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Modification of a commercial pyrolysis probe to improve its temporal and spatial temperature profiles

Performance evaluation using model polymers

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Abstract

A coiled-filament probe of a commercially available pyrolyzer (Chemical Data Systems, CDS Pyroprobe 120) was modified to change the temporal and spatial temperature profiles delivered by the probe. The modification changes the geometry of the heating filament: it is coiled tightly and a light coating of a ceramic cement is applied to maintain its dimensional stability while minimizing the possibility of developing an electrical short. The modified pyroprobe produced a reproducible and uniform temperature profile over a ~3-mm long pyrolysis region and had near-perfect emissivity (~0.95) for monitoring temperature with an optical thermometer. To conduct experiments off-line we also designed a glass housing for the tightly-coiled pyroprobe (TC-pyp). The housing has provisions for making a gas-tight seal with the pyroprobe, for introducing a gas to control the pyrolysis atmosphere and provide a rapid sweep of the pyrolysis region and for interfacing with a pre-trap to collect pyrolysates. To evaluate the results obtained with the TC-pyp we compared mass and temperature dependencies of Kraton D1107P pyrograms with those generated by a Pt ribbon-pyroprobe (PtR-pyp) and an unmodified coil pyroprobe. In addition, we report on the use of the instrumentation for quantitative analyses of model polymers. © 1997 Elsevier Science B.V.

Keywords: Pyrolyser; Pyroprobe; Polymers

1. Introduction

Analytical techniques based on thermally-induced processes, e.g., thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and pyrolysis–gas chromatography (Py–GC), are commonly used for the characterization of synthetic polymers and other non-volatile organic samples. Importantly, the quality of results achievable with the different techniques is dependent on supplying heat to a sample under carefully controlled con-

ditions. For this reason, a large amount of effort has been devoted to the design of instrumentation capable of subjecting the sample to a carefully controlled temperature or heating profile.

When performing pyrolysis, two main approaches have emerged as the preferred means to induce the thermal decomposition of a sample: by the delivery of heat at a constant temperature (continuous mode), or by applying a well-defined heating pulse (pulse mode) to the sample. In the continuous mode, the sample is reproducibly introduced to a well-controlled high-temperature environment, while in the pulse mode the sample is rapidly heated to a final

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temperature by means of a filament. However, regardless of the approach chosen, achieving reproducible inter- and intra-laboratory results requires definition and control of both spatial and temporal temperature profiles, as well as the final temperature experienced by the sample.

The continuous mode is common to other thermoanalytical techniques in addition to pyrolysis and is often used to obtain detailed degradation kinetics, to investigate reaction mechanisms and to screen samples for thermal stability. However, approaches based on continuous-mode heating are generally time consuming and usually measure gross physical effects, e.g., as in TGA. Thus, to obtain chemical information it is necessary to interface the thermoanalytical instrument to other instruments capable of providing molecular structure information, e.g., mass and IR spectrometers. In general, techniques using continuous-mode heating may not be readily adaptable to situations where high-volume, rapid characterization of polymers is required.

The development around 1970 [1–3] of pulse-mode pyrolyzers with well-defined heating characteristics suggested the potential of those pyrolyzers as a convenient means to rapidly and reproducibly analyze polymers. Heating a surface rapidly and reproducibly, e.g., at $>100^{\circ}\text{C/s}$, served to rapidly decompose the sample and produce a pyrolysate of well-defined composition. Improvements in the instrumentation contributed to the popularization of this approach. Today, the two most common methods of performing pulse-mode pyrolysis include resistive heating of a platinum element e.g., a filament, a ribbon, or a coiled filament enclosing a quartz tube insert to hold the sample [4] and inductive heating of a ferromagnetic material, e.g., a wire or foil placed in the induction coil cavity, heated by means of an applied radio-frequency field [3]. Because volatile products are presumably released instantaneously from the reaction zone, the release approaches an ideal injection plug for gas chromatography. Thus, the interface of pulse-mode pyrolyzers to a gas chromatograph was a natural step in the development of a new technique, pyrolysis–gas chromatography (Py–GC).

While approaches based on resistive and inductive heating have intrinsic advantages and disadvantages [5], there are several factors that affect, in general, the reproducibility of pulse-mode Py–GC [6].

1.1. Temperature profile: rise time and actual pyrolysis temperature

Degradation by several temperature-dependent, competing pathways may occur as the sample is heated. Therefore, different decomposition products may predominate depending on the rate of temperature change and/or pyrolysis temperature. This means that to obtain a reproducible pyrolysate the sample must experience a well-defined and reproducible temperature profile as a function of time [5,7]. An exception is the case in which the rate of heating is much faster than the rate of thermolysis. In that case, the pyrolysate composition would be determined by the final temperature of the heating device. To meet the experimental requirements, rapidly heating devices, $\sim\leq 20$ ms, have been developed and are commercially available. Most of these devices are small filaments, e.g., wires, thin ribbons or foils. Smallness is a necessity if one is to minimize the effect of heat capacity on the rate of heating. As a consequence of their small mass, this type of heating element will not tolerate a large sample size.

1.2. Sample size

Small samples (<100 μg) are more likely to pyrolyze in a uniform and reproducible way [5,8–10]. Moreover, depositing a sample from solution is the preferred means of depositing the sample: presumably, the solution deposits a thin and uniform film, in close contact with the pyrolyzer surface, after solvent evaporation. However, the pyrolysate composition of a sample deposited as a thin film may also be affected by any catalytic activity of the pyrolyzer surface. Interestingly, the molecular mass of a polymer may also affect the composition of the pyrolysate [11].

1.3. Catalytic effects

The heating filaments of most resistively-heated pyrolyzers are made of platinum, while the filaments of inductively-heated pyrolyzers are made from alloys of iron, nickel and cobalt. Catalytic effects and secondary reactions occurring on these hot metal surfaces may be a cause of irreproducible results [6]. In those situations it may be advantageous to use a quartz surface to shield the sample from the metal. In

an implementation of this concept, a thin-walled quartz tube containing the sample is inserted in a cavity made by coiling a heavy-gauge heating wire made of platinum (CDS, platinum-coil pyroprobe, PtC-pyp). A consequence of this design is that the combined masses of wire and quartz insert significantly change the heating characteristics of the device compared to foils operated with the same power supply module. Importantly, the distance between the heating coils of the commercial pyroprobe suggests the existence of 'cold' spots between coils. Furthermore, the design makes it difficult to place samples at the same position relative to a given coil within the probe. To minimize temperature gradients and enhance our ability to reproducibly place a sample within the heating environment, we developed the tightly-coiled pyroprobe (TC-pyp).

The characteristics of commercial pyroprobes and the TC-pyp, with emphasis on the effects of heating rates, geometry and surface on the composition of pyrolysates of block and model synthetic copolymers, are reported in this communication.

2. Experimental

2.1. Materials

Kraton D1107P (styrene–isoprene block copolymer, 14/86) was obtained from Shell (Oak Brook, IL, USA). Capillary GC/GC–MS grade solvents (B&J GC²) were obtained from Baxter Diagnostics (McGaw Park, IL, USA). Samples of hydrogen (H)- or deuterium (D)-containing polymers were prepared as block copolymers, synthesized to have a nominal composition of H-polystyrene/D-polystyrene, H-PS/D-PS=90K/10K, D-PS/H-PS/H–polymethyl methacrylate, D-PS/H-PS/H–MMA=5K/45K/50K and H-PS/D-PS/H–MMA=5K/45K/50K. A mixture of H-polystyrene and D-polystyrene (H-PS–D-PS, 83.3:16.7, w/w) was prepared by weight to check accuracy. Solutions of the polymers, made in B&J GC² solvents, were used to deliver samples to the pyrolyzers.

2.2. Equipment

Pyrolysis experiments were performed with CDS

pyroprobes (ribbon and coil pyroprobes, CDS Analytical, Oxford, PA, USA) and the modified pyroprobe, i.e., a tightly-coiled pyroprobe (TC-pyp). Chromatographic measurements were made with a Hewlett Packard (HP) Model 5890 Series II GC, equipped with flame ionization (FID), HP 5971 mass-selective (MS) and HP 5965B infrared (IR) detectors. MS and IR signals were processed using the CHEMSTATION software and FID data were processed by a Perkin Elmer Nelson system (PE, TURBOCHROM-3 software). A methyl silicone column (Rtx-1 Restek), 60 m×0.32 mm I.D., 1- μ m film thickness, served as the analytical column. This instrumentation, conditions and the large-volume injection system (LVIS) used to introduce samples generated by off-line pyrolysis, were described previously [12].

2.3. Measurement of the temperature profile of pyroprobes

Two kinds of transducers, a J-type thermocouple made from 40 ga. wire (TG-J-40, OMEGA Engineering, Stamford, CT, USA) and a micro infrared temperature transducer (abbreviated IR-Tm in the text, cat. OS42-RS232C-close focus, output=1 mV/°C, Omega), were used to measure probe temperatures. A small-mass thermocouple (\leq ~0.5 mg, 0.5-mm diameter) was attached to the inside wall of the quartz insert and/or heating filaments of the pyroprobes using a small amount of ceramic cement. The IR-Tm was mounted on a special housing made of glass to maintain a constant temperature, an inert atmosphere (helium) and proper focusing distance between the transducer and the heating element. Signals from these transducers were stored in a Fluke 9750 MHz Scopemeter (Fluke International, Everett, WA, USA). To collect and store the data, the scope and the pyroprobe controller were triggered sequentially using a calibrated delay provided by a one-shot multivibrator. Stored data were downloaded to an Excel spreadsheet (Microsoft) for further processing.

2.4. Off-line pyrolysis

2.4.1. TC-pyp and glass housing

To modify the PtC-pyp and transform it into a TC-pyp, it is necessary to push the Pt coils of the heating element together, so that they virtually touch

(<0.5 mm distance between coils). This is done while using the quartz tube insert as a mandrel to preserve the internal volume of the coils. The result is that the existing 15 coils of the PtC-pyp are concentrated in a 5-mm distance, for a reduction of ~50% in the length of the heating zone compared to the commercial unit. A ceramic cement (Ceramabond 569, Aremco Products, Ossining, NY, USA) was used to apply a thin coating to the coils to preserve their dimensional stability and minimize the possibility of a short circuit. The cement was diluted ~1/10 with water and applied with a brush. After drying, successive coats were applied until the surface looked white. We estimate the mass of cement added to the heating element at <100 mg. Thus, we expected the change in heat capacity of the heating element to be comparable or smaller than that caused by the quartz tube used to hold the sample. The pyroprobe body fits into a glass housing designed to facilitate the rapid sweep of the pyrolysis volume with helium (Fig. 1A). A heater cartridge for the glass housing was constructed using the same approach used for the pre-trap heater cartridge [13].

2.4.2. Sampling procedures

Polymers were dissolved in dichloromethane to

obtain solutions containing 1–10 $\mu\text{g}/\mu\text{l}$. In most cases the sample was spotted on the center of the pyroprobe heating element. This was done by touching the midpoint of the platinum ribbon, or touching the interior wall of the quartz insert, with the needle of a 10- μl syringe and gently expelling the solution. An effort was made to keep the spot diameter at ≤ 3 mm.

To observe temperature distributions of the heating elements, different procedures were used. Because the PtR-pyp is only 2-mm wide and 40-mm long, we chose positions near the middle: four spotting points, placed at ~10, 15, 20 and 25 mm from the end attached to the probe tip, were used. Because we estimated the actual heating zone of the PtC-pyp at ~12 mm, four samples were spotted, at ~3 mm intervals, bracketing the estimated middle of the heating zone. Thus, two samples were near the optimum placement, i.e., at $\sim \pm 1.5$ mm from the middle. Because the heated zone of the TC-pyp is only 5-mm long, we did not deliberately deviate from a constant spotting point, i.e., 5 mm from the end of the quartz insert. When inserted in the TC-pyp, the sample would be in the center of the heated zone within ± 1 mm.

After depositing the sample, the probe was in-

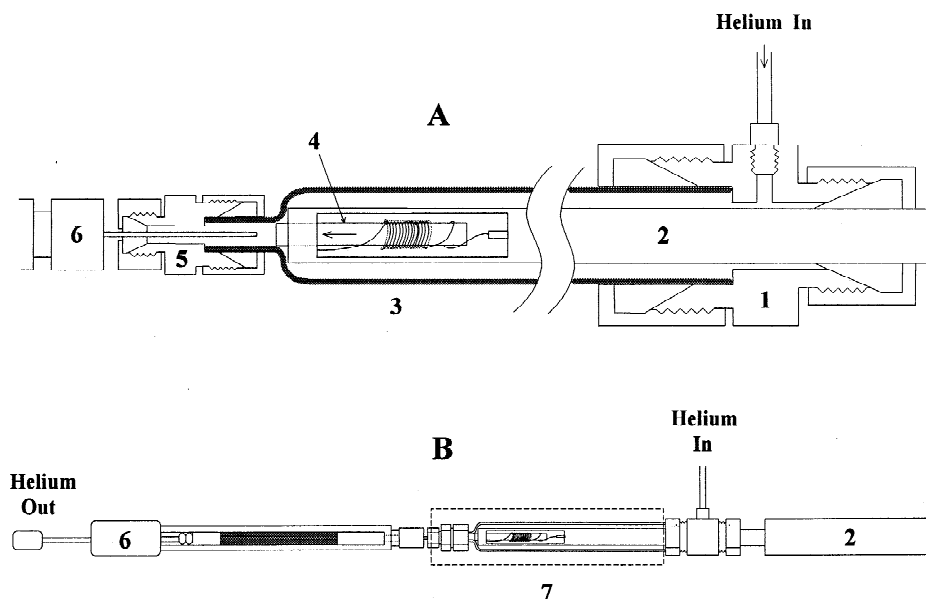


Fig. 1. Schematics of TC-pyp and glass housing (A) and set-up used to collect volatile pyrolysates (B): 1=3/8"-1/4" Swagelok ss-reducing union; 2=pyroprobe; 3=glass housing; 4=quartz insert; 5=1/8"-1/16" Swagelok ss-reducing union; 6=pre-trap; 7=heater cartridge.

serted in the heated (200°C) housing, while flushing the housing with helium at 20 ml/min. An air-tight seal between housing and probe was achieved by means of a PTFE ferrule. The solvent was fully evaporated prior to starting any pyrolysis. Then, pyrolysis was conducted for 20 s, under different heating conditions as needed to study different effects, e.g., temperature rise time, final temperature. Pyrolysis products were collected in a pre-trap, packed with ~150 mg of Tenax TA, by passing a 100-ml volume of helium (20 ml/min for 5 min) through the housing/pre-trap system shown in Fig. 1B.

2.5. Chromatographic analysis of pyrolysates

The equipment and procedures used were described in a previous communication [12]. A brief description of the steps required, using the LVIS, follows. After collection, the contents of the pre-trap were desorbed (at 180°C, while flowing dry helium at 15 ml/min for 8 min) and transferred into the cryogenic concentrator, kept at -140°C during the transfer. After the transfer, the sample was released from the cryogenic concentrator by heating (to 200°C, at 15°C/s), followed by transfer to the analytical column for analysis. GC-MSD/IRD/FID: The following experimental conditions were used. GC: Inlet temperature 250°C; oven temperature 50°C for 2 min, then programmed to 280°C at 6°C/min, followed by an isothermal period of 5 min. The column effluent was split ~1/10 between the MS and IR detectors using an SGE glass-lined splitter. MS detection: Transfer line 280°C; MS temperature 185°C; electron energy 70 eV. Mass range m/z 20–300 (2.5 scans/s) for 20 min, followed by scanning from m/z 30–350 (2.2 scans/s) for the remainder of the run. IRD/FID: Transfer lines 250°C; light-pipe cell 250°C; source power 21.0 W. IR spectra were obtained by scanning the range 750–4000 cm^{-1} (1.5 scans/s at a resolution of 8 cm^{-1}). The effluent from the IR detector was introduced to the FID via a fused-silica transfer line. The FID temperature was set at 280°C and the FID area response for hydrocarbons used to calculate absolute recoveries. The only exception was the case of MMA monomer, where the actual FID response factor of the compound (0.58) was established to ensure accuracy. Recovery was calculated by converting FID area to

mass and dividing the calculated mass by the mass delivered to the probe.

3. Results and discussion

While Py-GC is a well-established analytical technique, questions remain regarding the inter- and intra-laboratory reproducibility of the results. Those questions remain unanswered because it is difficult to measure and/or control all the parameters involved in the pyrolysis process, e.g., sample heating rate and actual pyrolysis temperature, dependency of process on sample mass, catalytic effect of surface, etc. In an attempt to create a homogeneous heating environment, possessing a well-defined heating rate and inert surfaces, we modified a commercially available PtC-pyp. To benchmark its properties, we studied a number of experimental variables and compared it to existing units.

3.1. Temperature profile of pyroprobes

3.1.1. Pt-ribbon pyroprobe (PtR-pyp)

Measurement of actual pyrolysis temperature or heating rates of a PtR-pyp is difficult when using either a thermocouple or micro-infrared thermometer. For example, when using a thermocouple, its mass may be significant compared to that of the foil or sample (a thermocouple constructed with 40 ga. iron-constantan wire (~0.5 mm diameter) would have a mass $\text{ca.} \leq 0.5$ mg). Thus, it is likely that the added mass would change significantly the temperature of the measurement site on the ribbon.

There is another problem associated with the measurement site that also affects the IR measurement: the foil changes position as it is being heated due to the linear expansion of the foil. As a consequence, the contact point of an unattached thermocouple and the focal point of an infrared thermometer would change, producing a concomitant change in readout temperature. Attempts to attach a thermocouple to the foil with ceramic cement to prevent loss of contact with the surface as it moves during heating were only partially successful.

Another set of problems unique to IR monitoring of temperature are caused by the small width and construction of the Pt-ribbon. The low emissivity of platinum (0.05–0.10) over the temperature range of

interest (500–1000°C) and the difficulty of keeping a tight focus on the small surface make calibration and monitoring difficult. Thus, we could only obtain an estimate of the nominal heating rate: the rise time of the probe is fast; the final temperature, 700°C, was reached within 80 ms when the maximum heating rate ($>20\,000^\circ\text{C/s}$) was used. We conclude that the actual heating rate over which most of the pyrolysis will occur, e.g., 300–600°C, is larger than $10\,000^\circ\text{C/s}$. In addition, the final temperature of the Pt-ribbon was constant during the heating period following pyrolysis, e.g., 1–20 s.

3.1.2. TC-Pyp and conventional Pt-coil pyroprobe (PtC-pyp) with quartz insert

Inter- and intra-laboratory reproducibility is likely to be more dependent of heating rates than final temperature [7]. For this reason, we chose to work on optimizing the heating uniformity and the measurement of the heating rates of the coil pyroprobes.

The actual temperature of the quartz insert is measurable with either a small-mass thermocouple and/or an IR thermometer. This is true because the quartz insert has enough mass (~85 mg) to keep its temperature constant when a small-mass thermocouple is attached to its inside wall and because it also has a high IR emissivity (~0.8). In addition, when using the TC-pyp we cover the Pt coils with a thin coat of a ceramic cement which has near-perfect IR emissivity (0.95); thus, commercial IR thermometers can be used without recalibration.

Using either method, a constant-temperature region, e.g., $800 \pm 3^\circ\text{C}$, over a 3-mm long distance, was measured with the TC-pyp design. This compares to the commercial PtC-pyp temperature variations of ca. $\pm 10^\circ\text{C}$ over the same number of coils (~6 mm). Interestingly, we observed differences in temperature between two probes, i.e., the TC-pyp and a PtC-pyp, when operated by the same power supply module and operated at the same set point temperature (e.g., the TC-pyp was lower by 80°C and 50°C, at 200°C and 1000°C, respectively). The reason for this difference is not clear. Although the differences in the actual temperature of the two probes may be due to the larger mass (heat capacity) of the TC-pyp due to its ceramic coating, it is also possible that differences in resistance between the two probes may be responsible. In either case, the actual temperature is easily measurable with a small thermocouple.

The temperature rise time of the TC-pyp was also measured, using the IR-thermometer and a thermocouple, for two different nominal heating rates, e.g., $>20\,000^\circ\text{C/s}$ and 1000°C/s . This is shown in Fig. 2. As expected, the rise time is significantly slower than that attainable with the ribbon probe: it took ~600 ms to change the temperature from 300°C to 600°C at the fastest rates available with our unit ($>20\,000^\circ\text{C/s}$). The slope of the temperature vs. time profile of the TC-pyp, at a setting of 1000°C/s , was actually 290°C/s . Importantly, these rates are easily measured and should be readily reproduced by other equipment.

3.2. Evaluation of TC-pyp and conventional pyroprobes using Kraton D1107P

3.2.1. Effect of heating rate and probe geometry

The yield and distribution of Kraton pyrolysate and by inference, the mechanism of pyrolysis, were expected to be a function of pyrolysis temperature and/or heating rate. For example, Levy and Walker [14] reported a 'linear' increase in isoprene/dipentene ratio with temperature and attempted to use it as a means to calibrate the pyroprobe temperature. To study the effect of heating rate and temperature on product distribution and yield, we pyrolyzed samples at a constant nominal value (700°C), while changing rise time and probe geometry. The nominal value was selected because we believed it to be far in excess of the expected pyrolysis temperature of Kraton ($\leq 550^\circ\text{C}$).

Relative compositions and absolute recoveries are shown in Table 1. In general, the relative yield of monomer, as measured by the ratio of isoprene to dipentene, increases as the rate increases. We conclude that the increased monomer yield is a consequence of the existence of competing mechanisms and their dependence on actual sample temperatures during the course of the reactions. Also shown in the table are the absolute recoveries. Absolute recoveries are constant (R.S.D. $< 10\%$) for a fixed heating rate. The observed R.S.D. values probably reflect the ability to deliver a constant mass with a microliter syringe. Thus, the increased recovery observed for the Pt ribbon (55.6–82.7%, or ~25%) is also a function of heating rate. Note that recovery is

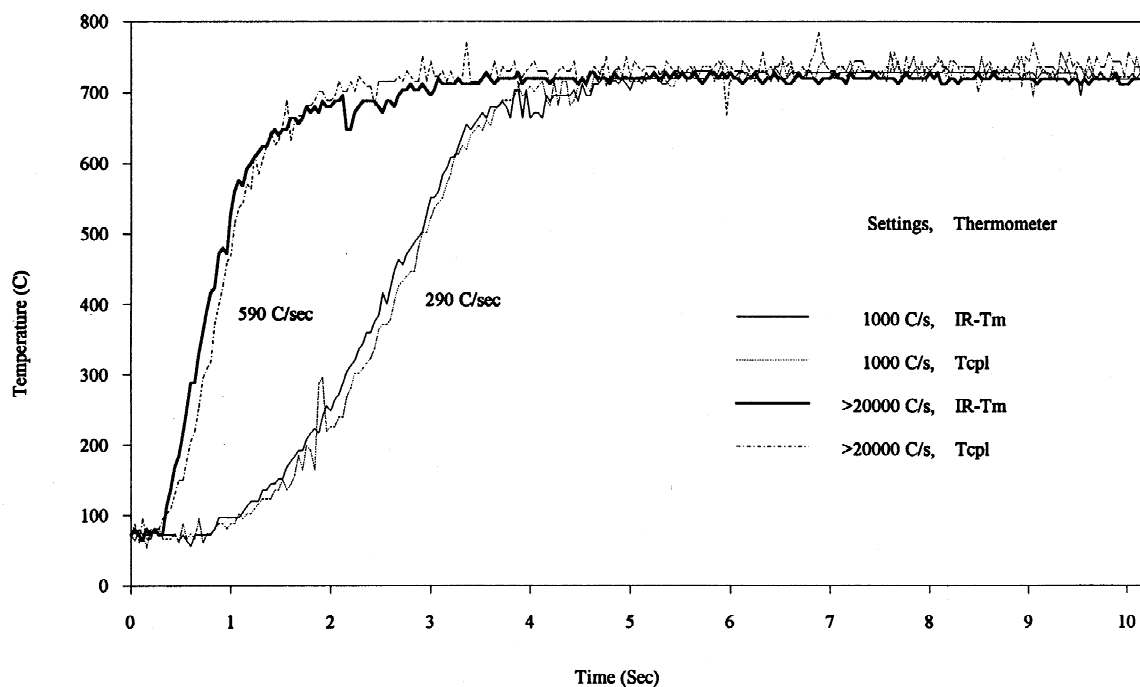


Fig. 2. Heating rate of TC-pyp as a function of power supply settings and measurement tools. Heating rates in °C/s (C/s). Measurement tool: IR-Tm=IR-thermometer, Tcpl=thermocouple.

essentially constant for the TC-pyp (69.7 and 65.1%).

We believe the reason for the near-constant recovery found for the TC-pyp and the increased recovery found for the Pt-ribbon as a function of heating rate, may be the same. As pyrolysis occurs,

there is an explosion of mass from the surface as gaseous materials are released from the sample. The explosion of mass includes intact fragments of sample; thus, in the case of the ribbon, they would no longer be available for pyrolysis. However, in the case of the TC-pyp, the intact fragments have a

Table 1
Effect of heating rate and probe geometry on yield and distribution of Kraton pyrolysates

Probe type	PtR-pyp		PtR-pyp		TC-pyp		TC-pyp	
	>20 000 ^a		1000 ^a		590 ^b		290 ^c	
Heating rate (C/s)	Relative %	R.S.D.	Relative %	R.S.D.	Relative%	R.S.D.	Relative%	R.S.D.
<i>Products</i>								
Isoprene	66.5	1.6	49.1	2.3	51.9	4.1	45.9	0.8
Styrene	19.0	8.1	25.4	4.6	22.7	7.1	25.5	0.8
DMVCH	4.1	2.0	4.9	0.5	5.0	1.3	5.4	0.7
Dipentene	10.5	3.9	20.6	0.5	20.4	2.4	23.2	0.9
Isoprene/dipentene ratio	6.36		2.38		2.54		1.98	
Recovery (%)	82.7		55.6		65.1		69.7	

Heating rates in °C/s (C/s). R.S.D. values established with $n=3$. DMVCH=1,4-dimethyl-4-vinyl-1-cyclo-hexane.

^a Sample amount 5 µg, nominal temperature 700°C.

^b Sample amount 5 µg, actual temperature 705°C.

^c Sample amount 1 µg, actual temperature 705°C.

chance of encountering a hot surface where they would undergo further pyrolysis. The higher yields found for the Pt-ribbon at the higher heating rate are probably due to the pyrolysis rate being faster than the mass loss due to the explosion.

3.2.2. Effect of sample position on pyroprobes

The effect of depositing a sample on a pyroprobe would depend on the reproducibility of the temperature profile delivered by the pyroprobe. We tested the effect with ribbon pyroprobes because we expected their temperature profiles to be more sensitive to position [2] than those of coil probes since their thermal mass is significantly smaller. The results are shown in Table 2. Depositing samples over a ± 8 -mm distance from the center of the ribbon produced a relative composition with R.S.D. values ranging from ~ 10 to 20%. By contrast, when care is exercised to deposit the sample at the same point near the middle, the R.S.D. values drop to $\sim 1\%$ or better. The average yield also increased and approached the values reported in Table 1. Therefore, regardless of the probe used, we made an effort to always position the sample within a 3-mm region of the chosen spot.

3.2.3. Effect of final temperature on product distribution

In a seminal communication, Farré-Rius and Guiochon [7] stated that ‘in most cases pyrolysis is completed at a temperature well below the equilibrium temperature of the heat source and thus, that the heating rate is of paramount importance in flash pyrolysis’.

At a constant mass (1- μg sample) and heating-rate ($\sim 290^\circ\text{C}/\text{s}$), the distribution is dependent on final temperature setting as shown in Table 3. For example, when using the TC-pyp, the isoprene/dipentene ratio changed from 1.77 to 2.13, or $\sim 20\%$, over a temperature range $\sim 300^\circ\text{C}$. The changes suggest that the heating rates are a function of the final temperature setting of the device: higher heating rates are the likely result of increasing the final temperature setting.

At a chosen final temperature, the distribution R.S.D. values for data obtained with the TC-pyp are slightly better than those observed for the conventional probes ($\leq 4\%$ vs. $\geq 5\%$). While the devices are capable of producing highly reproducible results, e.g., at $\sim 600^\circ\text{C}$, the R.S.D. values become progressively worse at higher and lower temperatures. However, the preponderance of data suggest the TC-pyp is capable of producing a more uniform and reproducible temperature profile than either of the conventional probes and that reproducible profiles are more difficult to achieve at the higher heating rates. For this reason, we chose an easily achievable and measurable heating rate of $290^\circ\text{C}/\text{s}$ for the remainder of the work.

3.2.4. Effect of sample mass and surface activity of pyroprobes on product distribution and yield

At constant temperature ($\sim 600^\circ\text{C}$) and heating rate ($\sim 290^\circ\text{C}/\text{s}$), the product distribution is virtually independent of mass when pyrolysis is performed with the TC-pyp, as shown in Table 4. This property is important when characterizing unknown polymers.

Table 2
Effect of sample position on a PtR-pyp: yield and distribution of Kraton pyrolysates

PtR-pyp Products	Different positions ^a		Same position ^b	
	Relative %	R.S.D.	Relative %	R.S.D.
Isoprene	33.5	22.7	41.0	0.4
Styrene	34.0	19.1	31.1	0.7
DMVCH	5.4	11.6	5.3	0.5
Dipentene	27.1	15.4	22.5	0.4
Isoprene/dipentene ratio	1.24	1.82		
Recovery (%)	32.5	49.7		

Nominal heating rate = $1000^\circ\text{C}/\text{s}$, R.S.D. values established with $n=4$.

^a Average composition after depositing sample at four different locations on the ribbon (15 mm span).

^b Sample deposition within a 3-mm region of the chosen midpoint spot.

Table 3
Effect of final temperature of pyroprobes on yield and distribution of Kraton pyrolysates

Probe type	Products	Relative %	R.S.D.	Relative %	R.S.D.	Relative %	R.S.D.	Relative %	R.S.D.
TC-pyp	Actual temperature (C)	805		705		610		515	
	Isoprene	47.3	4.0	45.9	0.8	44.8	1.3	43.8	1.7
	Styrene	25.4	3.8	25.5	0.8	25.6	0.2	25.9	0.7
	DMVCH	5.1	3.6	5.4	0.7	5.4	0.9	5.5	1.4
	Dipentene	22.2	3.4	23.2	0.9	24.2	2.3	24.8	2.6
	Isoprene/dipentene ratio	2.13	–	1.98	–	1.86	–	1.77	–
	Absolute recovery %	72.6	–	69.7	–	65.3	–	66.8	–
PtC-pyp	Actual temperature (C)	760	–	670	–	585	–	500	–
	Isoprene	49.1	6.1	48.7	5.3	43.6	0.4	39.9	2.6
	Styrene	25.7	7.5	23.5	7.0	26.3	1.0	23.1	4.8
	DMVCH	5.1	2.2	5.4	1.1	5.4	0.9	5.9	1.0
	Dipentene	20.2	5.8	22.4	4.2	24.7	0.4	31.2	0.4
	Isoprene/dipentene ratio	2.43	–	2.18	–	1.77	–	1.28	–
	Absolute recovery %	87.9	–	73.2	–	67.2	–	56.2	–
PtR-pyp	Nominal temperature (C)	800	700	600	500				
	Isoprene	44.8	4.0	41.4	0.8	41.0	0.4	40.3	1.8
	Styrene	32.4	5.5	33.3	2.9	31.1	0.7	27.6	2.2
	DMVCH	4.3	3.7	4.8	5.8	5.3	0.5	5.8	0.9
	Dipentene	18.5	2.8	20.6	3.5	22.5	0.4	26.4	2.3
	Isoprene/dipentene ratio	2.42	–	2.01	–	1.82	–	1.53	–
	Absolute recovery (%)	44.3	–	44.5	–	49.7	–	42.1	–

Sample amount=1 µg, R.S.D. values established with $n=3$. Heating rate: TC-pyp ~290°C/s (actual), PtC-pyp ~600°C/s (estimate), PtR-pyp 1000°C/s (nominal).

Furthermore, a constant product distribution is indicative of an inert pyrolysis surface. Thus, it is possible to pyrolyze as little as 0.25 µg of sample when a quartz surface is employed.

This is in contrast to the product distribution observed with a Pt-ribbon pyroprobe: large changes in the isoprene and styrene distribution occur when masses <1 µg are pyrolyzed. We believe this is a consequence of using a catalytic surface to hold the sample during pyrolysis. This view is supported by the distribution at higher masses: as the mass increases, the distribution approaches values comparable to those obtained with the quartz surface. Thus, when using the larger masses ≥1 µg, the catalytic activity would be confined to the few layers in close proximity to the surface and the total fraction undergoing catalytic decomposition would become a smaller fraction of the total mass. This explanation is also congruent with the absolute yield of products: a

constant recovery of 60±5% was measured with the quartz surface as opposed to values ranging from 13% to 57%, for low (0.25 µg) and high mass (10 µg), respectively, measured with the Pt-ribbon.

3.3. Applications of TC-pyp pyrolysis to the quantitative measurement of polymer composition

Because the TC-pyp is capable of producing reproducible and quantitative results, we wanted to evaluate its potential for the characterization of polymers. In addition, the pyrograms may contain information regarding polymer microstructure and this information may be accessible if small peaks in the pyrogram are reproducible. For example, the pyrogram of a specially-designed H-styrene/D-styrene block co-polymer should contain information on the microstructures at the co-polymer junctions,

Table 4
Effect of sample mass and surface activity of pyroprobes on yield and distribution of Kraton pyrolysates

Probe type	Sample mass (μg) Products	0.25		0.5		1.0		5.0		10.0	
		Relative %	R.S.D.	Relative %	R.S.D.	Relative %	R.S.D.	Relative %	R.S.D.	Relative %	R.S.D.
TC-pyp	Isoprene	44.0	0.7	43.7	0.5	44.8	1.3	44.1	1.6	45.8	3.0
	Styrene	26.1	2.8	25.9	1.3	25.6	0.2	26.8	1.6	25.9	3.7
	DMVCH	5.4	1.9	5.4	0.9	5.4	0.9	5.4	0.5	5.3	0.4
	Dipentene	24.5	1.8	24.9	1.8	24.2	2.3	23.7	1.4	23.0	2.0
	Isoprene/Dipentene Ratio	1.79		1.75		1.86		1.86		1.99	
	Absolute recovery %	58.6		55.4		65.3		63.3		63.2	
PtC-pyp	Isoprene	43.8	3.3	43.4	0.5	43.6	0.4	46.6	5.8	45.9	4.6
	Styrene	26.6	3.6	25.9	1.4	26.3	1.0	24.7	7.6	24.9	4.0
	DMVCH	5.3	0.3	5.4	0.7	5.4	0.9	5.3	0.5	5.3	2.2
	Dipentene	24.3	2.0	25.2	0.5	24.7	0.4	23.4	3.4	23.9	5.4
	Isoprene/Dipentene Ratio	1.81		1.72		1.77		1.99		1.92	
	Absolute recovery (%)	56.5		55.1		67.2		65.7		60.4	
PtR-pyp	Isoprene	25.8	3.8	34.8	9.2	41.0	0.4	44.9	0.4	46.5	0.3
	Styrene	45.3	3.9	38.5	10.7	31.1	0.7	27.9	0.3	26.9	1.4
	DMVCH	5.7	7.4	5.1	4.6	5.3	0.5	5.3	0.3	5.2	0.5
	Dipentene	23.1	10.1	21.6	3.3	22.5	0.4	21.9	1.0	21.5	1.1
	Isoprene/dipentene ratio	1.12		1.61		1.82		2.05		2.17	
	Absolute recovery (%)	12.8		30.4		49.7		56.9		56.2	

Probe temperature: TC-pyp 610°C (actual), PtC-pyp 585°C (actual) and PtR-pyp 600°C (nominal). Heating rate: TC-pyp ~290°C/s (actual), PtC-pyp ~600°C/s (estimate), PtR-pyp 1000°C/s (nominal). R.S.D. values established with $n=3$.

Table 5
Quantitative assessment of polymer composition

Mixture	D-PS/H-PS			H-PS/H-PMMA			H-PS/H-PMMA		
	Relative (%)	R.S.D.	Nominal (%)	Relative (%)	R.S.D.	Nominal (%)	Relative (%)	R.S.D.	Nominal (%)
D-Styrene	16.5	0.2	16.7	–	–	–	–	–	–
H-Styrene	83.5	1.1	83.3	50.6	1.0	50.0	33.2	1.1	33.3
H-MMA	–	–	–	49.4	1.0	50.0	66.8	0.6	66.7

Block copolymer	D-PS/H-PS (10K/90K)			D-PS/H-PS/H-PMMA (5K/45K/50K)			H-PS/D-PS/H-PMMA (45K/5K/50K)		
	Relative (%)	R.S.D.	Nominal (%)	Relative (%)	R.S.D.	NMR (%)	Relative (%)	R.S.D.	NMR (%)
D-Styrene	8.7	0.1	10.0	2.7	0.9	2.4	3.6	5.2	2.8
H-Styrene	91.3	1.3	90.0	40.0	1.0	41.7	34.9	1.7	37.4
H-MMA	–	–	–	57.2	0.7	55.9	61.6	0.9	59.8

TC-pyp temperature 705°C, heating rate ~290°C/s, sample amount 1 μg , R.S.D. values established with $n=3$.
Molecular weight in kilodaltons, K.

e.g., dimers (H–H, D–D and H–D) and trimers (H–H–H, H–H–D, H–D–D, D–D–D). This topic will be the subject of another communication.

Quantitative results obtained on physical mixtures of deuterated polystyrene (D-PS) and the hydrogenated polymer (H-PS), as well as two mixtures of H-PS and polymethyl methacrylate (PMMA), are shown in Table 5. Mixture analyses are both reproducible and accurate to ~1% or better. Analyses of block copolymers showed comparable reproducibility, as shown also in Table 5. Accuracy was checked against results obtained by NMR [15]. In order to obtain mass distribution, it was necessary to use the FID response factor of MMA monomer (0.58) and transform the NMR results from volume/volume to weight/weight using the densities tabulated in the paper [15]. Agreement between the distributions calculated by both methods is within 2%. However, compared to the NMR results, pyrolysis data are easily obtained and interpreted.

4. Conclusions

The TC-pyp offers some advantages over existing units: it is more inert than ribbon pyroprobes and offers better temperature uniformity than conventional pyroprobes. These advantages should facilitate interlaboratory comparisons because a temperature profile, reproducible both in time and space, in addition to a non-catalytic surface, are important factors in achieving reproducible pyrolysis.

In general, results showing reproducibility and accuracy in the 1–2% range were achieved when the heating rate was kept at 290°C/s and the final temperature was kept between 600 and 700°C. In addition, a wide range of sample masses (0.25 – 10 µg) could be accommodated while relative composition remained essentially unchanged.

The off-line method reported here, coupled with the large-volume injection system [12], works well when analyzing products as volatile as isoprene (a C₅ compound with a boiling point of 34.1°C). In addition, the off-line pyrolysis method used in this work may offer advantages when using reactive atmospheres (e.g., hydrogen or ozone), when derivatizing pyrolysates, or when using external standards.

The instrumentation, comprising the TC-pyp and

the LVIS/GC/FID/MS/IR system, is a powerful tool for the characterization of polymers and other substances, as illustrated in a previous communication [12]. In this paper we emphasized the use of the FID in obtaining quantitative results; however, the instrumentation was applied to resolving mixtures of D- and H-containing compounds resulting from the test polymers. In those cases, both the MS and IR spectrometers provide needed information to properly interpret the results. This type of study will be the subject of another communication.

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