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Investigation of polymers by a novel analytical approach for evolved gas analysis in thermogravimetry

Gas chromatography comprehensively coupled to single photon ionization mass spectrometry

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Abstract A newly developed measurement technique for evolved gas analysis in thermogravimetry, viz. a thermo balance coupled to comprehensive gas chromatography/single photon ionization mass spectrometry (TG–GC × SPIMS), has been applied to investigate the thermal degradation of two polymers (polycarbonate (PC) blended with ABS and PVC). This detection method provides a two-dimensional analysis of the evolved gaseous products. TG relevant data is obtained as well as an improved resolution power to separate isobaric molecular structures without losing any fraction of the samples. In addition, this solution is not associated with any extension of the measurement time. The assignment of the substance pattern to distinct species is improved compared to solely using MS without a preceding separation step. Furthermore, hitherto undetected compounds when compared to applying TG–SPIMS without GC such as benzonitrile and its methylated derivatives have been found in the evolved gases from the thermal degradation of PC/ABS blend. Finally, a first estimation of the limit of detection has been carried out, yielding 400 ppt for styrene and 500 ppt for toluene from the thermal decomposition of PC/ABS blend.

Keywords Evolved gas analysis · Mass spectrometry · Gas chromatography · Photo ionization · Polymers

Introduction

Thermal analysis (TA) is a valuable technique for chemical and material analysis as well as for industrial process control. Measured variables as a function of temperature comprise mass loss [thermogravimetry (TG)], first derivative of the mass loss curve (DTG) and enthalpy changes [differential scanning calorimetry (DSC)]. These parameters are useful to characterize temperature-dependent material properties, to evaluate thermo dynamical conversions and thermophysical parameters as well as to observe chemical reactions. For more thorough and detailed investigations of the sample composition, a chemical investigation of the evolved gases, i.e., evolved gas analysis (EGA), is indispensable [1]. Depending on the requirements, EGA can be realized by off line coupling of TA methods with sequentially working analytical techniques such as gas chromatography (GC) [2–4] or with on-line real-time detection such as fourier transform infrared spectroscopy (FTIR) [5] or mass spectrometry (MS) [6, 7]. The latter can be realized by either a capillary coupling [8] or a skimmed super sonic expansion [9]. The ionization method utilized most frequently is electron ionization (EI). However, depending on the chemical class of the investigated molecules EI mass spectra hardly contain molecular ion signals, but are dominated by fragment peaks due to the introduced high excess energy by the electrons. Despite

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some of these fragment signals are characteristic for specific classes of molecules or functional groups and, therefore, can be used for identification purposes, especially for complex samples this would lead to overlapping signals. Hence, identification and quantification could become very complicated or even impossible. To overcome this difficulty, soft ionization has been applied in TA–MS hyphenation, e.g., chemical ionization (CI) [10], field ionization (FI) [11], meta stable atom bombardment (MAB [12–14], which is based on Penning ionization [15] and photo ionization (PI) [16–22].

These spectra are easier to interpret, since almost no fragment peaks are present. First, thermal decomposition measurements and pyrolysis studies using laser-based photo ionization have been carried out [23–26]. Vacuum-UV lamps such as deuterium or krypton discharge and electron beam pumped excimer light sources (EBEL) are an attractive alternative as photon sources. Arri et al. [27] reported about the coupling of TG–PIMS using deuterium discharge lamps and QMS to investigate the behaviour of polymer decomposition. The hyphenation of a thermo balance with QMS as well as an oa-TOFMS for the assay of plastics and crude oil samples using an EBEL as photon source has also been reported by the presenting authors [28–33]. In these cases, single photon ionization (SPI) has been applied. Thereby, the photon energy determines the selectivity and acts as an energetic threshold, since all molecules can be ionized, as long as their ionization potential is below the photon energy. However, SPI together with the utilized mass spectrometers exhibiting moderate mass resolutions is not suited to differentiate between isobaric molecules. A possibility to account for this is the coupling of TA with a separation technique, e.g., GC, in combination with MS (TG–GC–MS and Py–GC–MS) [34–36] for EGA. Due to different retention behaviour the compounds from the sample reach the ion source of the MS at different times. Consequently the number of simultaneously ionized compounds is reduced.

However, the on-line character offered by the utilization of MS should not be lost by implementing GC. An online coupling of the TG–GC–MS can be realized using valve systems in combination with sample loops allowing a quasi continuous operation of the TG–GC–MS [37–39] system. Another approach is the application of modulators. Based on a setup presented previously, in which a TG/DSC device has been coupled to SPI/time-of-flight MS (SPIMS), a quasi comprehensive chromatographic separation step has been included using a modulator to chop, trap, refocus and re-inject the continuous evolved gas stream from the TG/DSC system into the GC. The eluted substances are subsequently analyzed by SPIMS, leading to a comprehensive two-dimensional detection method (GC × SPIMS) for the thermally evolved gases. The principle of this setup, a comparison to previous TG–SPIMS measurements without GC separation, and first basic applications comprising diesel fuel and ABS copolymer are presented elsewhere [40]. In this article, further applications of this technique in the area of polymer characterisation are shown.

Instrumentation and experimental setup

A STA 409 PG Luxx thermo balance (Netzsch Geraetebau GmbH, Selb, Germany) was used for TA. The samples were heated in an Al_2O_3 crucible from ambient temperature of the furnace (40 °C) to 1000 °C with a heating rate of 10 K min^{-1} in an N_2 atmosphere. The gas flow through the STA was set to 60 mL min^{-1}. A heated transfer line (Horst GmbH, Lorsch, Germany) enclosing a deactivated fused silica capillary (2.5 m × 250 µm ID) connected the thermo balance with a GC (Thermo Trace GC × GC, Thermo Fisher Scientific Inc.). The flow through this transfer capillary amounted to 1.4 mL min^{-1}. The GC oven is equipped with a two stage liquid CO_2 spray modulator for GC × GC measurements. The injection system of the GC system was not used and disconnected from the gas flow. The fused silica transfer capillary was further connected without a split to a BPX 50 GC column (3 m × 250 µm, 0.25 µm, 50% phenyl polysilphenylene-siloxane film, SGE) and was guided through the column holder of the modulator close to the modulator nozzles as pictured schematically in Fig. 1. The modulation period is dependent on the heating rate of the TG system, which is thus limiting the separation power of the GC. During one modulation cycle (30 s), the GC column is cooled by the CO_2 stream approximately to −79 °C at the second stage, whilst the first CO_2 spray is turned off. The solutes are trapped at this cold spot and can be concentrated, whilst the carrier gas (N_2) sustains the gas flow to the MS. After 15 s, the first stage is switched on, stopping the flow of the sample substances, and the second stage is switched off. The trapped substances at the second stage are mobilized again due to the temperature of the GC oven (temperature program of the GC oven: holding at 40 °C for 2 min, 10 °C min^{-1} to 70 °C, holding at 70 °C for 1 min, 10 °C min^{-1} to 120 °C, holding at 120 °C for 25 min, 10 °C min^{-1} to 260 °C, holding at 260 °C for 45 min) and can be separated by the GC column, before they are guided through the gas inlet system into the MS. The gas inlet system consists of a completely heated 30 cm long aluminium cylinder acting as a short transfer line between the GC oven and the ion source of the MS. The GC capillary was inserted into the vacuum chamber through a heated steel needle.

For PI, VUV light with a centre wave length of 126 nm (9.8 eV) was generated by a homebuilt EBEL. The

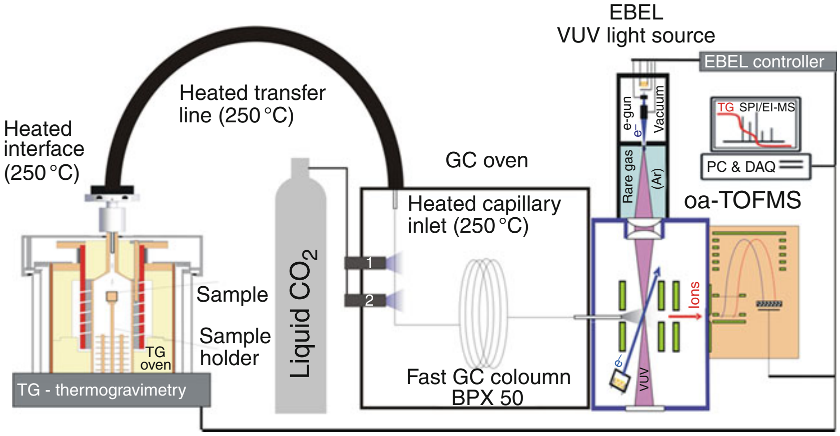

Fig. 1 Schematic drawing of the SPI/EI oa-TOFMS system

interface as well as detailed information about the EBEL is given elsewhere [41, 42]. The thermal degradation products of the polymers that were investigated in this study are well studied in literature and have already been investigated by our own group with TA–SPI-MS before, i.e., applying the same experimental setup without a GC in between. Therefore, the products are well known and the molecular ions are sufficient for identification of the main product peaks.

Results and discussion

The thermal decomposition behaviour of two polymers, namely Acrylonitrile–Butadiene–Styrene blended with polycarbonate (PC–ABS) as well as polyvinylchloride (PVC) has been investigated with the newly conceived measurement technique.

PC 0006 Bayblend T45 (PC–ABS blend)

Polymer blends and interpenetrating polymer networks such as copolymers are used to combine the properties of different polymers. For example PC is blended with a number of polymers including poly butylene terephthalate, poly ethylene terephthalate and ABS rubber to reduce the costs and to improve properties such as better processability and to reduce impact strength [43]. In this study, a PC blended with ABS has been investigated with the TG–GC × SPIMS technique. The TG and DTG curves are depicted in Fig. 2a. The maximum weight loss occurs at 445 °C, and the respective summed SPIMS spectrum (30 s, Fig. 2c) includes toluene (92 *m*/*z*), phenol (94 *m*/*z*), the isomeric xylenes (106 *m*/*z*), α-methylstyrene (118 *m*/*z*), benzenebutanenitrile (145 *m*/*z*) and benzene-C_5-nitrile (157 *m*/*z*) besides the base peak styrene (104 *m*/*z*). Focusing on the α-methylstyrene signal, it shows an unusually high signal for dehydrogenated α-methylstyrene (117 *m*/*z*) and consequently leads to the conclusion that there are overlapping peaks at 117 *m*/*z*. Figure 2b depicts the corresponding *m*/*z*-layer (117 *m*/*z*) with two signals overlapping in the *m*/*z* axis but separated clearly along the retention time axis. It also shows two different retention time behaviours due to the unequal molecules, namely, dehydrogenated α-methylstyrene and methylated benzonitrile. The two corresponding SPI mass spectra are pictured in Fig. 2d, e, respectively. The latter contains the α-methylstyrene signal and the expected isotope peak α-methylstyrene ($^{13}C{-}^{12}C_8{-}H_{10}$) beside the dehydrogenated α-methylstyrene (117 *m*/*z*). Figure 2e in contrast contains the MS signals of benzenebutanenitrile (145 *m*/*z*), benzenepropanenitrile (131 *m*/*z*) and the methylated benzonitrile (117 *m*/*z*), which obviously are thermal fragments due to the decomposition of ABS as they can also be determined by thermal degradation of pure ABS [40]. Due to the separation of these two species, a quantitative consideration of thermal fragmentation can be provided. Please note that the TG–SPIMS results can not differ between thermal fragmentation and fragmentation due to the ionization process. TG–GC × SPIMS in contrast provides results that lead to conclusions about the type of fragmentation. Signals deriving from thermal fragments differ in their retention time, whereas fragments due to the ionization process exhibit the same retention times as fragmentation takes place after the chromatographic separation.

For a more detailed look, two-dimensional plots of retention time versus temperature for selected *m*/*z* layers are displayed in Fig. 3. These are suggested to represent phenol (94 *m*/*z*), hydrogen reduced styrene/benzonitrile (103 *m*/*z*), styrene (104 *m*/*z*), C_2-alkylated benzenes (106 *m*/*z*), cresols (108 *m*/*z*), dehydrogenated α-methylstyrene/methylated benzonitrile (117 *m*/*z*), α-methylstyrene (118 *m*/*z*), vinylphenol/C_3-alkylated benzenes (120 *m*/*z*) and C_2-alkylated phenols (122 *m*/*z*). Using the knowledge of sample composition and the comparison of the *m*/*z* layers as mentioned above, identification of molecular species is now possible with this setup. Slides a, b and c show the

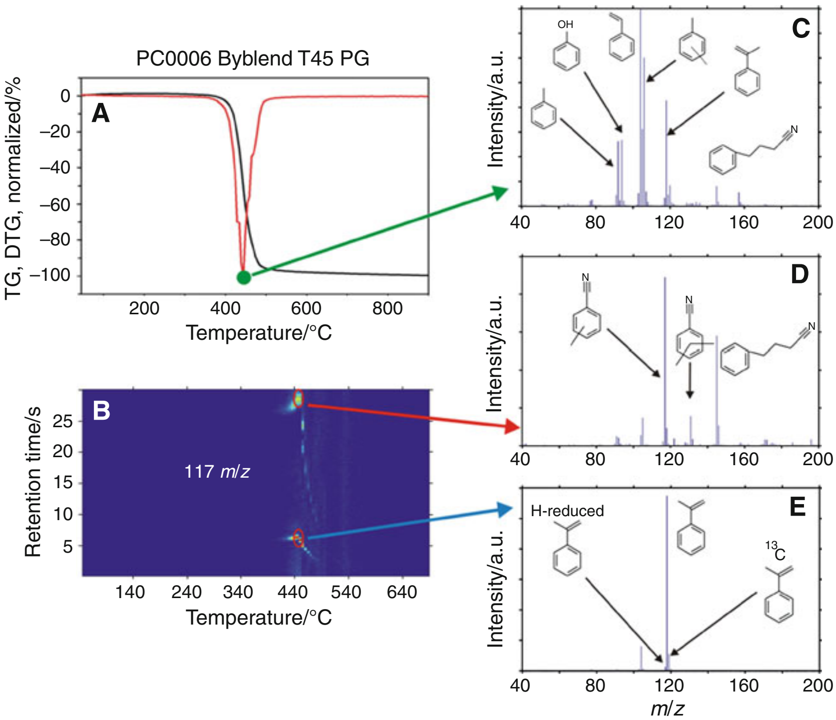

Fig. 2 **a** TG and DTG curve of PC–ABS blend, **b** retention times for the eluents with 117 *m*/*z*, **c** SPI-TOFMS spectrum at the temperature of the maximum mass loss and **d**, **e** SPI-TOFMS spectra recorded at different retention times at the temperature of maximum mass loss

typical retention behaviour for phenol and alkylated phenols. G and h correspond to dehydrogenated α-methylstyrene/methylated benzonitrile (117 *m*/*z*) and α-methylstyrene (118 *m*/*z*), respectively. Here, even without the SPI spectra it can be concluded, that the signal at the lower region of the layer (g) correspond to dehydrogenated α-methylstyrene, as it has the same retention time as α-methylstyrene (h) and therefore the signal at top has to be the methylated benzonitrile. The suspicion that benzonitrile (103 *m*/*z*) could also be a decomposition product of PC–ABS suggests itself, as the alkylated benzonitriles could be detected. However, the slides d and e demonstrate clearly that the signal at 103 *m*/*z* (layer d) can only be referred to the dehydrogenated styrene. Consequently, either benzonitrile is not evolving or the yield of the MS signal is lower than the detection limit provided by the device. The retention time value in addition to *m*/*z* information could be taken in account to address the ion signals in layer i. In comparison with the ion signal of C_2-alkylated benzenes (106 *m*/*z*) shown in layer f, the signal at the bottom is represented by C_3-alkylated benzenes. Compared to the phenol retention time behaviour presented in layers a, b and c, the signal in the middle may correspond to vinylphenol.

In addition to the improved resolving power of the TG–GC × SPIMS device, the limit of detection (LOD) should also be quite low. Due to the working principle of the modulator, substances are refocused to a sharp plug before they are re-injected into the GC device, which involves the entire evaporated part of the sample during 30 s. Consequently, the evolved compounds are preconcentrated, whilst the noise level remains constant. Furthermore, as compounds are separated along the GC column, the level of so-called chemical noise which can be related to sample impurity can be reduced. The online measured signal intensity of 10 ppm toluene standard gas in nitrogen (not modulated) was used as reference point for quantification. To determine the LOD of styrene, the cross section for SPI of styrene at 126 nm relative to toluene was measured. With the calculated styrene and toluene concentration *c*, the measured ion signals *S*, and the noise variance σ^2, a LOD of 400 ppt for styrene and 500 ppt for toluene could be evaluated [40], according to the IUPAC definition [44]:

$$\mathrm{LOD} = \frac{2 \cdot \sigma}{|S - B|} \cdot c$$

wherein *B* is the averaged noise.

PVC

PVC is one of the most common plastics worldwide. It is used in construction and building materials including window profiles, flooring, roofing membranes, pipes and plumping, as well as magnetic stripe cards and as isolation for electric cables etc. The waste management of PVC, which is also often carried out by thermal waste combustion, is one the most discussed and reported topics in the last decade. The investigation of the thermal decomposition and degradation products of PVC has been reported circumstantially elsewhere [45–47]. Marongiu et al. [48]

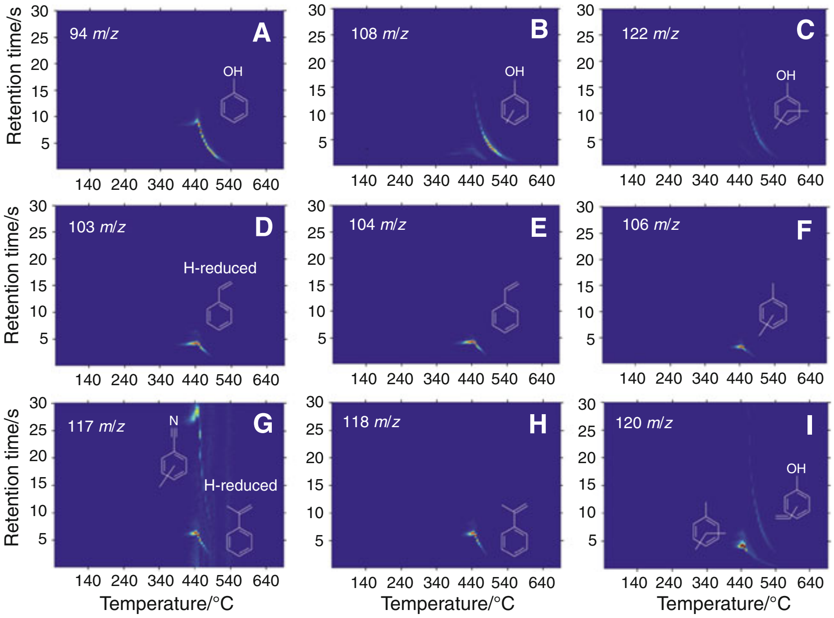

Fig. 3 Two-dimensional plots of retention time versus temperature for different mass traces for the thermal decomposition of PC–ABS blend. GC separation supports the identification of the compounds and reveals additional isobaric species

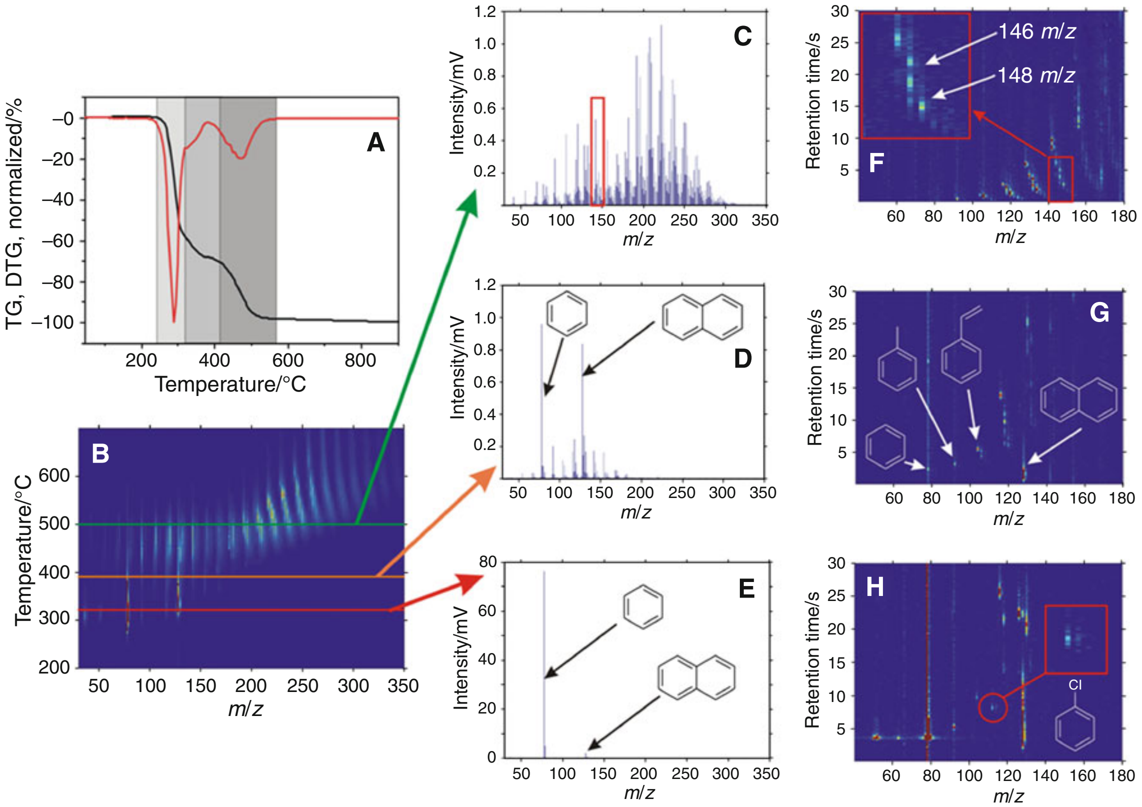

Fig. 4 **a** TG and DTG curves of PVC, **b** two-dimensional plot of temperature versus *m*/*z* (recorded with SPI-TOFMS) for the thermal decomposition of PVC depicting the whole TA at a glance, **c** SPI-TOFMS spectrum recorded at 500 °C, **d** SPI-TOFMS spectrum recorded at 390 °C, **e** SPI-TOFMS spectrum recorded at 320 °C, **f–h** retention time as a function of *m*/*z* at the same temperatures as in **c–e** depicting the two-dimensional detection with comprehensive GC × SPI-TOFMS for EGA in the thermal decomposition of PVC

described the thermal degradation of PVC through a semi-detailed kinetic model. PVC is believed to decompose in a two stage degradation, which is reflected in the TG and DTG curves shown in Fig. 4. In the first step, occurring at about 300 °C, HCl is eliminated and a polyolefinic structure is left as residue [31]. From the polyolefinic moieties mainly benzene is formed beside naphthalene and toluene as it is presented in Fig. 4b. Bockhorn et al. [46] proposed a Diels–Alder-type reaction for the formation of benzene moieties and a radical chain mechanism for the dehydrochlorination (DHC) process. At higher temperatures, the residual polyolefin structure is believed to undergo cross-linking reactions, which subsequently break apart during the further decomposition process, and release a very complex mixture of alkylated monocyclic as well as condensed polycyclic aromatic compounds due to the temperature raise. The final residue then represents a char-like refractory material. The soft ionization mass spectrum as well as the corresponding temperature layer, recorded at 320 °C (Fig. 4e, h), depict predominantly benzene (78 *m*/*z*) and naphthalene (128 *m*/*z*) as organic decomposition products in accordance with the literature. Chlorobenzene (112/114 *m*/*z*) is also detected, due to the presence of high amounts of chlorine in the first decomposition step. The spectra at 390 °C (Fig. 4d) and at 500 °C (Fig. 4c) as well as the corresponding two-dimensional temperature layers (Fig. 4g, h) represent the decomposition results of the cross-linked polyolefinic structure. Here, a complex pattern of aromatic carbon structures evolves. In our study, we were able to detect the homologous series of benzenes, indanes, naphthalenes, biphenyls, fluorenes and phenanthrenes. In most cases, the C_1-substituend congener was the most abundant one. According to theory, the profile of the substitutions is determined by the cross-linked polyolefin. Jiao et al. as well as Adam et al. [25, 47] reported about chlorine substituted benzenes (e.g., dichlorobenzene 146/148/150 *m*/*z*) and phenols, respectively. Although in our study MS signals at 146 and 148 *m*/*z* could be detected (Fig. 4c, f), these signals are assigned to alkylated indanes (146 *m*/*z*) and alkylated benzenes (148 *m*/*z*). As these peaks show a dislocation along the retention time axes in the temperature layer, the measured signals can not belong to an isotopic pattern and therefore are related to two different chemical species. Under the current experiment conditions, neither chlorinated benzenes (PCBz) nor chlorinated phenols (PCPh) and aliphatics have been detected in the second pyrolysis step. In contrast to the preceding reported flash-pyrolysis experiments, we used an N_2 atmosphere, where the formation of phenol and substituted phenols is suppressed. The absence of the PCBz and chlorinated aliphatics (e.g., dichloroethylene) can be related to the experimental conditions, whereas the rapid heating of the sample to temperatures above 600 °C (flash-pyrolysis experiments), the previously described DHC process is overridden. Consequently, the breakdown of the PVC backbone occurs in the presence of high amount of chlorine, resulting in formation of chlorinated aromatic and aliphatic species.

Conclusions

Comprehensive EGA in TG using a thermo balance coupled to GC × SPIMS (TG–GC × SPIMS) provides the opportunity to obtain TG relevant data as well as an improved resolution power to separate isobaric molecular structures of complex samples without losing any fraction of the samples. In addition, this solution is not associated with any extent of the entire measurement time. The assignment of the substance pattern to distinct species can be improved and hitherto undetected compounds have been found in the evolved gases from the thermal degradation of polymers. For future applications, just by turning off the VUV light from the EBEL and turning on the electron filament of the ion source the ionization process can be switched from SPI to EI, providing additional information concerning the structure of the compounds.

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