

The Mass Spectra of the Low-Molecular-Weight Polymers of α -Methylstyrene

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Studies using mass spectrometry for polymer chemistry have been widely carried out; the analysis of the bond sequence of a polymer is one example. However, most of these have adopted the method of measuring the mass spectra of the low-molecular-weight products which result from the pyrolysis or other chemical degradation of high-polymers. If it would be possible to measure the mass spectra of polymers directly without the aid of the pyrolysis or other chemical degradation of the polymers, we might obtain new information about the polymerization mechanism, the bond sequence of the polymer, and other problems from these mass spectra. Of course, the mass spectra of organic compounds having a very high molecular weight cannot be measured easily, because it is extremely difficult for these compounds to be ionized in a mass spectrometer on account of their non-volatilities. This is the reason why the mass spectra of low-molecular-weight polymers of α -methylstyrene obtained by the anionic living polymerization method were measured as the first trial in this research.

Studies concerned with anionic living polymerization of α -methylstyrene in aprotic solvents have been carried out by Kuwata, *et al.*,¹ and many others. The mechanism of this reaction which was suggested by Szwarc, *et al.*,² has been examined on the basis of these results.

Richards, *et al.*,³ examined the structure of the tetrameric dianion of α -methylstyrene by using mass spectrometry and other methods. We used the low-molecular-weight polymers (below *ca.* 1000) of α -methylstyrene formed by

living polymerization as the samples to obtain the mass spectra. In this investigation we used the techniques of both electron impact and chemical ionization.

EXPERIMENTAL

Polymerization

α -Methylstyrene was polymerized by the Na-mirror method¹ in tetrahydrofuran solution at room temperature. After the usual distillation method, α -methylstyrene was purified by distillation *in vacuo*. Tetrahydrofuran was purified in a similar manner, after removing any trace of water with Na—K alloy. Methyl alcohol (CH₃OH) and deuterated methyl alcohol (CD₃OD: D-content at 99 atom%—E. Merck, A. G.) were used for killing agents.

The polymers which were killed immediately after polymerization contained the polymers with comparatively high molecular weights, so that after the fraction of high-molecular-weight polymers was precipitated by methyl alcohol, the low-molecular-weight polymers were obtained by removing the solvents from the filtrate (polymer I). When the solution under living polymerization was heated at 60°C (near the ceiling temperature), most of the polymers consisted of dimers and trimers (polymer II). Two ways were adopted for heating; the first was heating without removing the residual solid Na (polymer II-A), and the other was heating after removing the residual solid Na through a glass filter (polymer II-B). Dimers and trimers were separated by gas chromatography. In polymer I

the presence of dimers and trimers was identified, but these could not be collected separately because their amounts were too small.

Mass Spectra

The measurements of mass spectra were carried out by a HITACHI RMU-6M electron impact type mass spectrometer (maximum resolution 12,000) installed at Nara Women's University and by HITACHI RMU-6MC chemical ionization type mass spectrometer installed at Hitachi Naka Works. In the electron impact mass spectra (EI-MS) measurements, the ionizing voltages (V_e) were altered from 80 V to 10 V in several steps, the repeller voltage (V_r) was fixed at 0V, and the ion source temperature was kept at 100 to 150°C. In the chemical ionization mass spectra (CI-MS) measurements, methane was used as a reactant gas, the ionizing voltage was 100 V, and the ion source temperature was kept at 80 to 150°C.

RESULTS AND DISCUSSION

Mass Spectra of the Dimer

The EI-MS and CI-MS of the "dimer" obtained from polymer II-A are shown in Figure 1. Though many fragment ion peaks were found in the low-mass-number region (below m/e 100) in EI-MS ($V_e=80$ V), they were omitted from this figure because there was no necessity to use them for the structural analysis in this case. As a rule aromatic hydrocarbons give some

molecular ion peaks in their mass spectra: that is, molecular ion peaks are observed in α -methylstyrene monomer and in several compounds similar to this dimer. Further, the measurement of mass spectra at lower V_e is one useful method for finding a molecular ion peak. The results obtained from the V_e -variation experiments will be mentioned later. Consequently, the peak of m/e 236 was determined to be the molecular ion peak, and the peaks of m/e 237 and m/e 238 to be the corresponding isotope ion peaks containing natural ^{13}C . This finding suggests that this "dimer" contained one double bond in its chain, because the molecular ion would have to possess the mass number of 238 if it were saturated (the molecular weight of α -methylstyrene is 118). Moreover, the ion of m/e 235 found in CI-MS corresponded to $(M-1)^+$ ion, so that the molecular weight of this dimer was confirmed to be 236 (M^+ denotes the molecular ion).

The fragment ions derived from multi-scission of bonds can be diminished by lowering the ionizing voltages in EI-MS; then, the relative amount of the molecular ion is somewhat increased in most cases. At the same time the scission of the double bond is diminished markedly. Consequently, the structural analysis can be carried out more easily by combining the mass spectra obtained from such operations with the ordinary one ($V_e=80$ V), in many cases.

Since the "dimer" had one double bond, the five possible structures shown in Figure 2 had to be considered. As V_e was lowered, the molecular ion peak (m/e 236) became the largest peak, while both m/e 118 and m/e 119 remained as large as they were. First of all, the type-B structure could be omitted because of the impossibility of forming both m/e 118 and m/e 119 peaks. Secondly, the type-D structure might also be omitted, because the possibility of forming m/e 131 and m/e 133 was extremely small. Thirdly, the type-C structure can be omitted by comparing m/e 103 with m/e 105 and m/e 133 with m/e 131, because m/e 103 and m/e 133 found in the ordinary mass spectra were smaller than m/e 105 and m/e 131, respectively, especially at lower V_e , and this finding cannot be understood using the structure of C. Finally, on the other hand, if the possible structure were type E, m/e

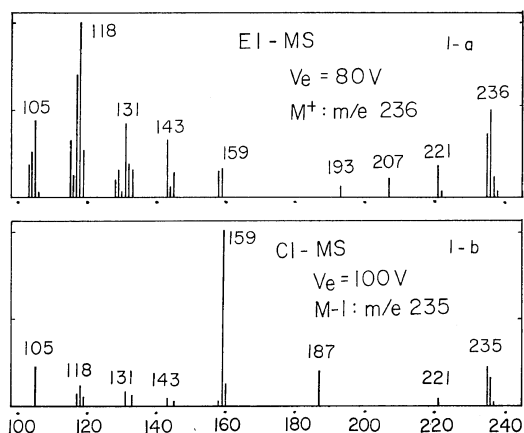


Figure 1. Mass spectra of the dimer obtained from polymer II-A.

Mass Spectra of α -Methylstyrene Polymers

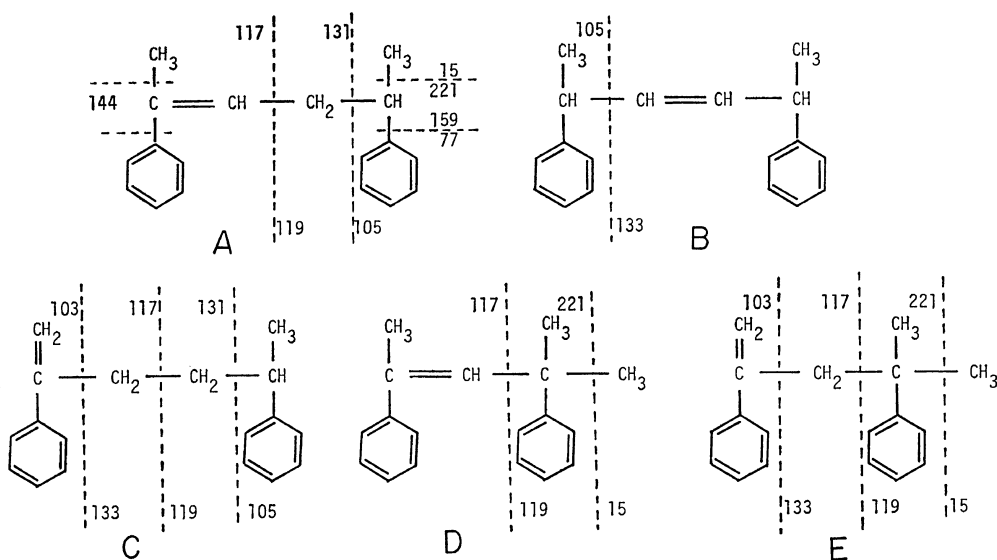


Figure 2. The structures of the dimers containing one double bond.

103 and m/e 133 peaks should become larger than m/e 105 and m/e 131 peaks, respectively. Thus, the four structures other than type A are inadequate, judging from the mass spectra: *i.e.*, this dimer might be deduced to have the type-A structure. This structure is not exactly the same as the dianion structure proposed by Szwarc,² because according to the mechanisms mentioned up to now, the dimer should be obtained for the saturated chain, namely the one having a molecular weight of 238.

The molecular weight of the dimer obtained using CD_3OD as a killing agent was also 236. This finding might suggest that the hydrogen used for the termination of the living polymer was not the hydrogen from methyl alcohol and that its hydrogen came through a quite different path.

The results from polymer II-B were the same as those given above.

Mass Spectra of the Trimer

The EI-MS ($V_e=15$ V) of the "trimer" obtained from polymer II-A is shown in Figure 3. In ordinary EI-MS ($V_e=80$ V) the main peak was m/e 105 and the molecular ion peak (m/e 354) was only 27% of the main peak, but at $V_e=15$ V the molecular ion peak became the main peak. From this spectrum the structure of the "trimer" was deduced in the same manner as for the "dimer" mentioned above. Since the structure of the "dimer" is type A, the structural type of the trimer might be pictured through adding a monomer unit to the type-A structure. A reasonable structure of the trimer is shown in Figure 4. The existence of relatively large peaks of m/e 131 and m/e 223 may support

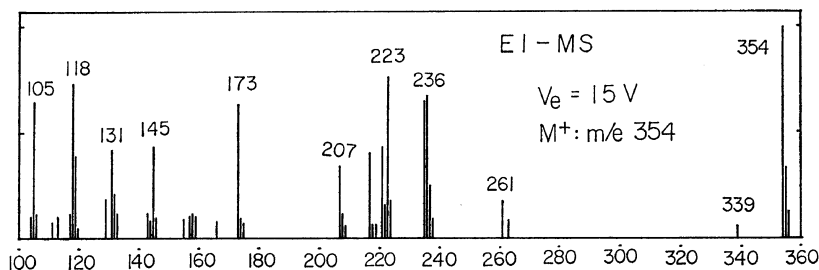


Figure 3. Mass spectrum of the trimer obtained from polymer II-A.

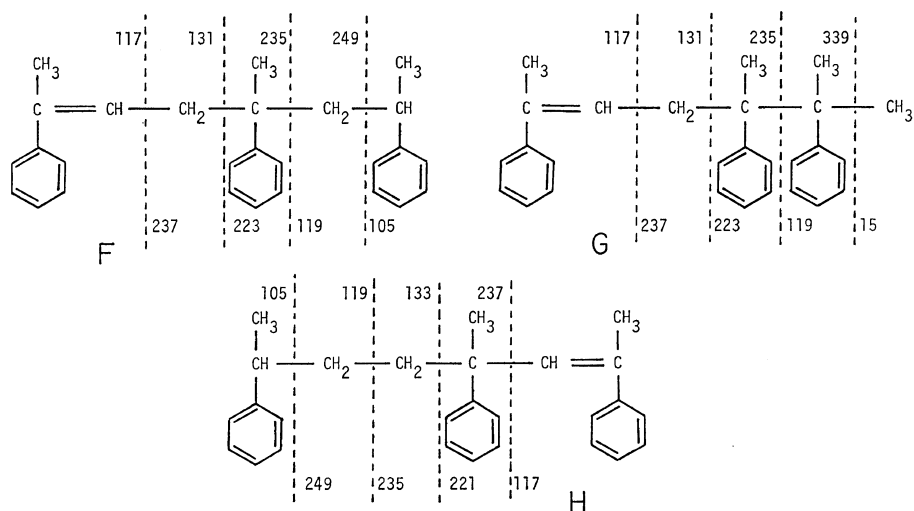


Figure 4. The structures of the trimers containing one double bond.

this structure.

Mass Spectra of the Polymer Mixtures

Since higher polymers than the tetramer could not be separated by gas chromatography, the mass spectra of the raw polymer mixtures were measured. The peaks m/e 472 and m/e 474 corresponding to tetramers and the peaks of m/e 590 and m/e 592 corresponding to pentamers could be found in every case. We have no direct evidence of a correspondence to each molecular ion of the tetramers and pentamers, respectively, if the fragmentation of higher polymers is taken into consideration. However, it may be reasonable to consider that these ions correspond to four molecular ions from the interpretations of the mass spectra of the "dimer" and "trimer" obtained by lowering V_e . The peaks of m/e 472 (118×4) and m/e 590 (118×5) correspond to a tetramer and pentamer containing one double bond in the polymer chain, and the peaks of m/e 474 ($118 \times 4 + 2$) and m/e 592 ($118 \times 5 + 2$) to a saturated tetramer and pentamer. In the case of CD_3OD killing, both m/e 472 and m/e 590 peaks also appeared, as in the case of CH_3OH killing. At that time m/e 475 appeared larger than m/e 474, while m/e 476 was about the same as m/e 474. If two deuterium atoms would be consumed at the termination, the mass shift from m/e 474 to m/e 476 by deuterium labelling should be accomplished

completely. In the m/e 475 ion peak, two ions might be contained: one is the molecular ion containing one deuterium atom and the other is the ion formed by losing one hydrogen atom from the molecular ion containing two deuterium atoms. It is difficult to show their abundance ratio. However, comparing these spectra with the spectra in CH_3OH killing, the result which includes the molecular ion containing one deuterium atom in the m/e 475 ion peak may be deduced.

The Mechanism of Polymerization

It is difficult to discuss the mechanism of the formation of a double bond and the termination of a living polymer from the results of mass spectra alone. And the fact that the polymer has one double bond in its chain may need an alternative mechanism for its explanation. Therefore, it might be considered that the formation of the double bond would be realized by the hydride ion transfer. If the double bond would be formed by a hydride ion transfer, the formation of two double bonds should be expected on the termination. Some other termination mechanism would have to be considered rather than the hydride ion transfer in order to explain the existence of only one double bond in the polymers. The polymers having one double bond did not show a shift by deuterium labelling in their mass spectra

Mass Spectra of α -Methylstyrene Polymers

from the consideration of the results of CD₃OD killing. This finding suggests that the hydrogen from the solvent might be related with the termination.

CONCLUSION

As mentioned already, it is useful to apply the mass spectrometry technique directly for studying the polymerization reactions without the degradation of polymers. However, the aid of mass spectra alone is insufficient to propose a new mechanism; but we are able to say that this new technique is useful to discuss the mechanism.

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