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Short communication

The development of pyrolysis–fast gas chromatography for analysis of synthetic polymers

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Abstract

The development of fast gas chromatography (fast GC) in recent years has brought an opportunity to speed up the separation process for all gas chromatography-related techniques. Pyrolysis–gas chromatography (Py–GC) is one of the techniques that heavily utilize the gas chromatograph to separate the pyrolysates. If all the applications in traditional Py–GC can be successfully replaced by Py–fast GC, the experimental time can be greatly decreased. The development of fast GC for pyrolysis applications in synthetic polymers has been summarized in this report. Several polymers have been demonstrated as examples to show the advantages of Py–fast GC. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Gas chromatography, fast; Polymers

1. Introduction

Improving the current analytical techniques to a more efficient stage is a constant effort for every analyst. In a chromatographic or separation discipline, if the resolution and sensitivity can be preserved or improved, the proficiency of the analysis is equal to the speed of the analysis, which is directly related to the speed of separation. One good definition of improvement of proficiency is “to decrease the experiment time or sample cycle time without reducing the quality of the result.” Pyrolysis–gas chromatography (Py–GC) is one of the techniques practiced in the analytical laboratory that would benefit by improving proficiency as a goal in technology development.

It is obvious that GC separation is the bottleneck

of the Py–GC operation. If the GC operation time can be reduced, the whole Py–GC proficiency can be improved. Historically, continuous operation of Py–GC is labor intensive and productivity limited. If proficiency of the Py–GC experiment can be improved to a point where GC separation is not the bottleneck of the whole operation, the labor-intensive and productivity arguments can be all resolved. However, what is the milestone for the improving proficiency at this time? How fast should a Py–GC experiment be to be called ‘fast’ enough [1]? By reviewing the Py–GC steps, if the time required for a GC separation can be reduced to the same order as the sample preparation, the GC step will not be the limiting step in the Py–GC operation.

The development of fast gas chromatography (fast GC) has been on going for several years [2–6]. Recent reports [7] show that the concept and technology development have reached a mature stage. Last year, major instrumentation companies started intro-

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ducing their new GC systems with ‘fast GC options’ [8]. These facts all indicate that fast GC has passed through its instrument development stage to an application oriented method development stage. Py-GC [9] is a technique that uses thermal energy (pyrolysis) to break down a polymeric sample to monomers, oligomers, and other fragments followed by the GC separation, detection and identification. In this study, the development of fast GC for pyrolysis applications in synthetic polymers has been summarized. Several polymers have been demonstrated as examples to show the advantages of Py-fast GC.

2. Experimental

2.1. Sample sources

The styrene-butyl acrylate copolymer was synthesized in the laboratory with a textbook method [10]. The acrylonitrile-butadiene-styrene terpolymer (ABS, catalog No. 43014-5), the vinyl chloride and vinylidene chloride copolymer (catalog No. 43710-7) were purchased from Aldrich (Milwaukee, WI, USA). All polymers purchased were used without further purification.

2.2. Py-GC conditions

(1) Pyrolysis conditions: Model CDS-2000 pyrolyzer; probe type, coil; Py temperature, 700°C; Py time, 20 s; interface temperature, 300°C.

(2) GC conditions: Model HP 6890 GC system; option, ‘fast-GC’ option; column type, DB-5, 15 m × 0.25 mm I.D.; film thickness, 1.0 μm.

(a) Conventional experimental conditions: oven temperature, 40°C/4 min—10°C/min—320°C/18 min; inlet temperature, 300°C; pressure, 10 p.s.i. (1 p.s.i. = 6894.76 Pa); split ratio, 25:1. Flame ionization detection (FID): temperature, 300°C; H₂ flow, 40 ml/min; air flow, 450 ml/min; make up, 45 ml/min He; sampling rate, 2 Hz.

(b) Fast experimental conditions: oven temperature, 40°C/0.4 min—100°C/min—320°C/6.8 min; inlet temperature, 300°C; pressure, 10 p.s.i./0.4 min—120 p.s.i./min—70 p.s.i./9.1 min; split ratio, 25:1. FID: temperature, 300°C; H₂ flow, 40 ml/min;

air flow, 450 ml/min; make up, 45 ml/min He; sampling rate, 25 Hz.

3. Results and discussion

In order to do the GC separation faster, four areas in the instrumentation and experimental conditions need to be addressed. These are a high efficiency inlet system, a programmable flow control system, a programmable oven temperature control system, and a high speed detection/acquisition system. The requirement of a high-efficiency inlet system is because the sample vapor stream needs to be re-focused into a narrower plug in the Py-fast GC experiments. The relative band width of the sample stream will directly reflect to peak width during the GC separation. In order to optimize the resolution of chromatogram or, in other words, to allow a number of peaks to be compiled in the early retention time region, the GC inlet system is required to have a high efficiency cryogenic trapping unit to re-focus the sample vapor stream while at the same time avoiding extra column band broadening. The inlet cryogenic trapping also serves as the sample accumulation and re-concentration site [11].

Fig. 1A shows the sample introduced in the conventional GC run. The FWHM (full width at half maximum) of peaks 1, 2, 3 and 4 are all approximately 10 s. The width of these peaks fully reflect the normal chromatographic broadening. Over a total 50-min chromatogram, the 10 s is only 0.33% of the total length of the chromatogram. There is no resolution issue in this early eluting part of chromatogram. Fig. 1B shows the fast GC run without cryo trapping. The FWHM of corresponding peaks 1, 2, 3 and 4 are 8 and 4 s. The peak is narrower because of the flow programming in the fast GC run. Over a total 5.0-min run, these 8- and 4-s peaks are 2.66 and 1.33% of the total length of chromatogram. Certainly, the peaks look broad, there will be a resolution problem when several components elute in the early portion of the chromatogram under these conditions.

The programmable flow control system, as well as the programmable oven temperature-control system, are important for the fast GC run [12]. Optimization of the oven temperature program as well as flow

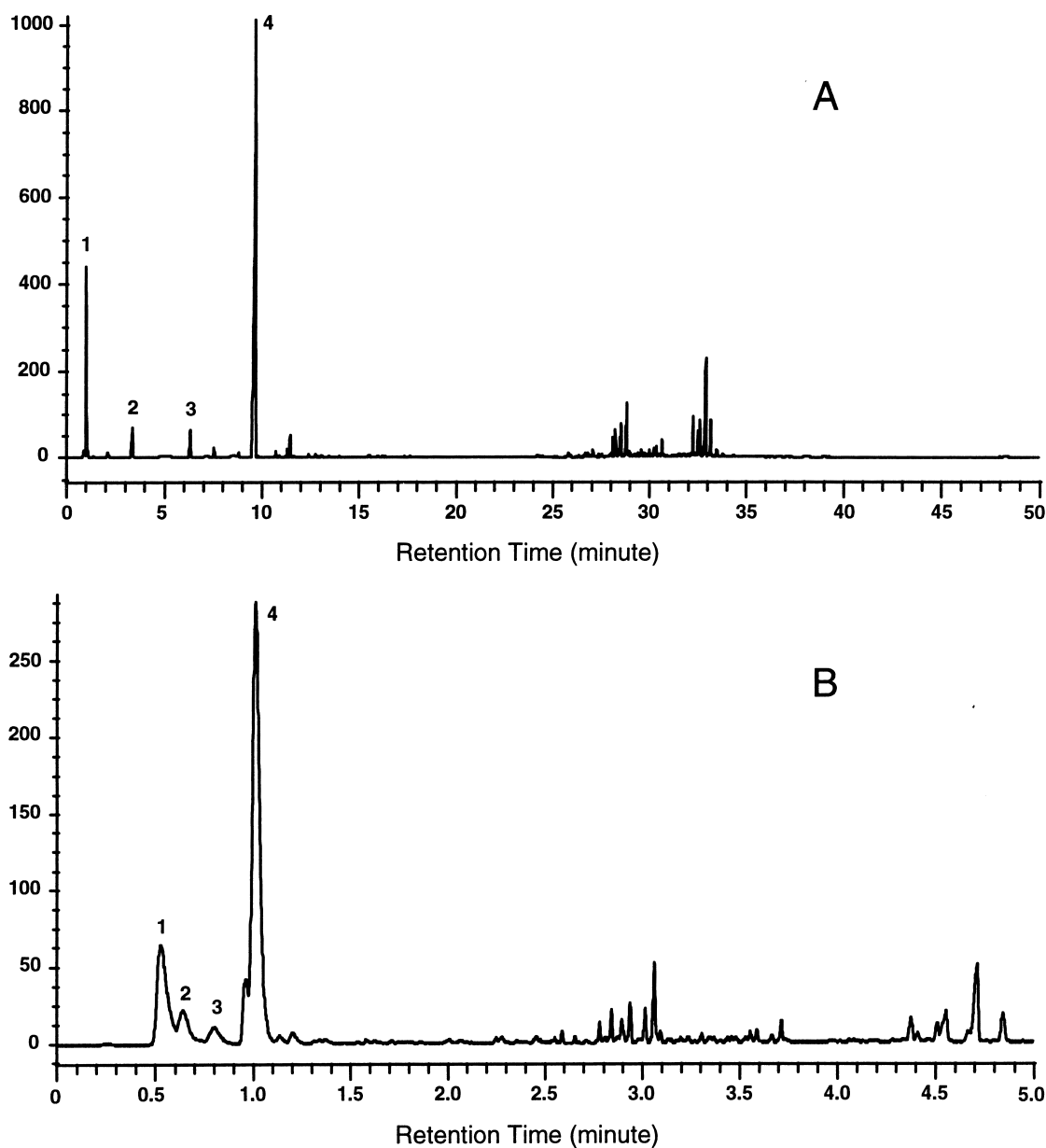


Fig. 1. The pyrogram of the styrene-butyl acrylate copolymer system with the conventional GC experimental conditions. Oven program is 40°C/4 min—10°C/min—320°C/18 min. (B) The pyrogram of the styrene-butyl acrylate copolymer system with the fast GC experimental conditions. Oven program is 120°C/0.5 min—100°C/min—320°C/7.5 min.

program to obtain the maximum resolution in the region of interest can be predicted by applying appropriate flow and temperature formulas. However, it is more convenient and easier to review their effect by direct experimental testing. An ABS ter-

polymer sample has been used as an example to demonstrate the advantages of flexible flow and oven temperature control (Fig. 2A–D). In all experiments, the first 10 min of the run were kept at the same conditions. Fig. 2A is a run in the conventional GC

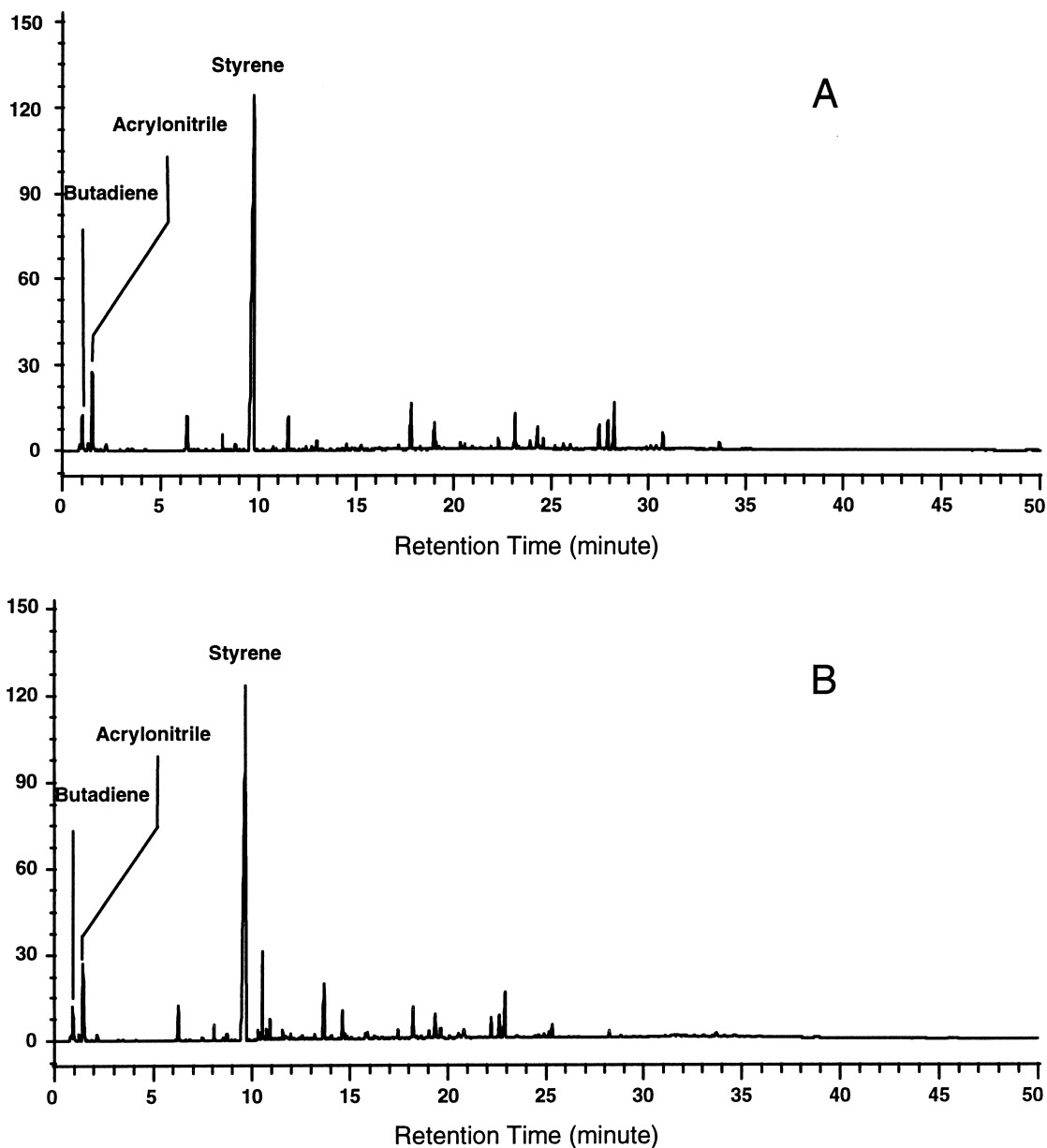


Fig. 2. The pyrogram of ABS terpolymer system. The head pressure is 10 p.s.i. through the entire run. The oven temperature program is 40°C/4 min—10°C/min—320°C/18 min. (B) The head pressure program is 10 p.s.i./10 min—120 p.s.i./min—70 p.s.i./39.5 min. The oven temperature program is 40°C/4 min—10°C/min—320°C/18 min. (C) The oven temperature program is 40°C/4 min—10°C/min—100°C/0 min—100°C/min—320°C/36.8 min. The head pressure is 10 p.s.i. through the entire run. (D) The oven temperature program is 40°C/4 min—10°C/min—100°C/0 min—100°C/min—320°C/36.8 min. The head pressure program is 10 p.s.i./10 min—120 p.s.i./min—70 p.s.i./39.5 min.

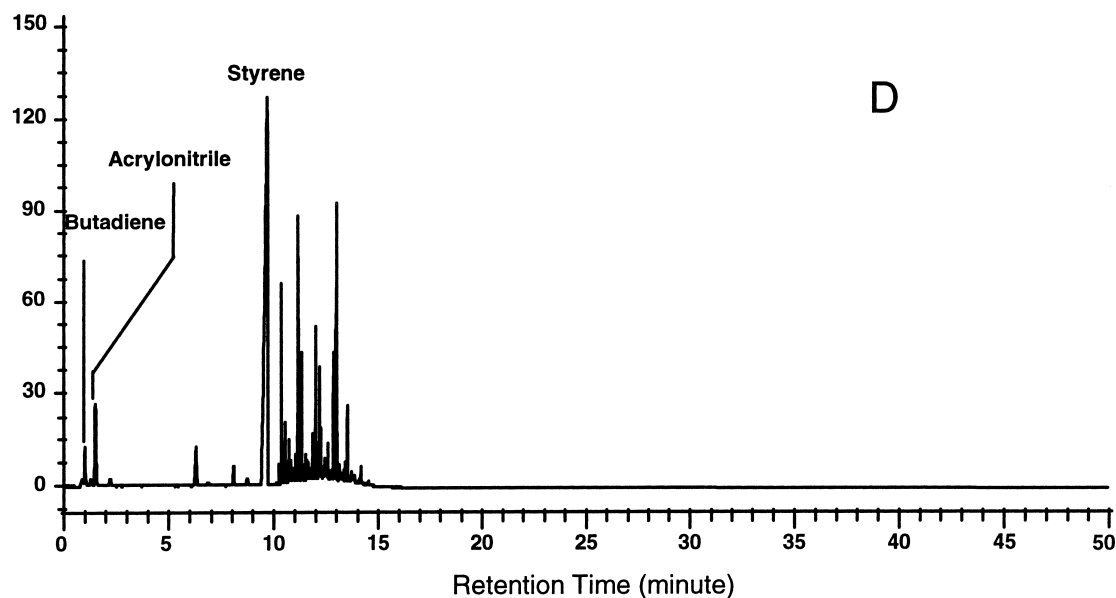
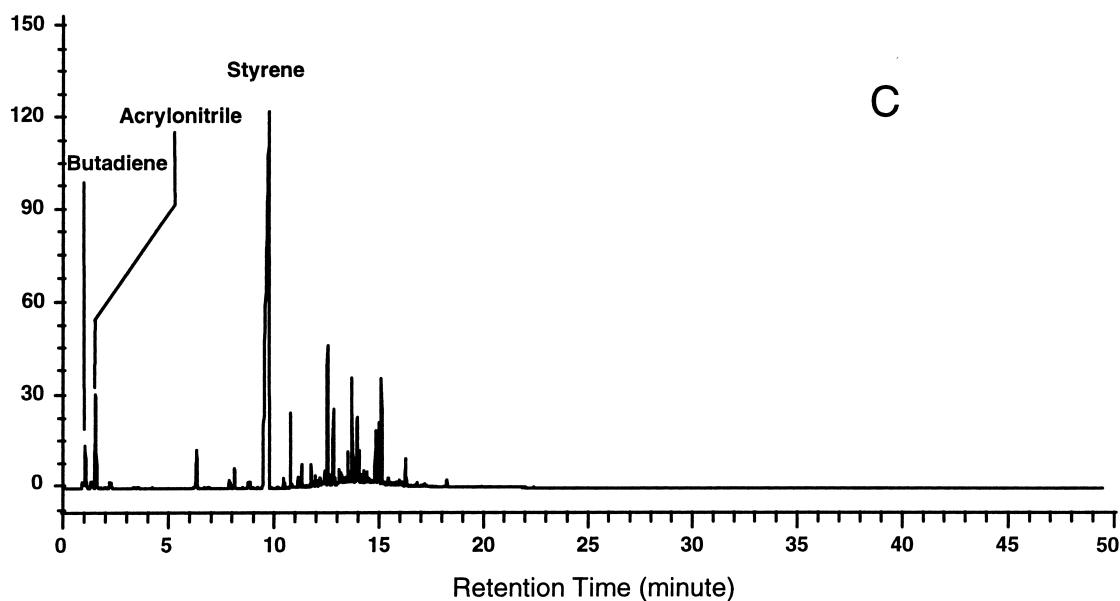


Fig. 2. (continued)

conditions. Fig. 2B shows the flow is rapidly increased after 10 min to see the flow effect on the component elution. Fig. 2C shows the temperature is rapidly increased after 10 min to see the temperature effect on the component elution. Fig. 2D shows both the flow and the temperature are rapidly increased after 10 min to see both the flow and the temperature

effect on the component elution. Apparently, the oven temperature has a much larger effect on components elution from the column.

A high-speed detection/acquisition unit is required for fast GC experiments. Because the total GC run time has been greatly reduced, the same amount of information must be compressed into a much smaller

time frame. This means that the signal variation obtained from the GC detector output will occur in a shorter time span. If the sampling rate is not fast enough, the data points collected for the fast GC experiment will not be able to adequately describe

the component peak [13], especially when the detector signal level varies dramatically in the peak and valley areas. This will cause poor peak area reproducibility, making quantitative analysis less precise. FID is capable of high-speed sampling rate. Most

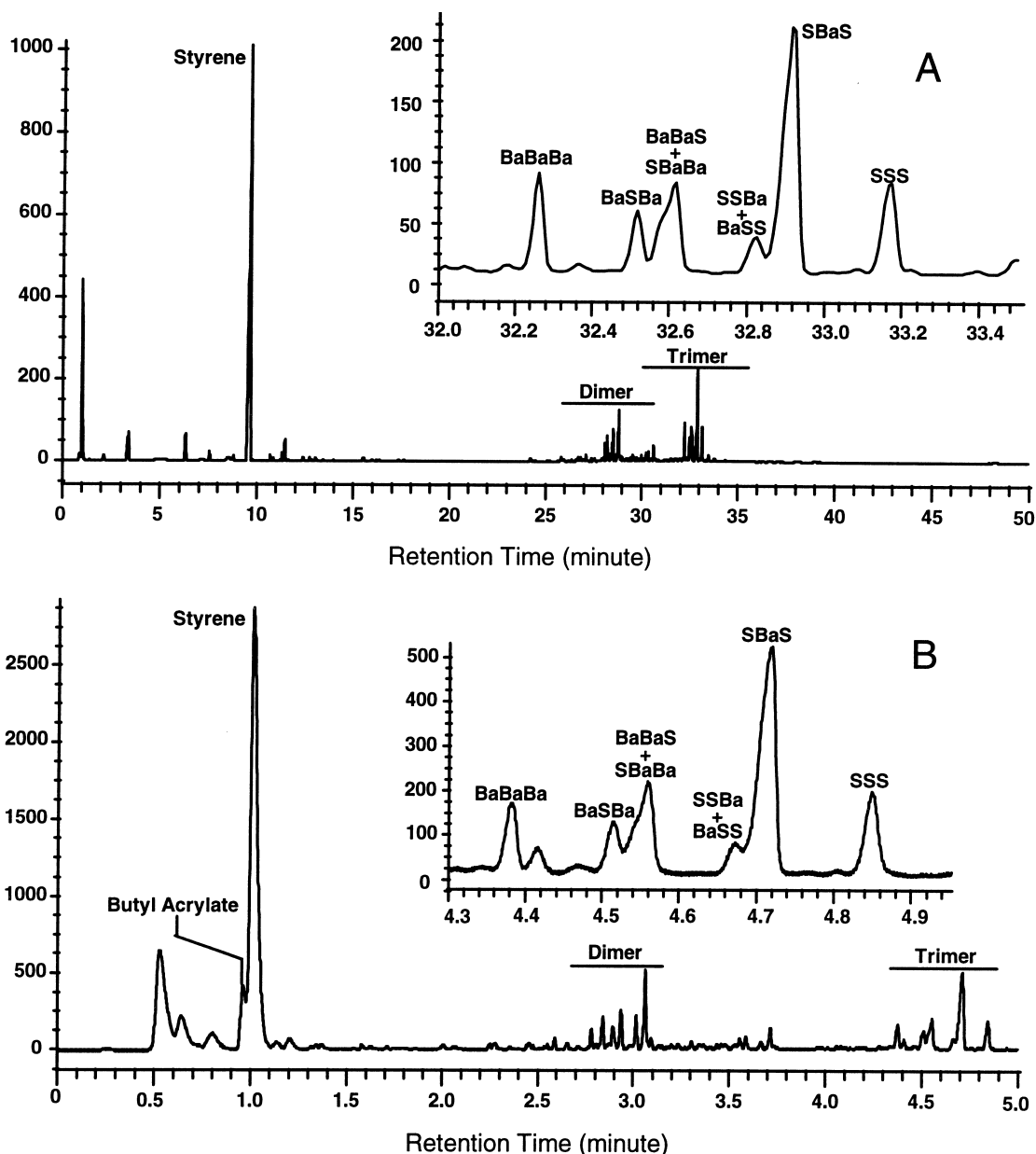


Fig. 3. The pyrogram of styrene-butyl acrylate copolymer system with the conventional GC experimental conditions. (B) The pyrogram of the styrene-butyl acrylate copolymer system with the fast GC experimental conditions. Oven program is 120°C/0.5 min—100°C/min—320°C/7.5 min.

quadrupole-based mass-selective detectors will not be able to sample signals faster than 2 Hz which is not suitable for fast GC detection/acquisition. Instead, a time-of-flight (TOF) mass spectrometry system [14] capable of detection/acquisition up to 500 Hz should be the choice as a mass spectrometry detector for fast GC.

Three examples have been presented in this study to demonstrate the feasibility of doing Py-fast GC experiments. All the examples presented here are runs without using the cryogenic focusing unit. A disadvantage of operation with a cryogenic focusing unit is the requirement of a certain type of coolant (either liquid carbon dioxide or nitrogen). This

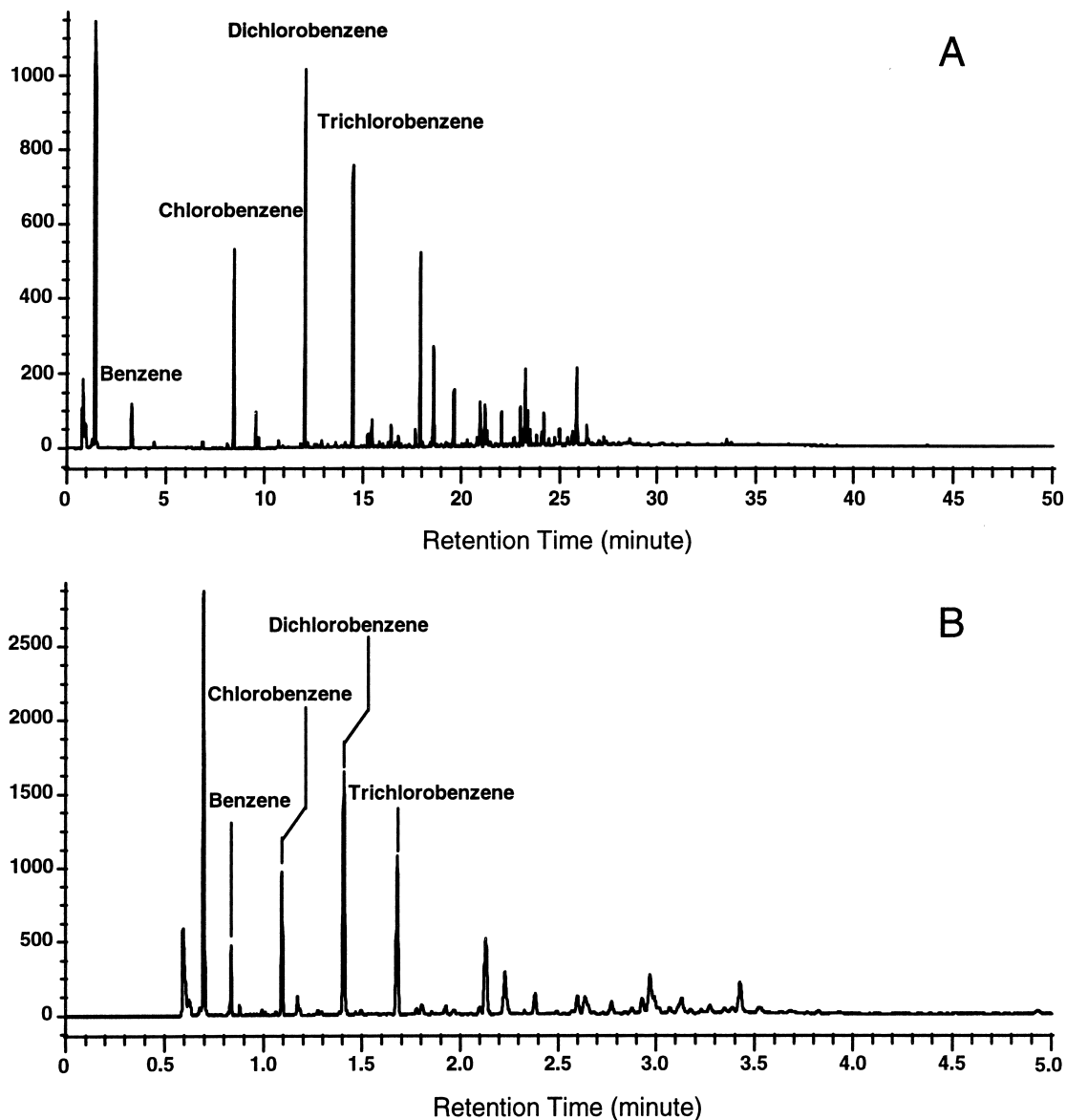


Fig. 4. The pyrogram of the vinyl chloride–vinylidene chloride copolymer system with the conventional GC experimental conditions. (B) The pyrogram of vinyl chloride–vinylidene chloride copolymer system with the fast GC experimental conditions.

situation may change, if the cryogenic focusing technology can be advanced to an electric cooling mechanism, such as Peltier electric cooling. At this time, the commercially available Peltier electric cooling unit can only cool down to -10°C , not enough to trap monomer units such as ethylene,

vinyl chloride, acrylonitrile and butadiene. Fig. 3A and B shows the pyrograms of conventional GC and fast GC runs of the styrene–butyl acrylate copolymer system. Even though the experimental time has been reduced from 50 to 5 min, the peak resolution in the region of interest (trimer peak areas, as shown in the

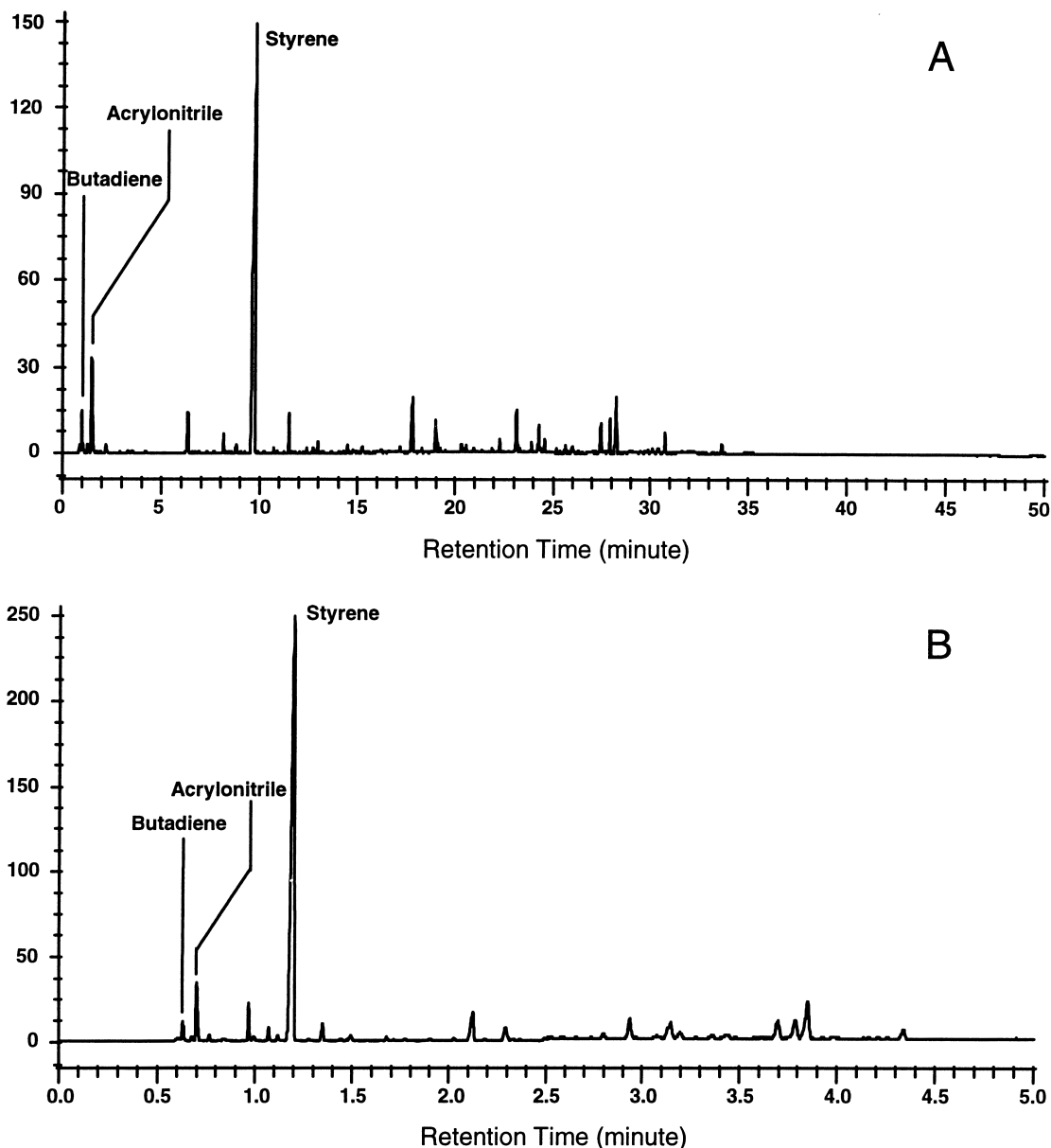


Fig. 5. The pyrogram of the vinyl acrylonitrile–butadiene–styrene terpolymer system with the conventional GC experimental conditions. (B) The pyrogram of the acrylonitrile–butadiene–styrene terpolymer system with the fast GC experimental conditions.

insert) is similar to the 50-min experiment. Fig. 4A and B shows the pyrograms of conventional GC and fast GC runs of the vinyl chloride and vinylidene chloride copolymer system. This copolymer system has been further tested for quantitative composition and structure analysis. The result obtained from Py-fast GC is in a very good agreement with the result obtained from conventional experimental conditions [15]. Fig. 5A and B shows the pyrograms of conventional GC and fast GC runs of the acrylonitrile, butadiene and styrene terpolymer system. All these examples show that the pyrograms match the desired goal, which was to reduce the experimental time without reducing the quality of the result.

The Py-GC experiment (sample preparation, pyrolysates separation and detection) takes an average of 1 h to generate composition information. With the development of Py-fast GC, the time required for the experiment will be greatly reduced to the same time as other spectroscopic experiments (5 min or less). Based on the information provided, the time required to generate the information and the cost of the experiment, Py-fast GC will be a good technique to choose in many polymer analyses. In addition to traditional qualitative and quantitative analysis, Py-GC has been recently developed to extend its capability to polymer structure determination [16], low-level monomeric units in polymer analysis [17], polymeric additive investigation [18], as well as functional group derivatization [19]. All these developments will be able to take advantage of the Py-fast GC development. In comparison to other polymer characterization techniques, there are even areas where those techniques have their specific superiority, Py-fast GC will have a superior time and cost advantage to other techniques yielding the same information.

4. Conclusions

The development of Py-fast GC has demonstrated that the time required to perform general Py-GC

experiments can be reduced to less than 5 min by adjusting flow and oven temperature programs. If the inlet system can be further modified with a cyro trap unit to re-focus the sample stream, the experimental run time can be further reduced. Based on the quality of information, from a time-saving and a cost-effective point of view, it is a success. Hopefully, this Py-fast GC success can encourage migration of other GC-related techniques to a more efficient stage.

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