results. Clearly, labeling studies are in order.

Poly-α-MS. Poly-α-MS shows a distinctly different cluster pattern than the other polystyrenes, as can be seen from Figure 1. The most striking feature is that the peak corresponding to $R_n + \Delta$ is greatly reduced in intensity and significant peaks appear at $R_n - 2\Delta$, $R_n - 3\Delta$, and $R_n - 4\Delta$. The major structural difference is that poly-α-MS has a methyl group replacing the benzylic hydrogen. This methyl group is labile, as indicated by MIKES/CAD studies of $C_9H_{10}^+$ isomers; loss of CH_3 from α-methylstyrene was 3–5 times greater than for any other $C_9H_{10}^+$ isomer studied.[23] Also, poly-α-MS showed the smallest hydrogen loss of any polystyrene in the present study (loc. cit.). Pulse radiolysis studies of poly-α-MS postulated that a rearrangement involving the methyl group is responsible for the chain unravelling mechanism.[9] This would require modification of Scheme I for poly-α-MS, as shown in Scheme IIA. The radical produced by initial chain cleavage (A-2) rearranges to form the more stable benzylic radical which loses a neutral to produce radical A-3. This type of reaction has been reported for the thermal degradation of polystyrenes.[11] Subsequent cleavage of A-3 yields only R_n or $R_n - \Delta$. Combining A-3 with A-1 from Scheme I correctly predicts loss of the $R_n + \Delta$ peak but also predicts that the pattern should contain only two clusters corresponding to R_n and $R_n - \Delta$ and in a 1:1 ratio. It should also be noted that rearrangement of the phenyl group instead of the methyl group would give exactly the same result. Clearly, something else is afoot.

Given the tendency for loss of the methyl group in α-methylstyrene, it is likely that loss of a methyl radical will initiate chain fracture rather than loss of a phenyl group; this is shown in Scheme IIB. This mechanism predicts only R_n and $R_n - \Delta$ clusters, which correlates with the lack of $R_n + 2\Delta$ and $R_n + 3\Delta$ clusters which are seen for poly-4-MS. A possibility which must also be considered is that several methyl groups could be lost from a given fragment and that the backbone chain does not fragment because hydrogen addition competes favorably with chain fracture. Such a possibility is shown in Scheme III. This process could account for the clusters at $R_n - 2\Delta$ to $R_n - 4\Delta$. If this were the case, however, one would expect that the intensities of peaks resulting from multiple losses would increase relative to R_n as the size of the fragment ion increased. Table I shows the relative cluster intensities for different patterns of poly-α-MS. Clearly, the $R_n - 2\Delta$ and $R_n - 3\Delta$ peaks *decrease* in intensity as the fragment size increases. The data in Table I extend to the highest mass that we could measure (m/z 3950) with an acceptable signal-to-noise ratio (S/N = 5). The $R_n - 4\Delta$ peaks were not included in Table I because of weak intensities. Thus, Scheme III

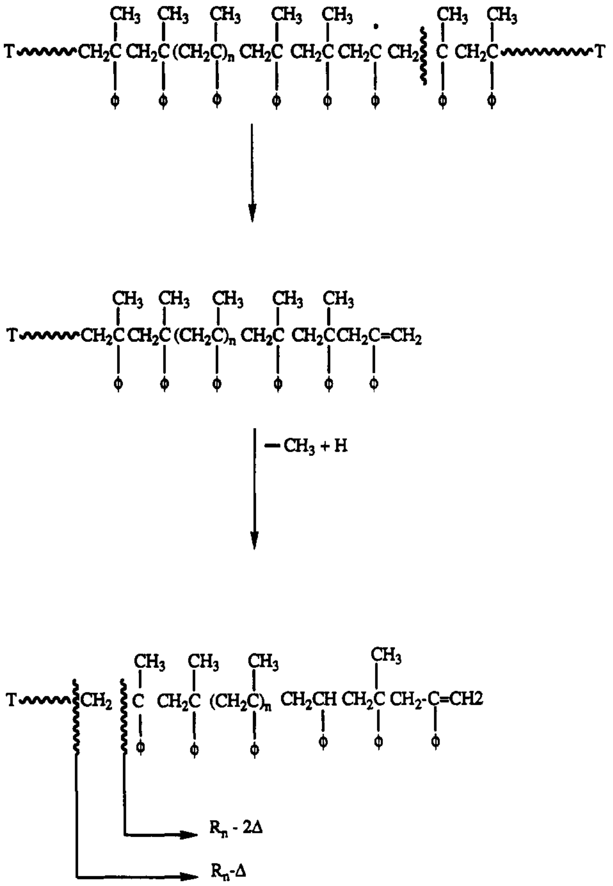
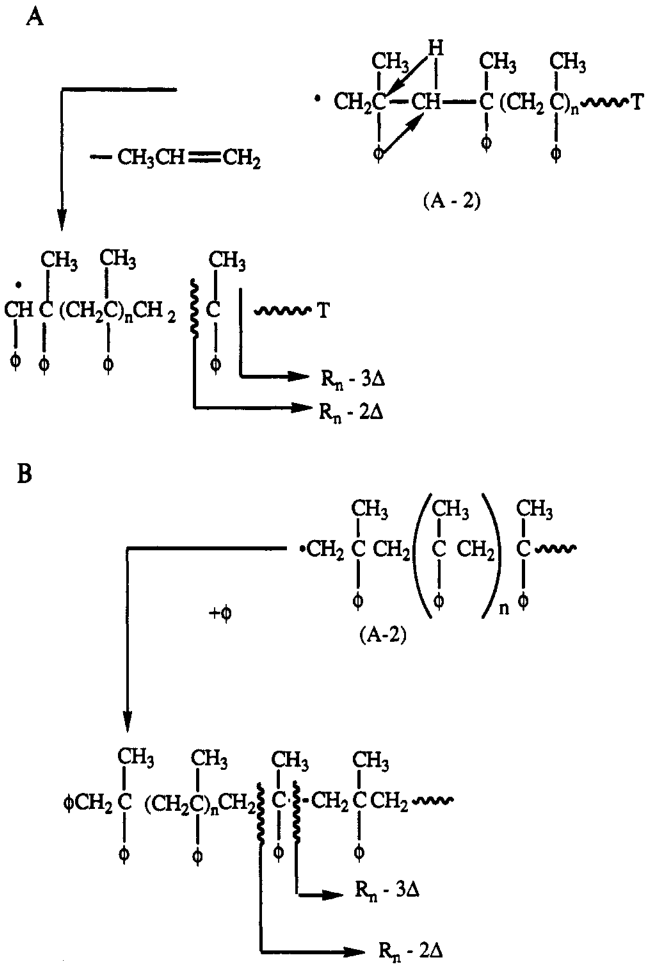


Table I
Relative Intensities of Poly(α-methylstyrene) Clusters

pattern no.[a]	−3Δ	−2Δ	−Δ	R_n[b]
6		74	219	100
8	43	215	105	100
10	82	77	74	100
12	48	44	64	100
14	31	36	59	100
18	13	24	50	100
24		18	56	100
32			50	100

[a] Pattern number is the number of monomers b. [b] Set to 100 for comparison.

Scheme IV



we can conclude that detachment of multiple methyl groups from a fragment ion is not a viable mechanism. After possible mechanistic schemes were considered, the inescapable conclusion was that the second chain fracture must depend on the nature of the radical produced by the initial chain-breaking event. This argues for a cyclic intermediate in which the radical end of the chain causes the second detachment. This is consistent with our analysis of cluster structure (loc. cit.).

The peaks at $R_n - 2\Delta$ and $R_n - 3\Delta$ are best explained by considering phenyl group transfer during chain fragmentation. This could occur by a number of different mechanisms, and presently there is no evidence to favor one over another. Scheme IV presents two such mechanisms to illustrate the types of structures and reactions necessary. In Scheme IVA rearrangement of the radical from A-2 occurs along with elimination of propene. Cleavage of the resulting radical yields fragments of $R_n - 2\Delta$ and $R_n - 3\Delta$. In Scheme IVB the A-2 radical abstracts a phenyl group from some point down the chain. Subsequent scission accompanied by H atom transfer accounts for two fragments at $R_n - 2\Delta$ and $R_n - 3\Delta$. This particular mechanism is consistent with a cyclic intermediate and has the advantage of predicting lower intensities of the $R_n - 2\Delta$ and $R_n - 3\Delta$ peaks as the fragment size increases. The "hot" end has further to reach to grab a phenyl group. However, it should be stressed again that the reaction presented is purely illustrative.

The $R_n + 4\Delta$ peak is problematic. No combination of the processes shown in Schemes I–IV can account for its presence. It could arise by cleavage at sites produced by backward addition in the original polymerization, but this idea does not fit with the data of Table I. Also, its intensity is greater than would be expected for the number of such sites generally found in polymer chains.[24]

Cluster Distributions. The relative intensities of the different clusters are summarized in Table II for the polystyrenes studied. The data given are for average cluster distributions obtained by averaging values for five patterns for each polymer. The values in parentheses are the standard deviations. Clearly, the relative cluster intensities differ for the various polystyrenes; polystyrene and poly-4-MS are similar, poly-α-MS is different, and the others fall in between.

Figure 3 shows the variation of cluster intensity as a function of fragment size for polystyrene, poly-4-MS, and poly-α-MS. Clearly, the variation in cluster intensity is more dramatic for poly-α-MS than for the other two. Once again, poly-α-MS is the outlier.

It is interesting to attempt to correlate the relative cluster intensities with the mechanism outlined in Scheme I for polystyrene and poly-4-MS. This can be done by calculating branching ratios for the reactions shown in the scheme to account for the observed spectral intensities. This is accomplished by solving a set of simultaneous equations relating the various pathways to spectral peak

Table II
Relative Cluster Intensities for Polystyrenes[a]

polystyrene	-2Δ	$-\Delta$	R_n	$+\Delta$	$+2\Delta$	$+3\Delta$
polystyrene[c]		23.7 (3.3)	29.9 (1.9)	22.9 (2.5)	12.9 (2.3)	10.7 (1.3)
4-methyl[c]		28.0 (3.4)	29.6 (2.4)	21.7 (2.6)	11.6 (1.5)	9.0 (1.3)
α-methyl[b,c]	16.1 (10.3)	28.8 (12.1)	38.7 (13.4)	4.4 (3.7)		
4-methoxy[d]	8.6 (0.5)	25.0 (1.0)	30.1 (1.5)	18.5 (0.8)	12.8 (0.3)	5.0 (0.3)
2,4-dimethyl[d]	5.5 (0.4)	29.6 (1.4)	28.1 (0.1)	16.9 (0.5)	12.7 (0.8)	7.1 (0.6)
2,5-dimethyl[d]	4.5 (0.5)	22.1 (3.8)	26.3 (0.5)	16.1 (1.2)	22.5 (2.4)	8.5 (0.4)
2,6-dimethyl-4-*tert*-butyl[d]	7.5 (0.6)	24.7 (1.4)	34.6 (1.4)	18.3 (2.2)	9.2 (0.8)	5.7 (0.2)

[a] Data given as percent of total intensity. [b] $-4\Delta = 3.6$ (3.8); $-3\Delta = 8.3$ (7.5). [c] Data obtained from an average of five patterns. [d] Data obtained by averaging all measurable clusters.

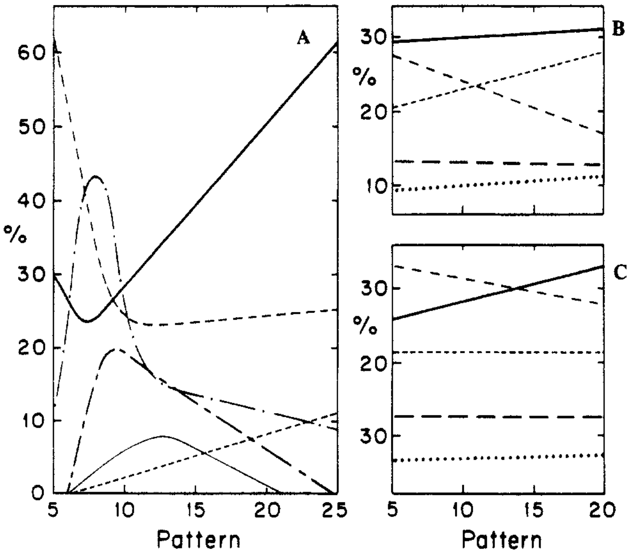


Figure 3. Relative cluster intensities for polystyrenes as a function of pattern number: (A) poly(α-methylstyrene); (B) polystyrene; (C) poly(4-methylstyrene). The data are shown as smooth curves, but the standard deviations of the slopes range from ±3% to ±30%. Key: $R_n + \Delta$ (- - -); $R_n + 2\Delta$ (— — —); $R_n - 2\Delta$ (– · –); R_n (—); $R_n + 3\Delta$ (···); $R_n - 3\Delta$ (– - –); $R_n - \Delta$ (– – –); $R_n - 4\Delta$ (—).

Table III
Branching Ratios for Polystyrene Fragmentation

	coefficient					
polystyrene	A_{11}	A_{12}	A_{21}	A_{22}	B_{11}	B_{12}
polystyrene	26	24	3.5	23	13	11
4-methyl	22	28	1.3	28	12	9
4-methoxy	29	20	3.2	27	14	5.5
2,4-dimethyl	31	18	0.0	30	13	7.4
2,5-dimethyl	30	18	0.0	22	22	8.5
2,6-dimethyl-4-*tert*-butyl	29	21	3.0	27	11	8.4

intensities. The branching ratios are shown in Scheme I as A_{11}, A_{12}, etc. The results for calculation of the branching ratios are summarized in Table III. For example, the intensity of peak R_n must be the sum of A_{11} and A_{21}. Similarly, $R_n - \Delta = A_{12}$, $R_n + \Delta = A_{22}$, $R_n + 2\Delta = B_{11}$, and $R_n + 3\Delta = B_{12}$. The consistency between the coefficients (Table III) and cluster intensities (Table II) is apparent, for example, for polystyrene $A_{11} + A_{21} = 29.5$ and $R_n = 29.9$. Also, A_{11} and B_{21} measure the same reaction, as do A_{12} and B_{22}, given that they are for the same radical. Thus only the A coefficients were used for this radical.

The relationship between A_{11} and A_{12}, and B_{11} and B_{12}, is what might be expected for free radical reactions. The second chain fracture is equally probable for both fragments. This is not the case for A_{21} and A_{22}; the ratio of A_{22}/A_{21} is 6.5 and 21 for polystyrene and poly-4-MS, respectively. This implies that there is preferential reactivity in chain fracture. Whether the process is simple fracture or involves hydrogen abstraction, A_{21} and A_{22} should be approximately equal. Thus it is likely that there is another process contributing to formation of $R_n + \Delta$ fragments. It is quite likely that it is a process competitive with A_{11} and A_{12} (mathematically this works out well) or that a completely independent mechanism of chain fracture is operative. Again, we will defer speculation pending more experimental data.

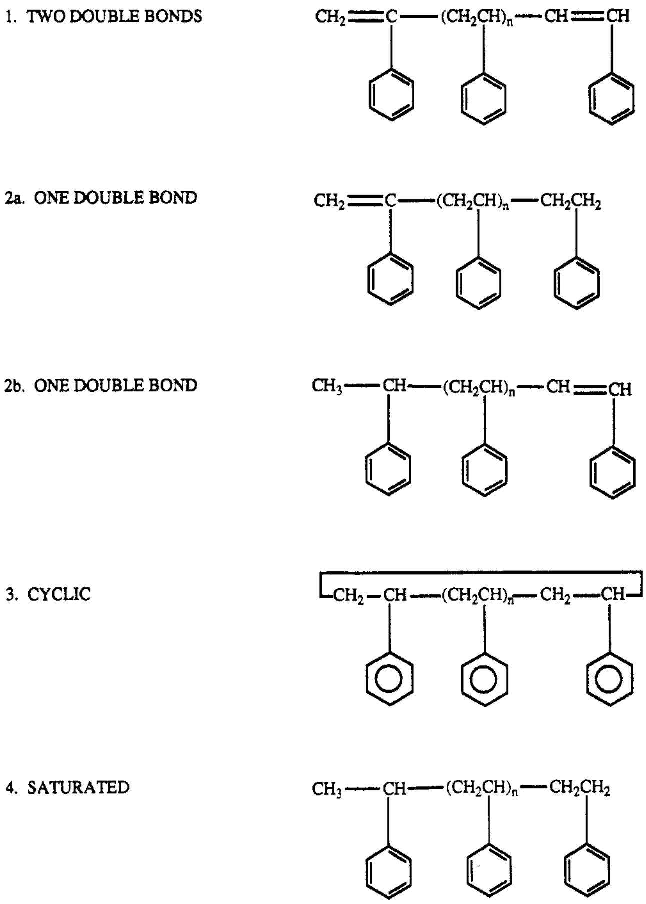


Figure 4. Structures illustrating unsaturation and ring formation for polystyrenes.

Cluster Structure. Figure 2 shows the detailed structure of the R_6 clusters for poly-4-MS and poly-α-MS. It is apparent that each cluster is resolved into a series of peaks separated by 1 amu. The clusters were analyzed by considering the carbon and silver isotope structure for single species. The number of peaks present in a cluster and their relative intensities require more than one species contributing to a given cluster. Each cluster contains sets of peaks that correspond to fragments containing zero, one, or two double bonds and/or rings; each fragment is cationized by silver. Figure 4 shows possible structures for the zero, one, and two double bond and cyclic structures for an R_n cluster of polystyrene. Note that there are two possibilities for structures having one unsaturation, they are isomers. A cyclic structure without additional un-

Table IV
Distribution (%) of Species[a] in Polystyrene Clusters

polystyrene	no. of unsaturations 2	1	0
polystyrene	26 (4.2)	45 (4.0)	29 (4.3)
4-methyl	26 (2.2)	37 (3.1)	37 (3.2)
α-methyl	9.2 (3.8)	86 (3.6)	4.6 (3.8)
4-methoxy	39 (2.3)	39 (2.3)	22 (2.3)
2,4-dimethyl	38 (3.5)	33 (3.4)	29 (3.5)
2,5-dimethyl	21 (3.0)	37 (2.9)	42 (3.0)
2-methyl-4-*tert*-butyl	17 (2.1)	33 (2.1)	50 (2.1)

[a] Relative standard deviations of the fits are given in parentheses.

saturation is also a possibility. These three will be considered as one fragment type. The relative abundances of the three fragment types are different for the various polystyrenes, as can be seen from the data of Table IV. The data of Table IV were calculated by averaging data for three successive sets of clusters, e.g. $n = 5$–7. The relative abundances of the species in Table IV vary somewhat as a function of cluster size. For example, for $n = 12$, the 2:1:0 ratios are 22:66:12 and 28:72:0 for poly-4-MS and poly-α-MS, respectively. Analysis of cluster peaks provides information about the mechanism of fragment-ion formation. We will consider two possible mechanisms of fragmentation, involving diradical and cyclic intermediates.

Diradical Intermediate. This model assumes that fragments are formed by two independent chain cleavages, generating a diradical which subsequently reacts with hydrogen. This is consistent with the simple statistical model given in Scheme I, path A, and would generate the structures shown in Figure 4 for an R_n fragment. This model predicts that two species will be formed which have one double bond (3–2 and 3–3), and there will be one species each for zero (3–4) and two (3–1) double bonds. Cyclic fragments are not considered.

There are two arguments which suggest that the 2:1:0 be formed in a 1:2:1 ratio. First, the heats of formation for all fragments must add to some constant value, because the total number of monomer units associated with the fragments and the number of double bonds will always be the same. This argument will not be affected by depolymerization because altering the chain length will only alter the final number of monomers in the fragment. Second, the number of hydrogens transferred between fragments must be equal since no hydrogen is added to the system. The energy associated with extraction of a hydrogen on either side of the chain break should be nearly the same.

Next, let us compare the abundance of the three types of species for the polystyrenes, as shown in Table IV. The data for Table IV were compiled using a least-squares fitting program. The anticipated spectrum was calculated for each species considering both carbon and silver isotope distributions. The cluster was fitted with increasing numbers of components and the residual examined for each additional component. When the residual was random, it was assumed that the correct number of species had been used. In all cases, three components were necessary to fit the data used for Table IV. It is clear from Table IV that the relative abundances for the polystyrenes differ from either 1:2:1 or 1:3:1, with the possible exception of polystyrene itself. The difference between poly-α-MS and the others is statistically significant. The difference for the 2-methyl-4-*tert*-butyl derivative is possibly significant.

The lack of agreement of the data of Table IV with predictions for a simple diradical intermediate correlates with the inability of Scheme I, path A, to explain fully the nature of the spectra. The disagreement cannot be due entirely to formation of cyclic fragments, because this would increase the monounsaturated derivative intensity at the expense of the other two. It should be remarked here that we assume the Ag^+ affinity of all three species is essentially the same. This assumption is justified in part by the fact that silver cationization is universal for almost all polymers,[18,25] and that accurate molecular weight determinations can be made from silver-cationized oligmer distributions suggests that discrimination in cationization is not a major factor. The results also very strongly indicate that some other fragmentation mechanism is operative under TOF-SIMS conditions. Although the diradical intermediate mechanism is not a major pathway it could be operative to a small extent, as suggested by the data for polystyrene.

Table V
Slopes of Least-Squares Plots of Intensity vs Monomer Number for Polystyrenes

derivative	slope
4-methyl	-1.62 ± 0.17
2,5-dimethyl	-1.78 ± 0.08
4-methoxy	-2.15 ± 0.17
2,4-dimethyl	-2.23 ± 0.10
styrene	-2.32 ± 0.07
2-methyl-4-*tert*-butyl	-3.18 ± 0.06
α-methyl	-4.87 ± 0.20

Cyclic Intermediate. We will now consider a cyclic intermediate in which fragment formation occurs, after initial chain breaking, by subsequent attack of the free radical end on some other portion of the same chain to cause the second cleavage. The kinetics of polystyrene cyclization in solution have been studied extensively.[26–28] It was found that the rate of cyclization decreases with the number of monomers in the polymer. The relationship is given by

$$k_{cy} = AM^{-\gamma} \tag{1}$$

where k_{cy} is the rate constant for cyclization, M is the monomer number, and A and γ are constants.[26] Normalized plots of cyclization rate vs monomer number were found to have slopes between −1.3 and −2.0, depending on solvation conditions.[28]

The treatment of eq 1 should apply to polymers whether forming in solution or being broken after ion-beam fracture. Log–log plots of total cluster ion intensity as a function of monomer number yielded slopes having values between −1.6 and −4.8, as shown in Table V. Five of the seven slopes fall in the range −1.6 to −2.3, showing good agreement with the solution results. The two polymers which have slopes outside this range (poly-α-MS and poly-(2-methyl-4-*tert*-butylstyrene)) are the two which also showed apparent deviations in Table IV. This decrease in fragment-ion intensity with monomer number was noted previously,[21] but without explanation. Equation 1 indicates that the only factor determining the rate of cyclization is the chain length of the polymer and the chemical nature of the monomer. We believe that the similarity of the slopes reported here with values from solution studies constitutes strong evidence for involvement of a cyclic intermediate in polymer chain fragmentation. The results from the cluster intensity studies are consistent with a cyclic intermediate as is the distribution of intensities of the clusters within a pattern.

Conclusions

High-resolution TOF-SIMS spectra of polystyrenes have been interpreted on the basis of a cyclic intermediate model. The qualitative features of the spectra are explained in detail for polystyrene, poly(4-methylstyrene), and poly(α-methylstyrene). The spectra consist of repeating patterns of clusters; the pattern structure can be explained by limited chain fracture. The structure of the clusters is due to species having zero, one, and two double bonds; cyclic structures are not likely. The evidence indicates that polymer chain fracture proceeds by an initial chain break to yield mostly ends which are free radicals. These radicals are "hot", and subsequently attack other points on their chain to cause a second cleavage. The clusters observed within repeating patterns and the detailed structure of this clusters are consistent with this "hot spot" theory.

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE-8411835 and INT-9024775.

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Registry No. Polystyrene, 9003-53-6; poly(4-methylstyrene), 24936-41-2; poly(α-methylstyrene), 25014-31-7; poly(4-methoxystyrene), 24936-44-5; poly(2,4-dimethylstyrene), 25990-16-3; poly(2,5-dimethylstyrene), 34031-72-6; poly(2,6-dimethyl-4-*tert*-butylstyrene), 144182-38-7.