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PYROLYSIS-FLUORESCENCE SPECTROSCOPY, PYROLYSIS-MASS SPECTROMETRY AND PYROLYSIS-LIQUID CHROMATOGRAPHY OF LINEAR AND CROSS-LINKED POLYSTYRENES

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SUMMARY

The pyrolysis of linear and cross-linked polystyrenes is studied using molecular fluorescence spectroscopy, high-performance liquid chromatography (HPLC) with UV absorption and fluorescence emission detectors, and mass spectrometry. In common with many aromatic systems, polystyrene pyrolysis products show molecular fluorescence and also excimer emission. Styrene oligomers up to the dodecamer can be separated isocratically with isooctane eluent on a 10- μ m alumina column. Pyrolysis of linear polystyrene in an enclosed system is shown by HPLC to yield primarily monomers; pyrolysis in a continuous-flow system produces monomers but in addition oligomers up to at least the heptamer. Stepwise pyrolysis-mass spectrometry substantiates the HPLC results in more detail, and also provides an indication of head-to-head microstructure in the predominantly head-to-tail polystyrene.

INTRODUCTION

Analytical pyrolysis (Py) methods have been used successfully in characterizing diverse types of samples, including isomeric organic compounds¹, high-molecular-weight synthetic polymers^{2,3}, bacteria⁴, and the insoluble carbonaceous matter, kerogen, in sedimentary rocks⁵. Pyrolysis products are usually studied with gas chromatography (Py-GC)⁶, mass spectrometry (Py-MS)⁷, or GC-MS (Py-GC-MS)³. These methods are useful in fingerprint-type identification^{8,9}, characterization of polymer microstructure³, compositional analysis of copolymers^{10,11}, and mechanistic and kinetic studies of thermal stability^{12,13}. With GC analysis, however, only a fraction of the pyrolysis products is sufficiently volatile to elute; the balance could be viewed as lost information². Py-GC-MS has the same limitation. Direct Py-MS does allow one to obtain information about higher-molecular-weight fractions of the pyrolyzates¹⁴, but not every laboratory can afford to dedicate a mass spectrometer to pyrolysis studies.

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Recently we described^{2,15} the use of high-performance liquid chromatography (HPLC) for analysis of pyrolysis products (Py-LC). This is designed to overcome the limitations of Py-GC, *i.e.* with Py-LC one is able to detect thermally unstable pyrolysis products and low volatility pyrolyzates strongly retained on the GC column. We report here the first application of pyrolysis-fluorescence spectroscopy (Py-FS) to detect the formation of fluorescent pyrolysis products of polystyrenes; the use of stepwise Py-MS for monitoring the pyrolysis process; the finding of a mass spectral fragment of molecular weight 180 corresponding to 1,2-diphenylethylene, as evidence for the existence of head-to-head microstructure in primarily head-to-tail polystyrene; and a comparison of enclosed and continuous-flow pyrolysis systems using Py-LC.

Fluorescence is more selective than UV absorption because only a relatively small number of the compounds that absorb UV also fluoresce. Pyrolysis followed by fluorescence spectroscopy of the products could be used to study fluorescing polymers such as polystyrene and also non-fluorescing polymers that produce fluorescent pyrolyzates. For example, pyrolysis of non-fluorescent poly(vinyl chloride) produces primarily HCl and benzene, and also trace amounts of fluorescent polycyclic aromatic hydrocarbons (PAHs)^{16,17}. Py-FS might also be useful in environmental pollution studies, *e.g.* to study the formation of PAHs in laboratory models of incineration processes.

Direct interfacing of a pyrolyzer to a mass spectrometer allows one to look at higher-molecular-weight fractions of pyrolyzates, as does HPLC. For example, Udseth and Friedman¹⁸ used both electron impact (EI) and chemical ionization (CI) MS to detect polystyrene pyrolyzed on a probe filament heated at a rate of 100°C/sec. They found extensive fragmentation under EI conditions; styrene oligomers up to n (the degree of polymerization) = 11 were detected; under CI conditions using argon as the reagent gas, oligomers up to $n = 27$ were detected. Lower-molecular-weight styrene oligomers have also been studied directly¹⁹ using a heated direct insertion MS probe. Coloff and Vanderborgh²⁰ used laser pyrolysis and time-of-flight MS for rapid analysis of degradation products. Lattimer *et al.*²¹ identified styrene oligomers separated by LC with field desorption (FD) ionization to identify styrene oligomers separated by size-exclusion chromatography. Matsuo *et al.*²² reported FD-MS of polystyrene with peaks at 600, 2200, 4000, and 8000 a.m.u., and proposed the use of polystyrene as a mass calibration reference for masses up to 10,000 a.m.u.

EXPERIMENTAL

Pyrolysis

Pyrolysis was carried out both in an enclosed system and in a continuous-flow system². With the enclosed system, about 2 mg of sample was sealed inside a 15 mm × 2.0 mm O.D. glass tube, and pyrolyzed 4 min at 400°C, using a CDS Pyroprobe 100 pyrolyzer (Chemical Data Systems, Oxford, PA, U.S.A.) with a Pt coil 15 mm × 3.0 mm O.D. × 2.0 mm I.D. After pyrolysis, the glass tube was broken in a small beaker containing 5 ml of isooctane, and the solution analyzed as described below. With the continuous-flow system, the same amount of sample was loaded into an open-ended quartz sample tube, 15 mm × 2.0 mm O.D., and pyrolyzed for 4 min at 400°C in the Pyroprobe 100. The pyrolysis products were swept continuously out of the pyrolyzer with helium at 30 ml/min through a heated 1/16-in. O.D. stainless-

steel capillary tube into a solvent trap containing 5 ml of isooctane. Following the pyrolysis, the pyrolyzer was cooled to ambient temperature and another 5 ml of isooctane used to rinse the condensates from the walls of the quartz tube and the apparatus. These isooctane solutions were analyzed separately. In both systems, considerable amounts of insoluble, charred polymeric residue remained.

Fluorescence

A Perkin-Elmer 650-10S fluorescence spectrophotometer was used with a Perkin-Elmer Hitachi 057 *x-y* recorder. The 10- μ l fluorescence flow cell also served as a stopped-flow cell, so that excitation and emission spectra of eluting peaks could be obtained. For continuous LC monitoring, the excitation wavelength was 270 nm and fluorescence was read at 320 nm.

High-performance liquid chromatography

A Varian 8500 LC pump was used with a 25 cm \times 2 mm I.D. Varian 10- μ m Al-10-MicroPak alumina column at ambient temperature with 20 ml/h of isooctane eluent. The Varian UV detector was set at 254 nm. Aliquots of 1 μ l of sample solution were injected.

Mass spectrometry

A Varian MAT CH7 mass spectrometer was used to study step-wise Py-MS. The mass spectrometer has a 70-eV EI ionization source and is equipped with an electrically heated sample insertion probe and a 5 mm \times 2 mm I.D. gold sample tube. The sample, weighing about 0.1 mg, was placed in the sample tube and inserted into the mass spectrometer. The temperature of the sample probe was quickly raised to a preselected temperature, and the mass spectral scan started. The probe temperature was constant to within 5–10°C during the whole mass scanning process (about 1.5 min). Upon completion of the mass scan, the sample probe was again quickly heated to a higher temperature, and a second mass spectrum recorded. This procedure was repeated until a total of five mass spectra were obtained for polystyrene (at probe temperatures of 65, 110, 150, 210 and 280°C), and four mass spectra for Porapak Q (145, 220, 290 and 350°C).

Samples

Polystyrene standards of nominal molecular weights 800 and $1.8 \cdot 10^6$ (referred to below as PS800 and PS $1.8 \cdot 10^6$, respectively) were obtained from the Alfa Chemical Company polystyrene standard kit. Porapak Q (Waters Assoc.) is a cross-linked copolymer of divinylbenzene and ethylvinylbenzene.

RESULTS AND DISCUSSION

Py-FS

Figs. 1 and 2 show the fluorescence emission spectra of the 400°C pyrolysis products of Porapak Q and PS $1.8 \cdot 10^6$, respectively, obtained using the continuous-flow system. It is interesting to observe that there are two emission bands in each spectrum. The band at 290 nm corresponds to the molecular fluorescence band of the major pyrolysis products. The band at 320 nm corresponds to excimer emission

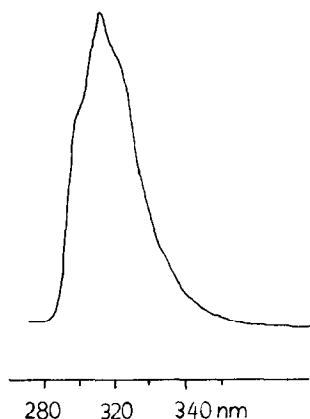


Fig. 1. Fluorescence spectrum of continuous-flow pyrolysis products of Porapak Q. Excitation wavelength 254 nm.

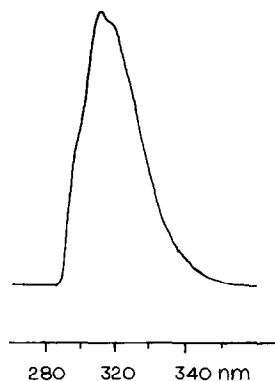


Fig. 2. Fluorescence spectrum of continuous-flow pyrolysis products of PS1.8 · 10⁶. Excitation wavelength 254 nm.

from these compounds. Excimer formation in high-molecular-weight polystyrene was first noted by Yanari and Bovey²³; excimer emission from small aromatic molecules has been discussed by Birks²⁴. We recently described excimer emission for each individual styrene oligomer in PS800 (monomer to dodecamer)²⁵. This is the first report of excimer formation in pyrolysis products of linear and cross-linked polystyrenes.

In general, excimer emission intensity is greater for isotactic than for atactic polymers²⁶⁻²⁸, and increases in the sequence atactic < atactic oriented < isotactic amorphous < isotactic crystalline, for polystyrene at 77°K (ref. 29); increases with polymer concentration in solution³⁰ and polymer molecular weight³¹; decreases with increasing temperature and solution intrinsic viscosity³¹; and increases on addition of poorer solvents, *e.g.* for poly(1-naphthylmethacrylate) in chloroform, both polar (methanol) and non-polar (cyclohexane) solvents increase excimer emission³¹. The effect of polystyrene tacticity on excimer formation has been attributed³⁰ to the formation of more stable configurations about the carbon skeleton in the isotactic form; in crystalline polymers, intra-chain regularity is the determining factor in enhancing excimer emission. That excimer formation also depends on both intrinsic viscosity and solvent composition indicates that chain contraction promotes excimer formation. The increase in excimer emission intensity in poorer solvents is related to the coiling and contraction of the polymer chain, which brings the aromatic groups into closer proximity. As molecular weight increases, a greater degree of intra-molecular interaction is possible, again contributing to excimer formation. The decrease in excimer intensity at higher temperatures is probably caused by increased internal conversion.

Py-LC

Figs. 3 and 4 show chromatograms of PS800 using alumina as the stationary phase, with UV detection and fluorescence detection, respectively. Although oligomer separations on alumina have not been reported previously, it is hardly surprising in

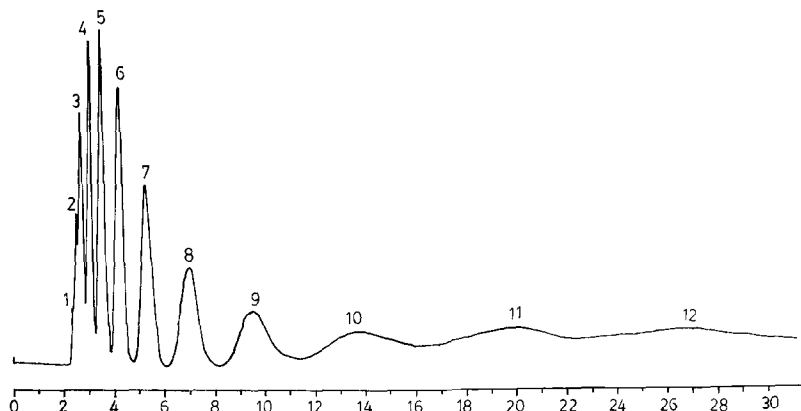


Fig. 3. Normal-phase liquid chromatogram of PS800 on 10- μ m alumina with UV-absorption detector (254 nm). Peak numbers correspond to degree of polymerization.

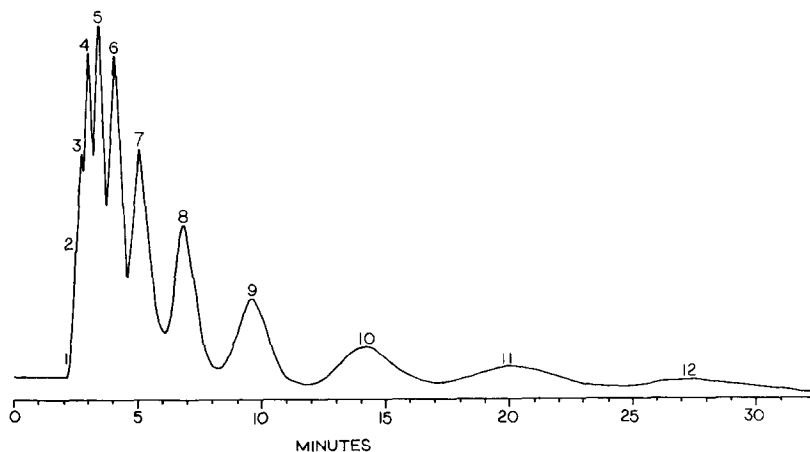


Fig. 4. Normal-phase liquid chromatogram of PS800 on 10- μ m alumina with fluorescence detector. Excitation at 270 nm, emission read at 320 nm. Peak numbers correspond to degree of polymerization.

view of the fact that polystyrene oligomers have been separated on a variety of reversed- and normal-phase HPLC stationary phases^{25,32-35}.

HPLC separations of the $PS1.8 \cdot 10^6$ pyrolyzates using continuous flow and enclosed pyrolysis at 400°C are shown in Fig. 5. Different pyrolysis product distributions were obtained for the two pyrolysis systems. Comparing the chromatogram of PS800 (Fig. 3) with Fig. 5, the enclosed pyrolysis system evidently yields primarily monomers (*i.e.* one-ring compounds including styrene, toluene, ethylbenzene, etc.), which are also found in the solvent trap of the continuous-flow system. The condensates rinsed out of the pyrolyzer correspond mainly to the dimer and trimer, with pentamer and heptamer peaks also in evidence (again, the exact identity cannot be deduced from the chromatogram, which provides only an indication of the relative molecular weight). The difference between the product distributions in the two pyrolysis systems is presumably caused by the localization of primary pyrolysis products

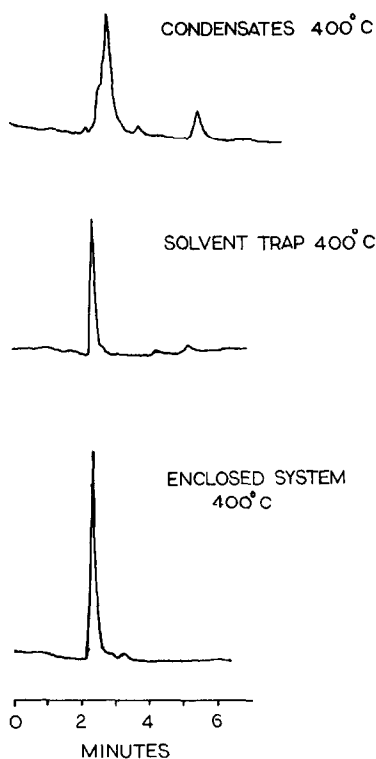


Fig. 5. Liquid chromatograms of 400°C pyrolyzates of polystyrene $PS1.8 \cdot 10^6$ on 10- μ m alumina with UV-absorption detector (254 nm). The upper chromatograms correspond to the condensates rinsed out of the pyrolyzer and tubing, and the lower chromatogram to the contents of the iso-octane solvent trap.

in the enclosed system, followed by the breakdown of the pyrolytic fragments into smaller compounds via secondary reactions. In the continuous-flow system, larger insoluble pyrolytic fragments either condense on the cool walls of the pyrolyzer or the tubing, or remain on the walls of the quartz tube.

Stopped-flow fluorescence spectra were obtained for each LC peak. All show fluorescence spectra similar to those in Fig. 2, differing only in emission intensity because of different concentrations.

Py-MS

Figs. 6-8 are plots of mass fragments of $PS1.8 \cdot 10^6$ as a function of pyrolysis temperature. The effective pyrolysis temperature, that of the mass spectrometer sample probe, is not readily comparable to the temperature of the Pyroprobe pyrolyzer coil, in view of the fact that the mass spectrometer inlet is operated at about 10^{-5} Torr. Because this alters product boiling points, products are more readily removed from the heated zone and can not undergo secondary reactions to the same extent. In any case, Figs. 6-8 indicate that the relative abundance of different pyrolytic fragments change with temperature, as did the stepwise Py-GC and stepwise Py-LC reported earlier². As might be expected, the abundance of fragments increases with temperature, reaches a maximum, and then declines. This is characteristic of stepwise

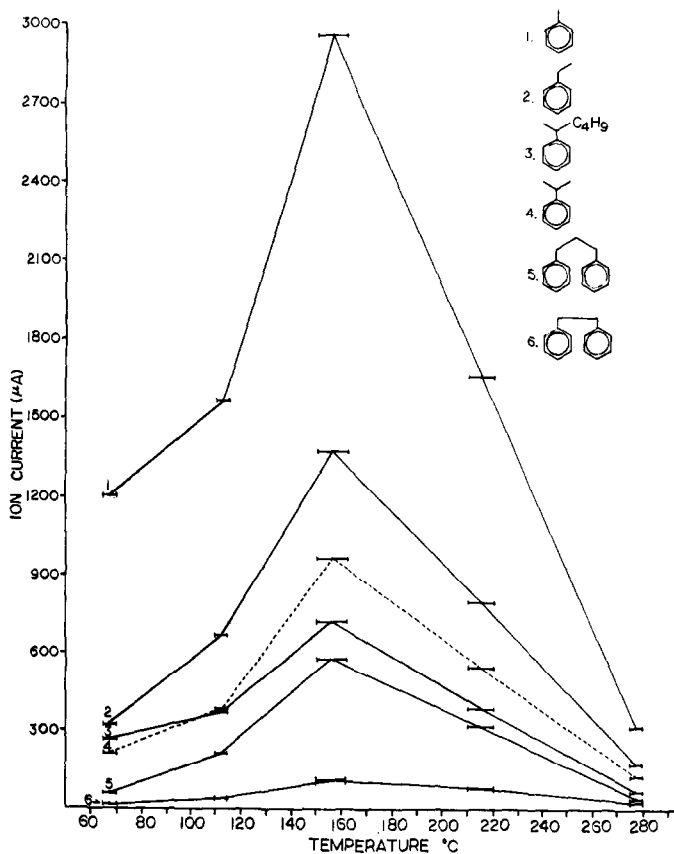


Fig. 6. Stepwise pyrolysis-mass spectrometry of $PS1.8 \cdot 10^6$. Distribution of some monomer and dimer ion peaks as a function of stepwise pyrolysis temperature change.

pyrolysis; the same sample is pyrolyzed at sequentially higher temperatures, so the amount of sample diminishes at each stage. The mass spectra at the lower pyrolysis temperatures show a substantial abundance of lower-molecular-weight compounds, which might indicate that at lower temperatures, the distillation of residual trapped monomers in the polymers as well as pyrolysis, is occurring. This also is consonant with our previous Py-GC results². Note the difference in ion current scales between Fig. 6 and Figs. 7 and 8. The distribution of monomers, dimers, etc. from the Py-LC results are consistent with the product distributions determined mass spectrometrically, although the former provides little detailed information.

The styrene oligomer fragments observed in these mass spectra presumably arise from random scission along the carbon chain of polystyrene. An interesting fragment (m/z 180) corresponding to 1,2-diphenylethylene, is observed. The appearance of this compound is evidence of some head-to-head microstructure, in agreement with previous work^{36,37}. The fragment at m/z 208 (2,3-diphenyl-1-butene or 1,4-diphenyl-1-butene) cannot, however, be used as evidence for a head-to-head styrene dimer, because the head-to-tail dimer (2,4-diphenyl-1-butene) has the same molecular

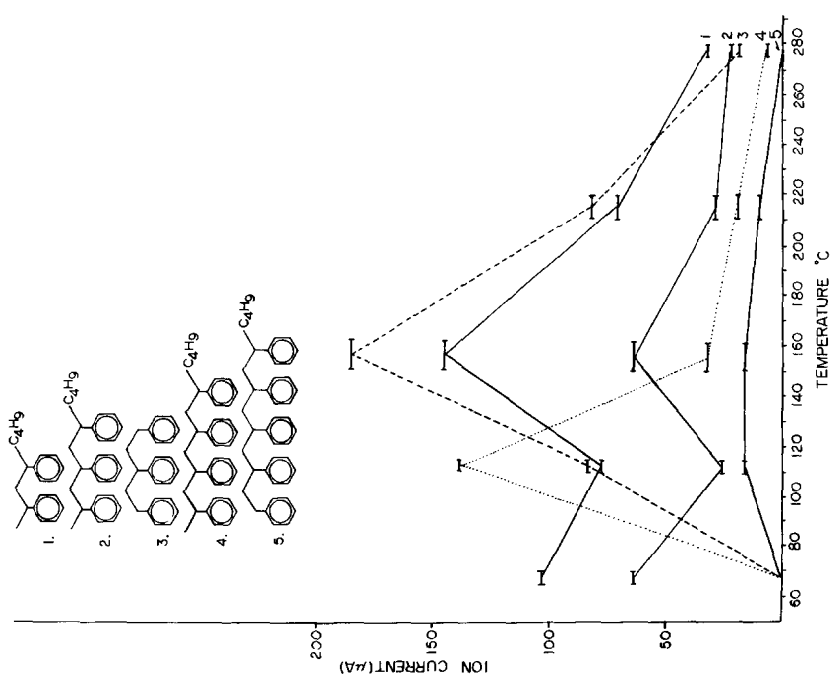


Fig. 7. Stepwise pyrolysis-mass spectrometry of $\text{PSI}.8 \cdot 10^{-6}$. Distribution of monomer, dimer, and trimer ion peaks as a function of stepwise pyrolysis temperature change.

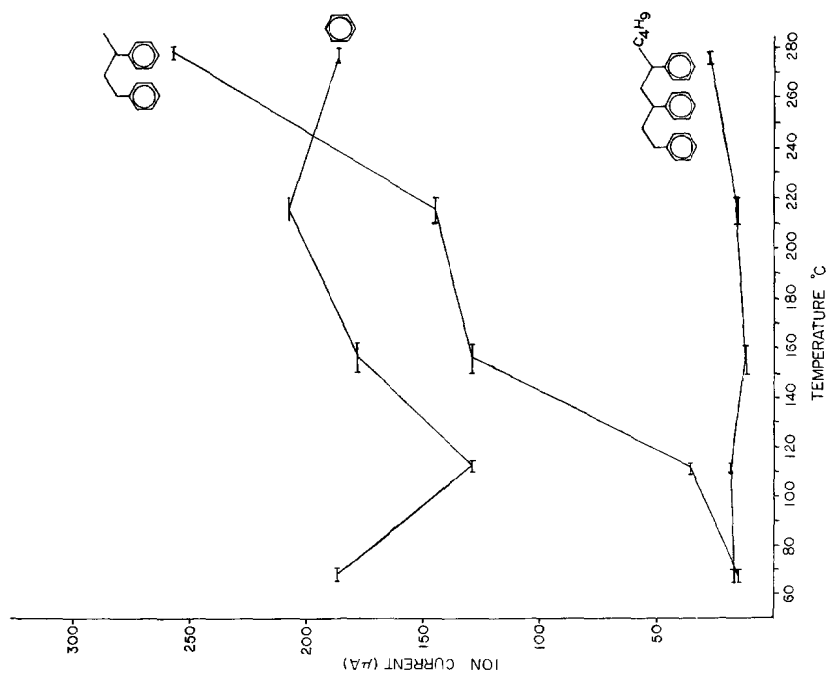
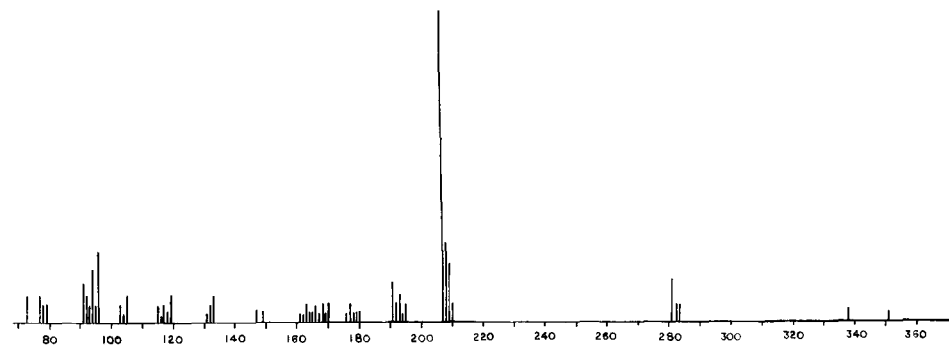


Fig. 8. Stepwise pyrolysis-mass spectrometry of $\text{PSI}.8 \cdot 10^{-6}$. Distribution of dimer, trimer, tetramer, and pentamer ion peaks as a function of stepwise pyrolysis temperature change.



220°C

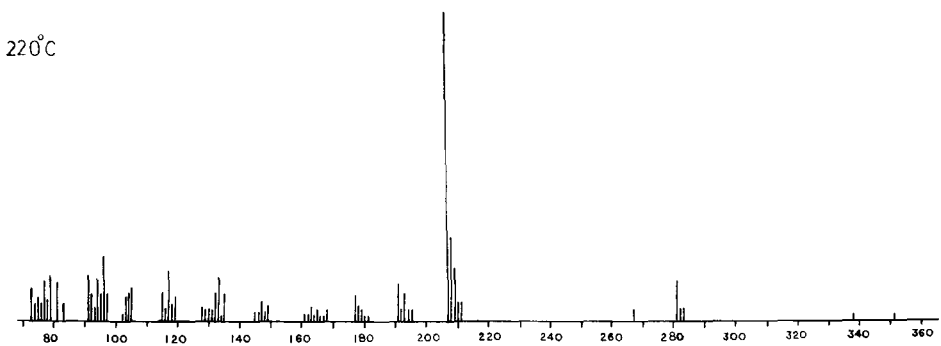
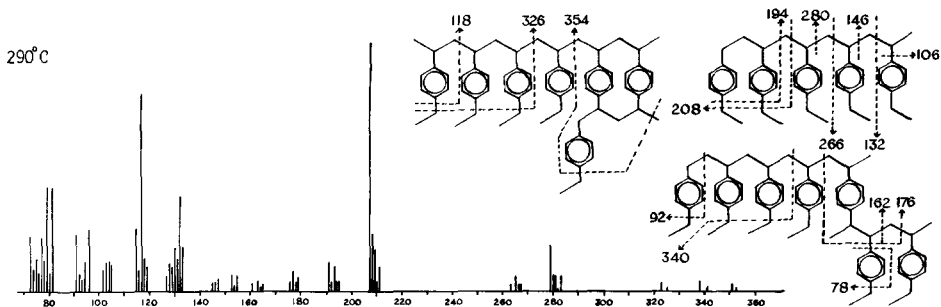


Fig. 9. Mass spectra of stepwise heated probe pyrolysis products of Porapak Q. Upper spectrum: pyrolysis temperature 145°C; Lower spectrum: pyrolysis temperature 220°C.

290°C



350°C

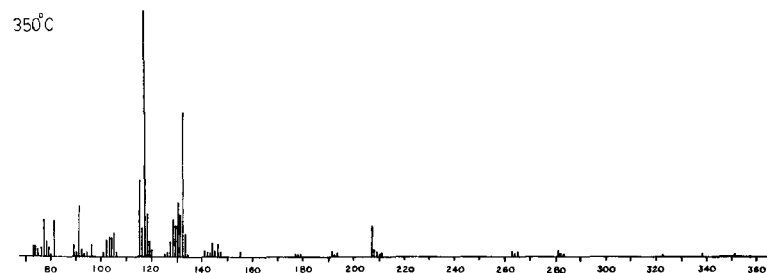


Fig. 10. Mass spectra of pyrolysis products of Porapak Q. Upper spectrum: pyrolysis temperature 290°C, with indication of possible chain scissions leading to prominent ions. Lower spectrum: pyrolysis temperature 350°C.

weight. The GC retention times of these isomers are different, however, which has been used both in Py-GC and Py-GC-MS to distinguish head-to-head from head-to-tail microstructure of polystyrene^{36,37}.

Figs. 9 and 10 show the mass spectra of Porapak Q, a cross-linked polystyrene. Pyrolysis products corresponding to random scission are observed in these spectra, as indicated on Fig. 10. These spectra indicate that pyrolysis temperature control in Py-MS is an important factor in obtaining reproducible results; samples should also be subject to controlled temperature rise rate, pyrolysis time, and mass spectral scan rate.

CONCLUSIONS

The straightforward combination of pyrolysis with fluorescence spectroscopy provides some qualitative insights, but does not offer much as a generally useful analytical technique. Chromatographic analysis of pyrolysis products produces fingerprint-type information, which can be useful if standards are available for calibration. As might be expected, the MS analysis of pyrolysis products gives the most detailed information, useful for polymer characterization. By themselves, however, mass spectra are not completely unambiguous, so that the combination of MS with high-resolution chromatographic techniques is still necessary for better understanding of polymer structure.

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