CHROM. 21 002

Note

Modified column system for pyrolysis capillary gas chromatography

HUWEI LIU, RUONONG FU*, ZHENXI GUAN and LINXIANG TIAN
Department of Chemical Engineering, Beijing Institute of Technology, P.O. Box 327, Beijing (China)
(First received June 21st, 1988; revised manuscript received September 20th, 1988)

Pyrolysis–gas chromatography (PGC) is now universally accepted as a powerful method in organic and polymer analysis. In recent years, pyrolysis–capillary gas chromatography (PCGC), known as high-resolution PGC[1], has been used in a variety of applications[2,3] and was demonstrated to be more efficient than packed column PGC, and even IR and NMR spectroscopy in special cases. Nevertheless, when a pyrolyser is attached directly to a gas chromatograph, the vaporizer of the chromatograph forms a dead volume, which results in a loss of resolution. On the other hand, column contamination is a serious problem affecting the separating capacity in PCGC, because tarry components, which are produced to various extents by the pyrolysis of high polymers, and residues of the sample may enter the capillary column.

To overcome these problems, several modified interfaces and techniques have been studied[3–6]. Sugimura and Tsuge[4] used a glass tube with a splitter and precolumn, which protected the capillary column from contamination. However, the chromatographic vaporizer constituted a dead volume and, morever, an additional module was needed to control the precolumn temperature. In the pyrolysis system employed by Raynor *et al.*[5], the injection port, fitted with a precolumn glass frit insert, was still empty although it was loosely packed with silanized glass-wool to prevent non-volatile material from entering the capillary column. Whiton and Morgan[6] utilized a modified capillary inlet with small dead volume, but the column contamination was not eliminated and the vertical positioning of the probe precluded the use of a coil filament probe with a quartz sample tube. Another technique, reported by Liebman *et al.*[3], cannot be used with a glass capillary column, in addition to the column contamination problem.

In this work, a modified column system was designed and constructed for PCGC, involving a precolumn placed in the injection port of the gas chromatograph. The system was applied to different polymers.

EXPERIMENTAL

Materials

Polystyrene (PS), poly(vinyl chloride), (PVC), isotactic polypropylene (Iso-PP), poly(methyl methacrylate) (PMMA), methyl methacrylate–styrene copolymer (MS), acrylonitrile–styrene copolymer (AS), butadiene–styrene copolymer (BS), acrylo-

nitrile–butadiene–styrene terpolymer (ABS) and methyl methacrylate–butadiene–styrene terpolymer (MBS) were used in the PCGC experiments. A mixture of isomers of mononitrotoluene (MNT), dinitrotoluene (DNT) and trinitrotoluene (TNT) was separated in conventional capillary GC experiments. The mixture was dissolved in toluene.

Instruments

A 150 Pyroprobe solid pyrolyser (Chemical Data Systems) was used consisting of a heated interface, a platinum coil probe and an electronic control module. The interface was connected to the chromatographic injection port via a thin stainless-steel tube. One end of this tube pierced the silicone-rubber septum and the other end was attached to the interface outlet by a tightly fitting septum and a nut. Fig. 1 is a schematic diagram of the pyrolysis system. All polymer samples were pyrolysed at 750°C for 20 s with the heating rate "off" and the interface temperature set at 250°C.

A GC-5A gas chromatograph (Shimadzu) with a flame ionization detector was employed. The instrument was equipped with a modified column system as indicated in Fig. 1. Its injection port was fitted with a stainless-steel precolumn, which was packed with 8.3% OV-101 on Celite (60–80 mesh). The temperature of the precolumn was controlled by use of the original controller of the gas chromatograph. Separations were performed on a 50 m × 0.28 mm I.D. glass capillary column coated with OV-101 by the static method[7]. In order to compare PCGC with packed column PGC, a 3 m × 4 mm I.D. stainless-steel column packed with 8.3% OV-101 on Celite (60–80 mesh) was also used in polymer pyrolysis. Nitrogen was used as the carrier gas; the GC conditions are given in the figure captions.
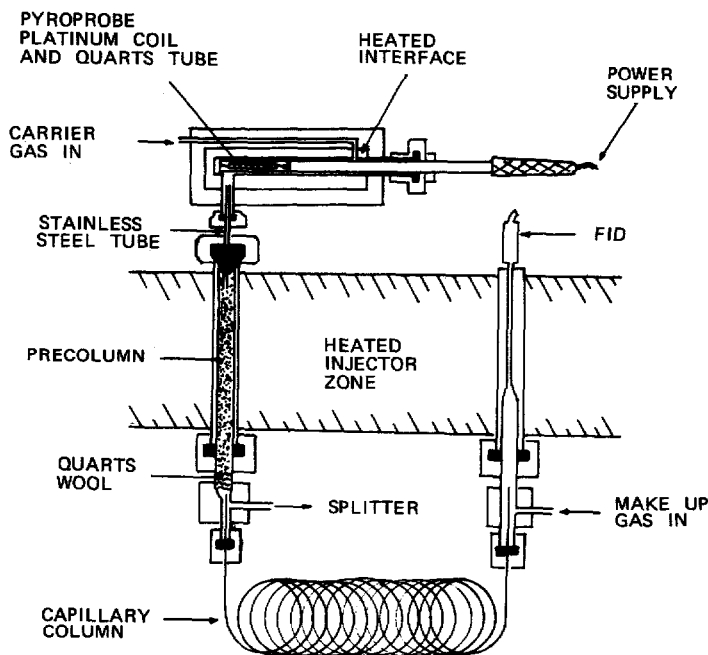

Fig. 1. Schematic diagram of the pyrolysis system.

When the precolumn was not packed and the pyrolyser was removed, the modified system was used for conventional capillary GC analysis, which was performed on a 16 m × 0.31 mm I.D. glass capillary column coated with cross-linked SE-54[8]. The experiments were performed under the following conditions: carrier gas, nitrogen at 25 ml/min; column temperature, programmed from 100°C (4 min) to 250°C at 4°C/min; splitting ratio, 40:1.

RESULTS AND DISCUSSION

Precolumn

It was reported[4] that a packed precolumn can prevent column contamination and improve the separation efficiency of the pyrolysis system. This was also demonstrated in these experiments. Some tarry substances were found in the precolumn after a period of operation and the separation efficiency of the system decreased. When the precolumn was repacked with fresh packing, the separation capacity increased again. If the precolumn temperature was properly set, the maximum molecular weight of pyrolysates eluted from the capillary column was controlled. The packing material should be renewed regularly, with the result that the precolumn can help to improve the separation power because the precolumn was packed with the same stationary phase as that in the glass capillary column.

Compared with the other techniques mentioned above, this modified system has additional advantages. First, it has a minimum dead volume because the precolumn is placed in the chromatographic vaporizer and it is commensurate with a short packed column. Second, it is simple and economic to construct because an additional module
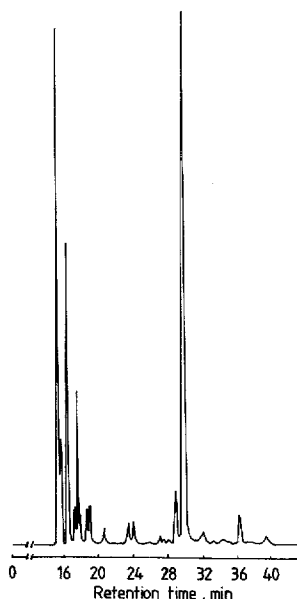

Fig. 2. Pyrogram of Iso-PP separated on a 50 m × 0.28 mm I.D. glass capillary column coated with OV-101. Experimental conditions: pyrolysis temperature, 750°C; pyrolysis interval, 20 s; heating rate, "off"; column temperature, 90°C; detection temperature, 250°C; carrier gas, nitrogen at 25 ml/min.
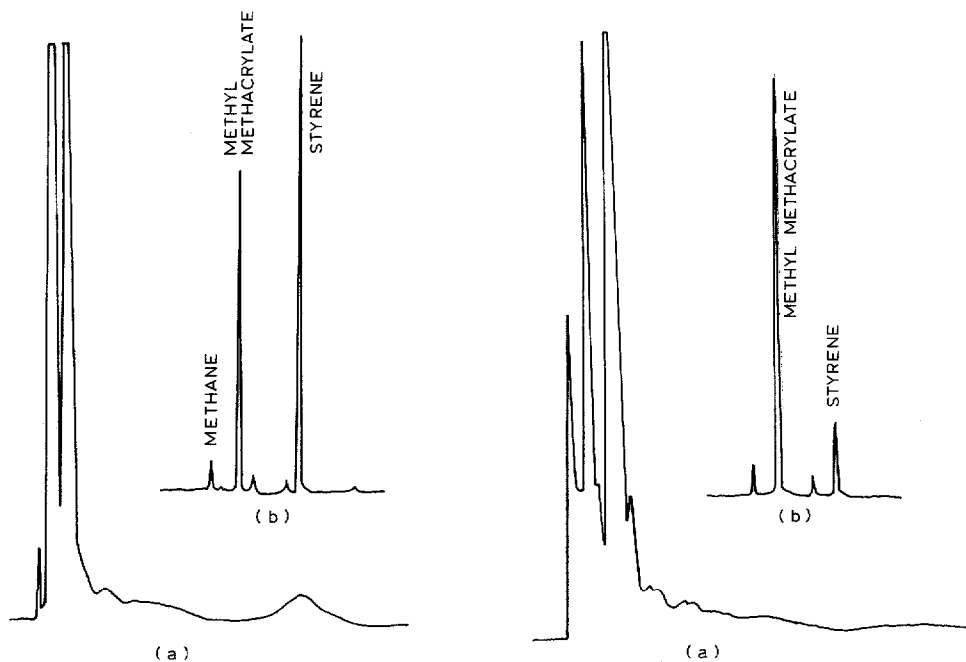
Fig. 3. Pyrograms of MS: separation on (a) the packed column and (b) the capillary column. Column temperature, 110°C; other conditions as in Fig. 2.

Fig. 4. Pyrograms of MBS: separation on a (a) the packed column and (b) the capillary column. Experimental conditions as in Fig. 3.

is not needed to control the precolumn temperature, this being controlled by the original controller of the injection port temperature. Finally, this system can also be used in ordinary capillary GC if the precolumn is not packed.

Separation capacity

The high efficiency of the PCGC system can be seen in Figs. 2–4, which show typical pyrograms of Iso-PP, MS and BMS, obtained under the conditions mentioned

TABLE I

REPRODUCIBILITY OF RETENTION TIMES OF PYROLYSATES OF MS

Experimental conditions as in Fig. 3; α = relative retention. The results were obtained by five repeated experiments.

Parameter	Methane		Methyl methacrylate		Styrene	
	t_R *(min)*	α	t_R *(min)*	α	t_R *(min)*	α
Mean retention	13.27	1.00	15.41	1.16	20.42	1.54
Standard deviation	0.0586	0.0000	0.0593	0.0045	0.0747	0.0084
Coefficient of variation (%)	0.4414	0.0000	0.3850	0.3855	0.3658	0.5413

TABLE II

QUANTITATIVE REPRODUCIBILITY OF PYROLYSIS OF PS

Experimental conditions as in Fig. 3; A = area percentage of chromatographic peak (normalization). The results were obtained by six repeated experiments.

Parameter	Toluene		Styrene		Methylstyrene	
	α	A (%)	α	A (%)	α	A (%)
Mean	0.82	1.7303	1.00	96.3060	1.24	0.8384
Standard deviation	0.0041	0.0567	0.0000	0.2695	0.0000	0.0573
Coefficient of variation (%)	0.5000	3.2769	0.0000	0.2798	0.0000	6.8380

above. It is obvious that the separation capacity of PCGC is much higher than that of packed column PGC at the same column temperature. These results show that the modified column system is applicable to the PCGC analysis of high polymers.

Reproducibility

The reproducibility of the modified system was measured. Table I shows the reproducibility of the retention times of the pyrolysates of MS. The standard deviation of relative retention is not greater than 1%. Table II illustrates the reproducibility of the quantitative analysis of PS.

From these results, it can be concluded that the quantitative reproducibility of the main pyrolysates can meet the needs of PCGC analysis. The yield of monomeric styrene was greater than 95%, and the coefficient of variation was very small although the standard deviation was slightly greater. Similar results were obtained for the other
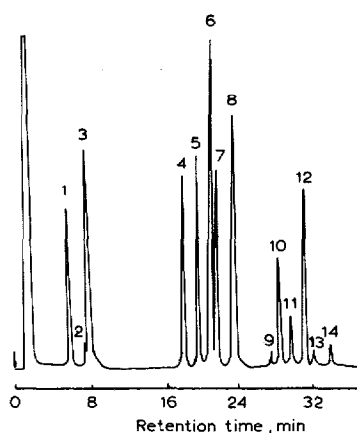

Fig. 5. Chromatogram of a mixture of the isomers of MNT, DNT and TNT separated on a 16 m × 0.31 mm I.D. glass capillary column coated with cross-linked SE-54. The column temperature was programmed from 100°C (4 min) to 250°C at 4°C/min. Detection temperature, 250°C; carrier gas, nitrogen at 25 ml/min; splitting ratio, 40:1. Peaks: 1 = o-MNT; 2 = m-MNT; 3 = p-MNT; 4 = 2,6-DNT; 5 = 2,5-DNT; 6 = 2,3-DNT + 2,4-DNT; 7 = 3,5-DNT; 8 = 3,4-DNT; 9 = 2,4,6-TNT; 10 = 2,3,6-TNT; 11 = 2,4,5-TNT; 12 = 2,3,5-TNT; 13 = 3,4,5-TNT; 14 = 2,3,4-TNT.

polymer samples. The reproducibility of the determination of the pyrolysates which were produced in low concentrations was not very good because of variations in the sample amounts and the power source. As for the modified system itself, the experimental reproducibility was satisfactory.

Applications

The modified system was successfully applied to the PCGC analysis of various polymers. It can also be used in conventional capillary GC analysis when the precolumn is not packed. In the previous capillary column system of the GC-5A chromatograph, there was a stainless-steel tube about 20 cm long between the injector and the capillary column and therefore the dead volume was high. However, in the modified system, the capillary column was directly linked with the vaporizer, and the empty precolumn corresponded to a lining in the injection port. As a result, the dead volume was greatly reduced and the separation efficiency was improved. Fig. 5 shows the chromatogram of a mixture of isomers of MNT, DNT and TNT, from which the high performance and thermal stability can be seen. Using a cross-linked glass capillary column, the baseline drift was only $1.8 \cdot 10^{-12}$ A when the column temperature was as high as 320°C. In this experiment, the splitting ratio was maintained essentially constant.

CONCLUSION

The modified column system can be used for both PCGC and conventional capillary GC analysis. The packed precolumn not only eliminates column contamination, but also reduces the dead volume and improves the separation efficiency of the pyrolysis system. The separation capacity and the experimental reproducibility are satisfactory. This system is simple to construct and easy to operate.

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