A New Curie-point Direct Injection Probe for Mass Spectrometry
2. Application to Synthetic Polymer Analysis

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A Curie-point direct injection probe to be coupled to a mass spectrometer was developed. Its flash heating, wide range temperatures (160 ~ l.040°C), reproducible temperature (± 1°C) and direct connection to the ion source of a mass spectrometer were effectively applied to the polymer analysis. Pyrolysis-mass spectrometry by use of this device enabled the discrimination between a copolymer and the corresponding blended polymer of {poly(styrene) and poly(fluorostyrene)}, because of the decreased secondary reactions among the pyrolyzates, when compared with pyrolysis gas chromatography (Py-GC). As compared with Py-GC, the new technique can elute larger pyrolyzates, only within a few minutes, which provide compositional and structural information of the polymer samples. The rapid analysis of an additive in a polymer is also reported in this paper.

1 Introduction

The concept of combining a pyrolysis inlet system with a mass spectrometer (MS) has been utilized to provide fingerprint analysis and to study thermal degradation of materials [1]. pyrolysis-MS (Py-MS) has found application in a wide range of analytical fields, including the study of synthetic polymers, biochemistry, geochemistry and environmental studies [2]. However, its development has been severely hindered by the lack of practical instrumentation, which has restricted the number of laboratories to access to this technique[3].

An ordinary furnace-pyrolysis probe is not suitable for some Py-MS analyses because of its low maximum temperature (about 300°C) and long temperature rise time (TRT). In addition, pyrolysis of thermally resistant polymers is very difficult in some instruments because of their low maximum temperature caused by an insulator between the heat source and the sample, or the remote sample cell location from the heat source. Curie-point pyrolysis provides a precise and reproducible method, with a maximum heating temperature of 1,040°C and a TRT of less than 0.2sec 4). Although Curie-point Py-MS systems have been described [3),5)], the detection limit of m/I values is quite low (200•`300) in those systems, which may be mainly caused by condensation of pyrolyzates on the surface between the sample cell and the ionization source of the MS, due to the long distance between them. A Curie-point direct injection probe (JDI-800) was developed in our laboratory for use with an MS6)·`8). At the top of this probe. a small silver tube which served as a thermal conductor and allows the sample cell to be closer to the entrance of the ion source was inserted. This prevented condensation of higher boiling point pyrolyzates, which enabled to analyze synthetic polymers. Some applications of the Py-MS system equipped with the JDI-800 to the analysis of synthetic polymers is described in this paper.

2. Experimental

2.1 Materials

A styrene-2-nuorostyrene copolymer [P(S-FS)] and poly(2-fluorostyrene) (PFS) were synthesized by radical polymerization in solution. The content of 2-flouro-styrene (FS) units in the polymer was 49.7%, as determined by elemental analysis. Polystyrene (PS) with Mn=l3,000 was a standard sample purchased from Pressure Chemical Co., USA.

A series of styrene-divinylbenzene-pyrenonyl propyonic isopropylether copolymers were polymerized in an aqueous suspension, and purified with water, glacial acetic acid, acetone and chloroform to remove the residual monomers. The pyrene contents in the copolymers were analyzed by fluorescence spectrometry using an internal standard.

A poly(phenylene sulfide) (PPS) used as the standard polymer was obtained from Polyscience, Inc., USA.

A commercial grained polypropylene (PP) containing trace amounts of an antioxidant, di-i-butyl-4-hydroxytoluene (BHT), and a polyphenylene oxide (PPO), were supplied by Mitsui Petrochemical Industries Ltd. and General Electric Co.. USA, respectively.

2.2 Curie-point direct injection probe

The Curie-point direct injection probe assembly JDI-800, was described in detail elsewhere 7).8). It consisted of an injection probe and a radio frequency power (RF) supply.

At the top of the probe, there is a small silver tube which serves as a thermal conductor and allows the sample to be closer to the entrance of the ion source. This prevents condensation of higher boiling point fractions, and hold the pyrofoil® tightly to ion source while the injection probe is inserted into the MS. A cross section of the silver tube is shown in the previous papers). A slit in the silver tube can effectively prevent the sample cell from breaking and releasing the tube.

The Curie-point heating area of the injection probe was made of ceramics and metals. Organic material was not used in order to prevent noise. By unscrewing the two screws at the terminals, the ceramic bobbin with the RF coil could be separated from the shaft, and contaminants could then be removed by washing it with an appropriate solvent or baking at 300°C.

A quartz sample cell (9 mmx2 mm i.d.) was held inside the RF induction coil by a ceramic bobbin. A small Viton® 0-ring seal (without grease) was placed far from the Curie-point heating area, at the bottom of the sample cell inside the probe, to maintain the cell's position.

The power supply delivered 48 W at 10 MHz, and pyrolysis time was controlled from 0.1 to 10sec. Twenty kinds of pyrofoils® with Curie points from 160°C to 1,040°C and temperature accuracy of

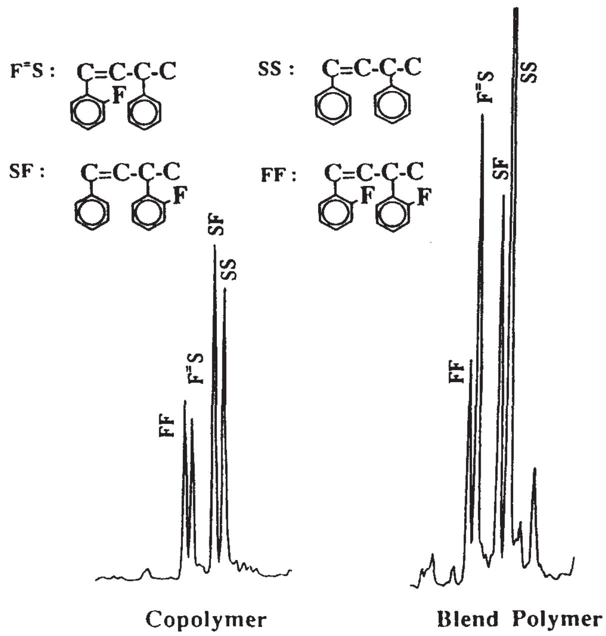

Fig. 1. Py-GC pyrograms of P(S-FS) and the related blend of polystyrene and poly(2-fluorostyrene), pyrolyzed at 500℃ for 8 sec.

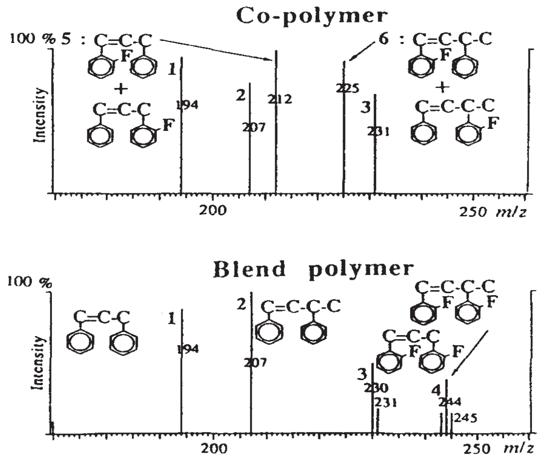

Fig. 2. Mass programs of P(S-FS) and the related blend of polystyrene and poly(2-fluorostyrene), pyrolyzed at 500℃ for 5 sec.

2.3 Mass spectrometry

The mass spectra were measured with a Shimadzu QP 2000A quadrupole MS which wasoperated with EI at 70 eV. The temperature of the ion source was 250°C and the scan rate was 0.5 see/scan.

2.4 Sample inlet

The amount of the sample injected was less than 2 ì g, to prevent contamination of the ion source. For soluble samples, I pl of sample solution (about 0.1 wt%) was placed on the center of a piece of pyrofoil® (1.8 X 8 mm, 50 ì m thick) with a micro-syringe, and was dried at 80°C in a vacuum oven. Then the sampled pyrofoil® was put into the standard cell.

For insoluble, or solid samples, the samples were wrapped in the Pyrofoil®. in tight contact with each other, and the pyrofoil® was then folded at the center and bent into "V" shape as described in elsewhere7). The sampled Pyrofoil® was set into the quartz sample cell with the silver tube, and then the ceu was inserted into the RF coil.

3. Results and Discussion

3.I Thermal degradation of styrene polymers

lt is well known that in the absence of oxygen, PS thermally degrades mainly to monomer, with some diners and trimers. The formation of the dimers and trimer has been said mostly to occur by intra-molecular transfers from the secondary macroradicals, followed by a-scission. On the contrary, Dean9) and Ohtani et al.10) recently suggested that the dimers and trimers may be formed to some extent by monomer recombination in the pyrolysis.

Figure 1 shows high resolution pyrolysis-gas chromatograms of P(S-FS) and mixture (1:1, in solution) of PS and PFS pyrolyzed at 500°C with a CDS 190 Pyroprobe coupled to an HP 5890 capillary gas chromatograph. The hybrid dimers (S-F and F-S) can still be seen on the pyrogram of the polymer mixture, which suggests

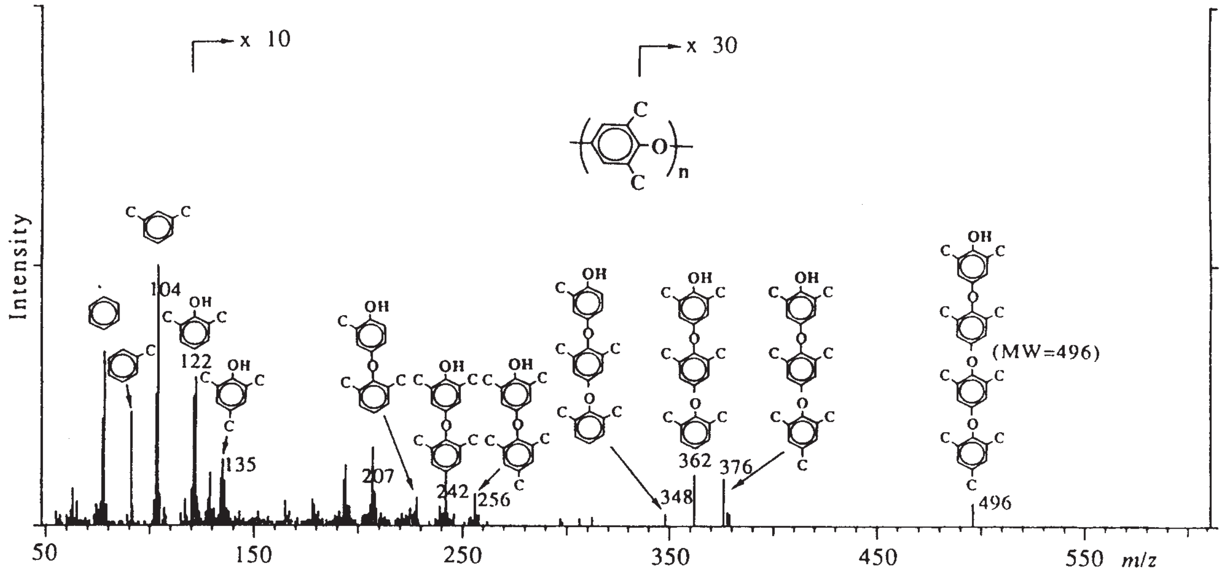

Fig. 3. Mass pyrogram of PPO, pyrolyzed at 590℃ for 5 sec.

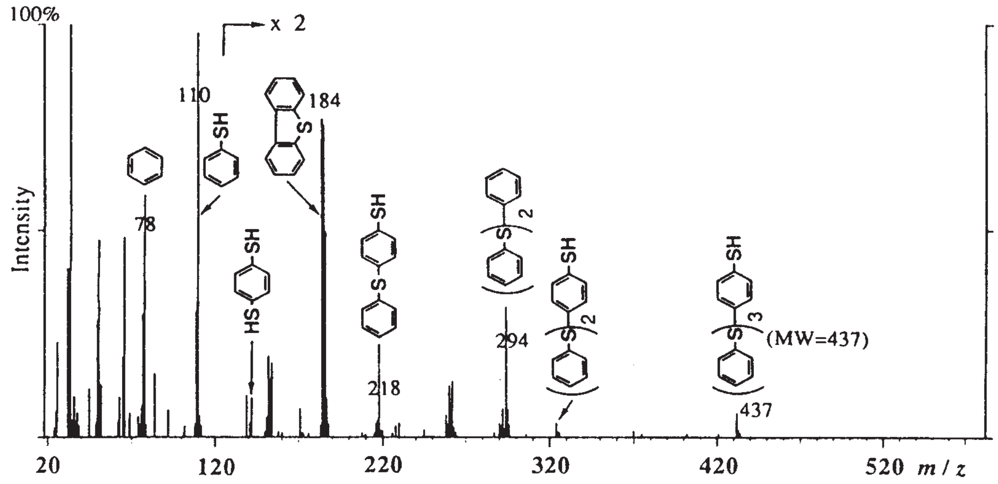

Fig. 4. Mass spectrum of PPS, pyrolyzed at 445℃ for 5 sec.

that the diner formation could have been caused by recombination in the pyrolyzer or in the transfer pipe, or both after degradation. Therefore, by this data it is impossible to distinguish the blend from the copolymer. Mass pyrograms of the same samples pyrolyzed at 500°C for 5 sec with a JDI-800 are shown in Fig. 2. In this case, no hybrid dimers were observed on the pyrogram of the PS-PFS blend. This indicates that the pyrolysis direct injection probe almost completely suppressed the secondary reaction. Thus. the copolymer can easily be distinguished from the polymer blend.

3.2 Polymer characterization

The larger fragments and oligomers in the pyrolysis products usually provide more detailed information regarding the microstructure (stereoregularity, conformation, sequence distribution. *etc.*). The pyrolyzates with higher molecular weight sometimes cannot be eluted by Py-GC because of condensation in the transfer pipe or the sparation column, or both$^{11)}$. However, by use of the pyrolysis direct injection probe inserted and connected

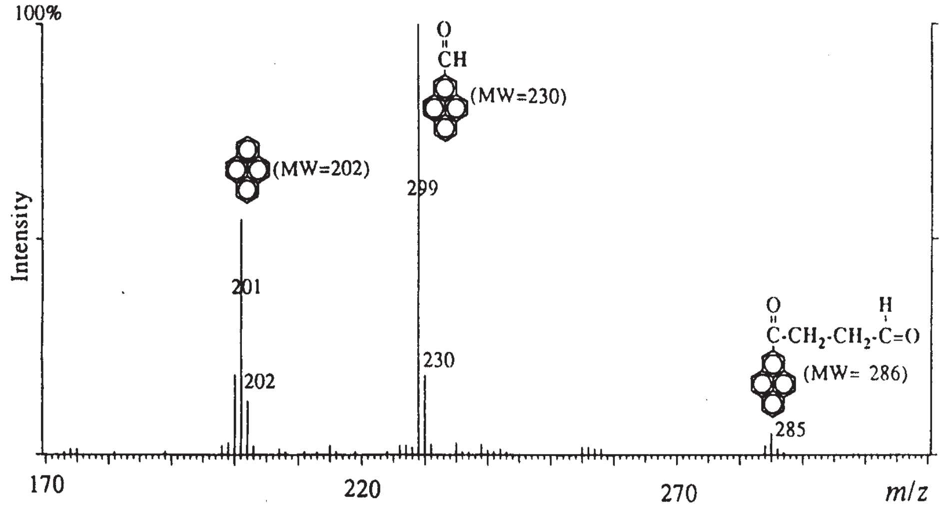

Fig. 5. Mass pyrogram of co(styrene-pyrenoyl propionic iso-propylether)polymer, containing 3% pyrene mol, pyrolyzed at 358℃ for 3 sec.

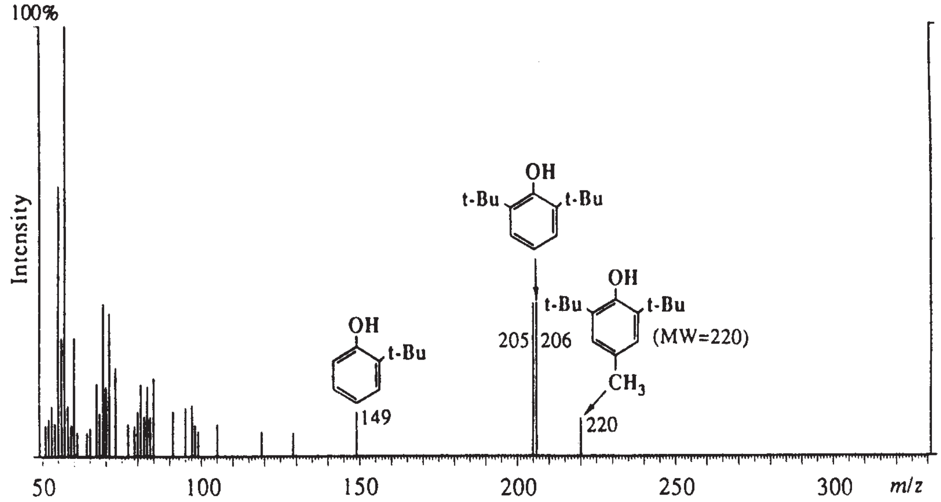

Fig. 6. Mass spectrum of volatile components from PP containing 0.5 mol% of BHT, heated at 220℃ for 3 sec.

directly to ion source of the MS, the condensation of the higher boiling point pyrolyzates is limited and they can be detected more easily than by Py-GC.

Figure 3 is a mass pyrogram of PPO. measured by the Py-MS system with the JDI-800, in which peaks up to tetramers are clearly observed. Therefore, this method gives more information for the microstructural analysis and for the investigation of thermal degradation of polymers.

Figure 4 is a mass spectrum of PPS, measured with the same system, in which up to the tetramer of phenylene sulfide is observed. When this analysis is done by Py-GC about 50 min is needed [12)] due to the column elution required to repeat the associated temperature programing for the column oven. With Py-MS, only three minutes elapsed from the time that the pps was put on the Pyrofoil® until the mass spectrum was recorded. The identified pyrolyzates were benzene, phenylmercaptan, 1.4-dimercaptobenzene, diphenylene sulfide, mercaptodiphenylthioether, trimer and tetramer.

Figure 5 shows the mass pyrogram of a

styrene-pyrene containing copolymer in which the pyrene content was 3% by mo1. The mass pyrogram of the copolymer, measured at 358°C had some characteristic peaks related to pyrene groups and the identification of trace comonomers in this copolymer was greatly simplified by this technique.

Figure 6 shows another application to the analysis of a polymer additive performed without any sample preseparation. PP was heated at 220°C for 3 sec, which was lower than the polymer pyrolysis temperature. On this mass spectrum, the molecular peak of the added antioxidant, BHT is clearly observed at m/z 220 in addition to its fragments at m/z 206, 205 and l49.

4. Conclusions

Curie-point Py-MS is a rapid and simple technique for the analysis of synthetic polymers. The data presented here indicate that this method can yield compositional and structural information. A copolymer is distinguished from the associated polymer blend by the Py-MS system which eliminates most of the secondary reactions.

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Keywords

Curie-point direct injection probe
Pyrolysis-mass spectrometry
Polystyrene
Polyphenylene oxide
Polyphenylene sulfide