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Characterization of ultra-thin polymeric films by Gas chromatography-Mass spectrometry hyphenated to thermogravimetry[☆]

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A B S T R A C T

Polymeric materials are widely employed to build up tunable nanomasks for nano-patterning technologies. Ultrathin polymer layers are involved in this process. A Thermo Gravimetric Analysis–Mass Spectrometry (TGA-GC-MS) method was optimised, validated and successfully applied to investigate the thermal behavior of ultrathin poly(styrene-*r*-methylmethacrylate) random copolymer layers P(S-r-MMA) grafted to a silicon wafer surface. The interface between TGA and MS is highly versatile since many instrumental parameters (i.e. loop volumes, pulsed sampling frequencies, acquisition modalities, carrier gases, flow rates) can be easily tuned. Samples featuring substantial scale difference, i.e. bulk materials, thick films (few μm thickness), thin and ultrathin films (few nm thickness) can be analyzed without any instrumental modification or sample pretreatments. The TGA-GC-MS analysis was used to highlight subtle differences in samples featuring different thicknesses, in the 2–6 nm range, and subjected to various thermal treatments, thus indicating that this hyphenated technique could be successfully applied to the investigation of ultrathin polymer films.

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1. Introduction

Thin film-based technology is at the core of many fast developing research and industrial fields, including the design of membranes and microelectronic devices. For the latter application, polymeric materials, and in particular self-assembling block copolymers, are employed to build up tunable nanomasks for subsequent nano-patterning processes. This approach is widely investigated since it is emerging as a simple, cost-effective, versatile, and scalable technique to generate scaffolds and templates for the fabrication of nano-structured devices [1,2]. In more details, the technology leading to lithographic nanomasks involves a multi-step thermal procedure [3–5] in which a block copolymers thin film (30 nm) is deposited on an ultra-thin layer (2–9 nm) of a grafted

functional random copolymer (RCP), which acts as surface modifier. Accordingly, the development of technical tools able to deep into the structure, thermal stability and degradation characteristics of the polymeric layer at the different steps of the nanopatterning process would be highly desirable to optimize the processing conditions including the process robustness.

The use of hyphenated thermal and mass spectrometric techniques is well established and many studies were addressed to the investigation of the polymer structures under distinct thermal conditions [6–8]. However, in most cases, the thermal conditions were set to induce a complete polymer degradation. Comparatively few studies were devoted to the assessment of the effects of relatively mild thermal treatments on the final polymer structure and stability [9–12]. This is particularly true when dealing with thin films. In most cases, the thermal studies were performed by TGA-MS (Thermo Gravimetric Analysis–Mass Spectrometry) combination [13–15]. However, this approach is affected by several limitations. The entire amount of the evolved gases is directly introduced into the MS detector, including the purge gas, which often has oxidative characteristics. This accelerates the deterioration of the ion
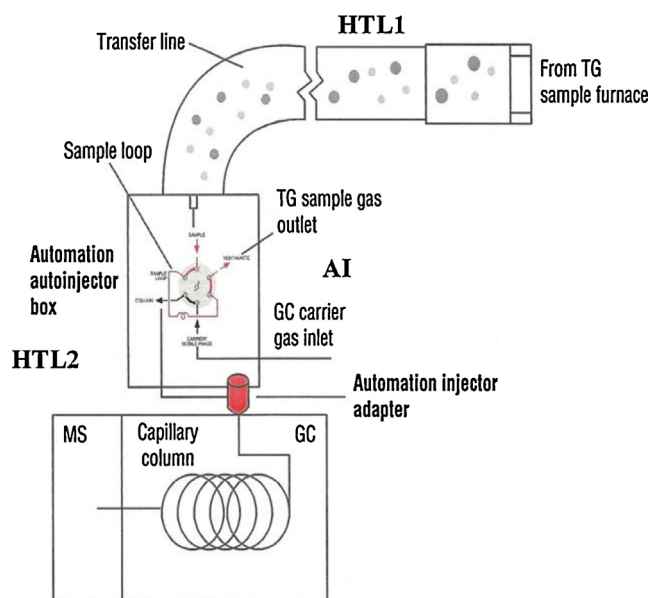
Fig. 1. Scheme of TGA-GC-MS interface configuration.

source thus affecting the analyzer performance [16]. In addition, the mass spectra include the entire set of products deriving from the thermal decomposition, thus further reducing the analytical performance. The addition of a Gas Chromatographic (GC) stage between TGA and MS could be highly effective in improving the analytical performance for material amounts to be analyzed at the nanoscale level. In the resulting TGA-GC-MS configuration, the TGA can operate to impart a precise and reproducible thermal history to the samples. Hyphenation of TGA with GC-MS allows the separation of the evolved gas mixture into single components [17,18] but in literature an application to ultra-thin film does not exist.

In the present work, a TGA-GC-MS method was optimised, validated and successfully applied to investigate the thermal characteristics of P(S-r-MMA) random copolymers, commonly used to neutralize the silicon wafer surface prior to block copolymer deposition and self-assembly. The random copolymers were studied in the form of bulk materials, thick films (few μm thickness) and ultra-thin film (few nm thickness). The proposed technique showed the capability to precisely and accurately discriminate the different thermal degradation behaviors.

2. Material and methods

2.1. Materials

Two hydroxyl end-functionalized random copolymers P(S-r-MMA) with styrene fraction (XS) of 0.62 (Number average molar mass Mn = 13500 g mol^{-1} and Poly Dispersity Index PDI = 1.26) and XS = 0.58 (Mn = 11400 g mol^{-1}, PDI = 1.64) were purchased from Polymer Source Inc. and used as received. These RCPs were marked as R62 and R58 where R stands for random and the number represents the percent styrene unit. KHCO$_3$ and all the other reagents and solvents were analytical grade and were purchased from Sigma–Aldrich.

2.2. TGA-GC-MS interface setup

Fig. 1 shows the interface (Automation s.r.l, Abbiategrasso, Mi, Italy) utilized in order to connect the GC-MS instrument to the TGA. The apparatus consists of three components, namely (i) a heated transfer line (HTL1) from TGA to an automatic gas sampling system

(autoinjector), (ii) an autoinjector (AI) equipped by a switch valve and a prefixed volume loop, and (iii) a second heated transfer line (HTL2) from the AI to the GC-MS injector port.

The two transfer lines (HTL1 and HTL2) are made by deactivated molybdenum-alloyed austenitic stainless chromium-nickel steel capillaries and are covered with a heating thermo-mantle to avoid gas condensation and to ensure uniform heating. The heating is performed and controlled by a series of thermocouples.

The AI controls the repetitive pulsed transfer of known amounts of the evolved gas, with the desired frequency, in the injector of the GC-MS instrument by a system consisting of a multi-position valve, switched by a nitrogen gas flux. The apparatus is equipped with a prefixed volume (from 0.5 to 5.0 mL) loop that can be interchanged without turning off the TGA and the GC.

The second heated transfer line (HTL2) from the AI enters directly in the GC-MS injector since it intercepts the carrier gas that flow in the GC column. The duration and frequency of the sampling of the evolved gas from the TGA are controlled by the LAN unit. Moreover, the above set up allows analysis in different modalities to be performed since the gas stream from TGA can be sampled either at regularly prefixed intervals or at different intervals during the thermogravimetric experiment.

2.3. Films preparation and characterization

The detailed procedure for sample preparation was previously reported [5]. Briefly, oriented silicon (1 0 0) substrates with a 50 nm thick thermal silicon dioxide layer were used as supports. The oxidized substrates (about 1 cm^2 surface) were cleaned with Piranha solution and rinsed in H$_2$O and dried under N$_2$ flow. Then, a solution of P(S-r-MMA) (18.0 mg in 2.0 ml of toluene) was spun on the substrates and the samples were thermally treated at different temperatures to promote the grafting reaction. The non-grafted P(S-r-MMA) fraction was removed by washing the samples with toluene using an ultrasonic bath.

The thickness of all the polymeric films was measured by means of a M-200U spectroscopic ellipsometer (J. A. Wollam Co. Inc.) using a Xenon lamp at 70° incident angle.

2.4. TGA-GC-MS copolymer characterization

All the TGA and TGA-GC-MS analyses were performed using a Mettler TGA/SDTA 851^e purged with a steady flow of inert gas at a scanning rate of 20 °C min^{-1} from room temperature to 1100 °C. For bulk materials, each sample was placed in an open alumina crucible. The polymeric films on the substrate were directly placed on the thermo-balance plate.

The GC-MS analysis was performed using a FINNIGAN TRACE GC-ULTRA and TRACE DSQ. The GC separation was carried out using a Phenomenex DB5-5ms capillary column (30 m, 0.25 mm i.d., 0.25 μm thickness). The injector temperature was set at 250 °C in the splitless mode and helium was used as carrier gas at a constant flow of 1.0 mL min^{-1}. The MS transfer line and the oven temperatures were set at 280 and 150 °C, respectively.

The evolved gas from TGA was transferred to the GC-MS using the interface described in the previous section. The optimised operating conditions were: HTL1 and HTL2 temperatures at 200 °C, AI temperature 150 °C, sampling frequency 1.0 min^{-1}. The sampled gas from the loop to the waste was switched after 10 s and the capacity of the injection loop was 2.5 mL.

The MS signal was acquired in EI + mode with ionization energy of 70.0 eV and at the ion source temperature of 250 °C. The acquisition was performed both in full-scan mode, in the 20–350 m/z range and in Single Ion Monitoring (SIM) mode by acquiring the signals corresponding to styrene (S) at m/z = 104, methylmethacrylate (M) at m/z = 100, of the dimers MM at m/z = 200, MS at m/z = 204, SS at
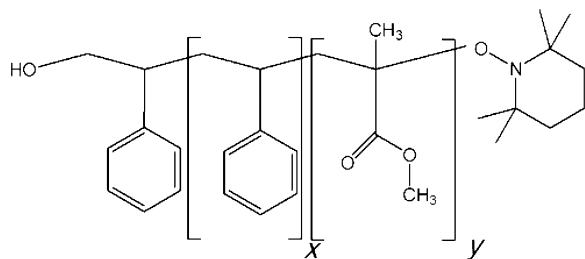
Fig. 2. Schematic representation of the hydroxyl terminated P(S-r-MMA).

$m/z = 208$ and of the trimer SSS at $m/z = 312$. Moreover, the signals of TEMPO and toluene were registered at $m/z = 156$ and 92, respectively. The identification of the evolved products was performed by comparison of the retention times and spectra of commercial standards analyzed in the same experimental conditions.

2.5. Validation procedure

The validation procedure was performed by the analysis of four different amounts of $KHCO_3$ (0.2, 0.5, 1.0, 3.0 mg) with the TGA-GC-MS setup optimized for the analysis of thin films as above reported. Each amount of $KHCO_3$ was heated at three different rates, namely 10.0, 20.0, and 40.0 °C min^{-1} with a He flow of 50 mL min^{-1} as purge gas in the TGA. All the experiments were performed in triplicate.

The acquisition was performed both in full-scan mode, in the 20–200 m/z range, and in SIM acquisition mode at $m/z = 44$ in order to monitor the CO_2 evolution. The SIM signal was used in the quantification process by the integration of the relative chromatographic peaks.

Moreover the standard deviations that affect the determination of the intensities and of the maximum of the ultrathin samples were evaluated.

The film analyses were performed in triplicate, and the standard deviation that affects the signal intensities was obtained by using the signal intensity corresponding to maximum of the degradation curve scaled for the volume of the grafted polymer to take into account the variability of the sample dimensions.

3. Results and discussion

Two hydroxyl end-functional P(S-r-MMA) R58 and R62, used for the surface neutralization step in the nanopatterning process, were investigated. These P(S-r-MMA) copolymers where prepared, with low molar mass and relatively narrow molar mass distribution, by a living free-radical polymerization technique, using the 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as radical controller. Accordingly, copolymers, with the structure reported in Fig. 2, terminated on one end with a moiety containing a hydroxyl (OH) group and on the other end with the TEMPO group, were obtained.

The studied samples were fabricated through a grafting reaction, which occurs between the HO—Si substrate and the hydroxyl groups of the functional copolymers. Then, the grafted substrates were washed with toluene to get rid of all the residual not bonded polymer chains. After this process, the thickness of the samples decreased from about 30 nm to about 2-6 nm, depending on the density of the polymeric chains effectively grafted to the substrate during the annealing process.

3.1. Interface setup development

Preliminary analyses were performed on bulk R58 and R62 to test the TGA-GC-MS setup on a simplified system without sensitivity problems. To guarantee the performances of the global setup we initially focus on the synchronisation of the working conditions of each instrumental components [18], i.e.:

(i) the chromatographic conditions
(ii) the acquisition mass spectrometric setup
(iii) the TGA heating scanning conditions
(iv) the duration and frequency of the auto-injector sampling step

Starting from the chromatographic components, a preliminary knowledge of the molecules that may evolve during the sample heating is necessary. From literature data [9], the formation of several degradation products was expected, including the TEMPO moiety, deriving from the terminal groups, M and S monomers, dimers and trimers as well as hybrid oligomers.

Several scouting experiments were performed by heating 1.0 mg of the bulk materials at a rate of 20.0 °C min^{-1} from room temperature to 500 °C. The mass spectrometric acquisition was set in SIM mode at the characteristic m/z values of TEMPO, M, S, SS, MM, MS, SSS, SMS, SMM. In addition we acquired the m/z signal corresponding to toluene, the solvent used in the synthesis of the macromolecules, which is still present in the commercially available samples. In the tested conditions, only TEMPO, S, and M monomers and toluene were detected whereas dimers, trimers or other oligomers, including the hybrid ones, were not observed. Consequently, in the following, only the isocratic condition was adopted. This choice is particularly suitable because it allows a very short interval between two consecutive injections to be employed, due to the lack of the GC column cooling time, thus finally resulting in an increased resolution of the product evolution profile along the temperature scale. Nevertheless, the mass acquisition conditions were set both in SIM and in full scan modes.

Different TGA heating rates were evaluated (10–40 °C min^{-1}) to find the best compromise between the analyte amount in the evolving gas, which increases as the heating rate increases, and the detection resolution which decreases as the heating rate increases. In addition, this choice should parallel the setup of the auto-injector parameters. In fact, the auto-injector controls the sampling and pulsed transfer of known amounts of the gas that evolves from TGA, at the required frequency, in the GC-MS injector by a multi-position valve. Each sampling is performed by a two-step procedure, including a collection step, in which the gas, that comes from TGA, fills the loop and an injection step in which the gas collected in the loop is transferred to the GC column and, at the same time, the gas deriving from TGA is switched to the waste. The frequency of the pulsed injection and the duration of the two steps are the parameters to be matched in order to synchronize the interface injection and the chromatographic run. This synchronization was ultimately obtained by setting the chromatographic run in the isocratic mode, the oven temperature at 150 °C, the TGA heating ramp at 20.0 °C min^{-1} from room temperature to 500 °C and the sampling frequency at 60.0 s^{-1}.

Provided these optimized conditions, the loop volume was 1.0 mL and the gas flow from TGA was of 50.0 mL min^{-1}. Finally, 10 s time of each collection step was employed to assure that the loop was overfilled without memory effects.

3.2. Bulk copolymer characterization

Fig. 3 collects the SIM TGA-GC-MS chromatograms obtained for toluene (92 m/z), TEMPO (156 m/z), M (104 m/z), and S (100 m/z) for the bulk R58 and R62 copolymers. The same figure reports the relevant Derivative Thermo Analysis (DTA) profiles (dashed lines). The chromatograms are the result of twenty-three repetitive injections, performed every 60 s, of 1.0 mL of the gas that evolved from TGA furnace. In this way, the gas evolution profiles had a resolution of 20 °C. The synchronization was successfully achieved since no peak
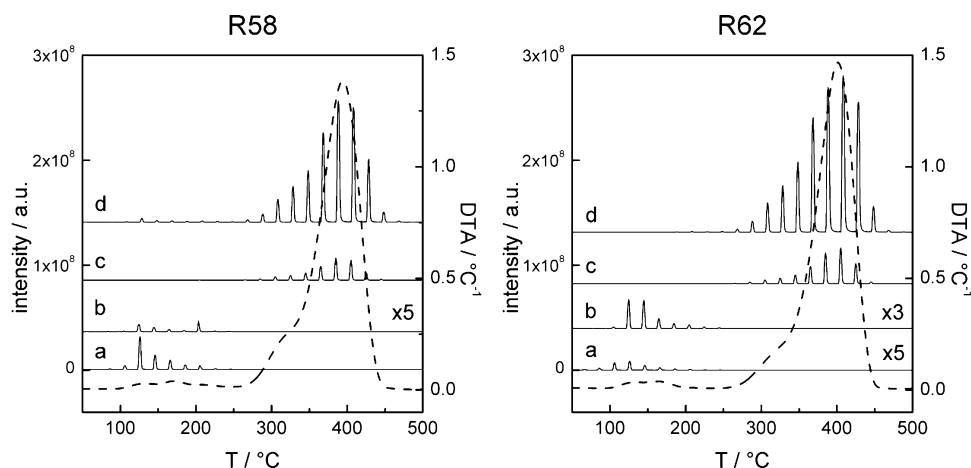
Fig. 3. Analysis of the copolymers in the bulk form. The dashed line is the DTA profile obtained for 5.0 mg of each copolymer (heating rate 20 °C min^{-1}). Continuous lines are the SIM TGA-GC-MS chromatograms obtained for (a) toluene, (b) TEMPO, (c) M, (d) S by analysis of 1.0 mg of each copolymer.

overlap was registered in subsequent injections. Consequently, the SIM chromatograms can be reported in the same temperature scale of DTA profile by appropriately re-scaling the chromatographic time axis over the temperature heating rate and the gas transfer line travel times.

A straightforward correspondence among the DTA peaks and the SIM chromatograms was observed. Comparison of the DTA thermograms with the SIM chromatograms allows identifying the species, that evolve in the temperature range between 130 and 200 °C. In particular, at 160 °C some S monomers start evolving, whereas M evolution starts from 170 °C. At higher temperatures, namely in the 240–450 °C range, the main degradation process occurs corresponding to the parallel loss of both S and M occurs. The styrene evolution closely parallels the TEMPO profile thus indicating that the bond between the polymer and the nitroxide is a weak link [8]. Moreover, some toluene was detected in correspondence of the low temperature weight loss due to the presence of some residual reaction solvent entrapped in the polymeric materials.

3.3. Thin films copolymer characterization

Ultra-thin films (thickness around 5 nm), obtained through the grafting of the random copolymers to the activated silicon surface, were directly placed on the TGA plate and analyzed using the same TGA-GC-MS set up conditions described for the bulk samples. It is important to point out that, due to the geometric constraints of the TGA furnace, the maximum size of the sample that can be analyzed is 1.0×1.0 cm^2.

Fig. 4 (upper row) illustrates the SIM chromatograms relevant to the S and M evolution. It is evident that further refinement is necessary to increase sensitivity and the signal to noise (S/N) ratio because only the S signal can be traced, featuring a poor sensitivity, whereas the M signal is lost in the background. The set up improvement was obtained both by increasing the loop size from 1.0 to 2.5 mL and by using helium instead of nitrogen as the TGA carrier gas. The 2.5 mL size loop represents the best compromise between the amount of injected material and the resolution loss due to the parallel peak width increase. As helium is the carrier gas employed in the GC-MS analysis, its use as carrier in the TGA allows the S/N ratio to be increased, because the auto-zero operation, performed at the start of the analysis, rules out the gas contribution in the background. Under these new conditions, the obtained SIM profiles are reported in the second row of Fig. 4. The S/N ratio value increases from about 1 to 4 and from 2 to 10 for M and S, respectively. In addition, a higher sensitivity is obtained.

3.4. TGA-GC-MS performance validation

Since the study of ultra-thin films is critical, because of the very low amount of analytes, a validation of the system performances is needed to assure statistical significance of the data. The validation process should be extended to several aspects of the analytical procedure. In particular, a high flow stability of the evolved gas through the entire instrumental apparatus is necessary to ensure reproducible results [15,19]. In addition, the intensity of the MS signal should not be affected by the heating rate of the TGA analysis [19,20]. Finally, the effect of the TGA-GC-MS coupling system on the TGA calibration and the method repeatability need to be investigated as well.

A modified validation procedure [12,18] was employed to quantify the performance of the TGA-GC-MS system. Accordingly, the calibration and the system performance evaluation were assessed by heating different amounts of a salt, that presents a well-known stoichiometric thermal decomposition reaction, and quantifying the evolved gas by the MS [20]. A high purity KHCO$_3$ sample was selected since it decomposes through a well-defined stoichiometric reaction in which H$_2$O and CO$_2$ only are simultaneously evolved [20]. Four different amounts of KHCO$_3$ (0.2, 0.5, 1.0, 3.0 mg) were employed using the TGA-GC-MS set up adopted for the thin film analysis. Three TGA heating rates, namely 10.0, 20.0, and 40.0 °C min^{-1} were tested and all the experiments were performed in triplicate.

As a typical example, Fig. 5 collects both the DTA curve and the chromatogram of CO$_2$ acquired in SIM mode (m/z = 44) by heating 3.0 mg of KHCO$_3$ at 20.0 °C min^{-1}. The sum of the areas of the chromatographic peaks was calculated and correlated to the theoretical amounts of CO$_2$ by the ordinary least squares linear regression. In this way, a calibration curve was obtained for each different heating rates. Table 1 reports the calculated equations together with the correlation coefficient values (R^2). The high correlation factors point to a high linearity of the mass chromatographic response respect to the amount of the gas evolved. Although the response linearity is fundamental to determine and quantify the CO$_2$ evolved in unknown samples, in the present context can be taken as a direct proof of the flow stability through the entire TGA-GC-MS system [20].

These data can be also employed in the estimation of the response factors of the instrument, defined as the ratio between the peak area and the amount of CO$_2$ expected from the stoichiometric decomposition of each of the KHCO$_3$ sample amounts. The mean response factor values (Table 1) result accurate since
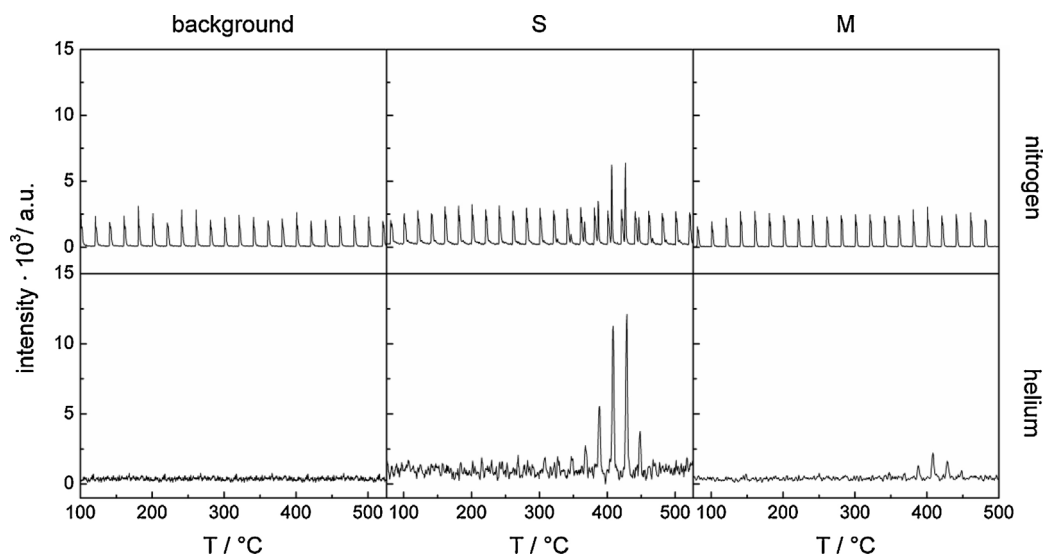
Fig. 4. Effect of the change of gas in the TGA furnace on the sensitivity and on the S/N ratio value for the determination of M and S evolution profiles. The samples were ultrathin films (5.5 nm of thickness) of R62 materials grafted at 220 °C for 15 min. The first raw reports the chromatograms obtained with nitrogen as the TGA carrier gas. The second raw reports the chromatograms obtained with helium as the TGA carrier gas.
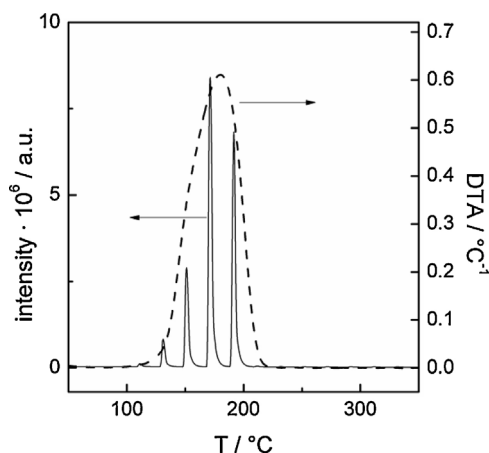

Fig. 5. DTA profile (dashed line) obtained for 3.0 mg of $KHCO_3$ with a temperature heating rate of 20.0 °C min^{-1}. The continuous line represents the SIM GC–MS chromatogram (44 m/z) obtained for CO_2 evolved during the same temperature program.

Percent Relative Standard Deviation (%RSD) values were determined to be lower than 4%. These results demonstrate that the interface, transfer line and sampling apparatus are adequate [15].

In addition, since different heat and mass transfer conditions are involved in the experiments using different TGA heating rates,

the low % RSD of the response factors indicates that mass transfer phenomena play minor effects on the chromatographic performances. Consequently, the above TGA-GC-MS analysis results under chemically controlled conditions.

The influence of the TGA-GC-MS coupling system on the TGA calibration was evaluated by monitoring the precision and the accuracy of weight losses and decomposition temperatures of the $KHCO_3$, in the absence and presence of the coupling system. The values of weight losses and decomposition temperatures at the various heating rates of TGA without the coupling system were taken as the reference values. The results of a t-test and F-test, at 95% confidence level performed on the data reported in Table 1, indicate that there is no significant systematic error or variance introduced by the TGA-GC-MS coupling system.

Finally, system repeatability was examined by monitoring repetitive sampling pulses of an inert purge gas. The area of repetitive short sampling pulses of gas at increasing TGA furnace temperature showed a %RSD lower than 1.8%. A % RSD lower than 0.36% was observed for the sampling period, thus indicating that the method features a high degree of repeatability.

3.5. Method applications

The method reliability was tested on films differing in thickness and thermal budget. Fig. 6 reports the S and M profile evolutions for the copolymer R62 spin coated from a concentrated solution onto the silica substrate (sample named "thick film"), the copolymer

Table 1
Data obtained in the validation procedure.

| Heating Rate (°C min^{-1})	Calibration Curves	R^2	Mean Response Factors (peak area mg^{-1}) ± %RSD	% Weight loss		Decomposition temperature (°C)	
				Without interface	With interface	Without interface	With interface
10.0	$y = 3.1\ 10^6$ $x + 9.6\ 10^5$	0.9980	$5.26\ 10^6 \pm 4.0\%$	31.47 ± 0.53	31.26 ± 0.86	175 ± 5.5	177 ± 5.7
20.0	$y = 1.2\ 10^7$ $x + 1.3\ 10^6$	0.9977	$2.66\ 10^7 \pm 3.8\%$	31.25 ± 0.67	31.14 ± 0.74	181 ± 4.9	182 ± 5.1
40.0	$y = 1.5\ 10^7$ $x + 1.6\ 10^6$	0.9969	$2.57\ 10^7 \pm 3.4\%$	32.02 ± 0.55	31.78 ± 0.67	192 ± 4.8	191 ± 5.3
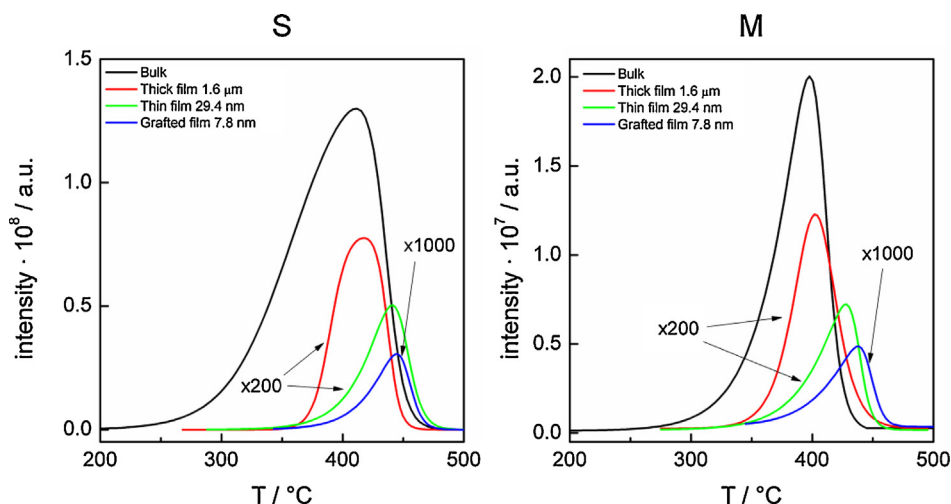
Fig. 6. S and M evolution profiles obtained from R62 copolymer samples differing in thickness and thermal history as well as the R62 bulk sample.

spin coated onto the silica substrate from a dilute solution (sample named "thin film"), and the thin film thermally treated at 270 °C for 15 min, to promote the grafting reaction, and washed to eliminate the not-bonded residual polymer (sample named "grafted film"). Fig. 6 reports also the monomer profiles for the bulk sample, for comparison purposes. In all cases, the measurements were performed using the set up optimized for the analysis of the thin films. In addition, the various profiles were build up by joining the points relative to the maxima of successive styrene or methylmethacrylate peaks in the relevant chromatograms in order to obtain a continuous curve describing the overall monomers evolution as a function of temperature. A decrease of the film thickness induces an increase in the thermal stability of the relevant samples as revealed by the translation of the thermal degradation profile toward higher values along the temperature scale. It is important to notice that the peak intensity of the sample featuring a thickness of 7.8 nm is still remarkable.

To further deep into the detection characteristics of ultra-thin films, several samples were obtained by performing the grafting reaction at temperatures ranging from 270 to 170 °C while still maintaining a grafting time of 15 minutes. As the grafting rate decreases with decreasing the grafting temperature, a series of ultrathin film samples with progressively smaller thickness from 5.0 nm at 270 °C to 2.6 nm at 170 °C are obtained.

Fig. 7 shows the evolution profiles of S and M for R58 copolymer ultrathin films. Very similar results were obtained for R62. From an analytical point of view, the comparison of the signal intensity for the various samples leads to a rough estimation of the thickness limiting detection which corresponds to a random copolymer layer of about 4 nm for M. Conversely the styrene signal is still well evident in 2.6 nm thick samples, even taking into account that the standard deviation of the intensity data is ±2%. This difference can be accounted for by considering that the M sensitivity is about five times lower than S in the mass spectrometric detection.

It is interesting to note that the data reported in Fig. 7 highlight also the capability of the system to detect subtle variation in the thermal characteristics of the grafted layer. Fig. 8 shows the evolution profiles corresponding to the chromatograms of Fig. 7. It is quite evident that the grafting temperature significantly affects the thermal characteristics of the grafted layer. The maximum of the thermal degradation profile moves toward higher temperatures when increasing the grafting temperature (Fig. 8). In particular, the maximum of the thermal degradation profile of the sample grafted at 170 °C results about 50 °C lower than the sample grafted at 270 °C. In contrast, the shape of the degradation profile results
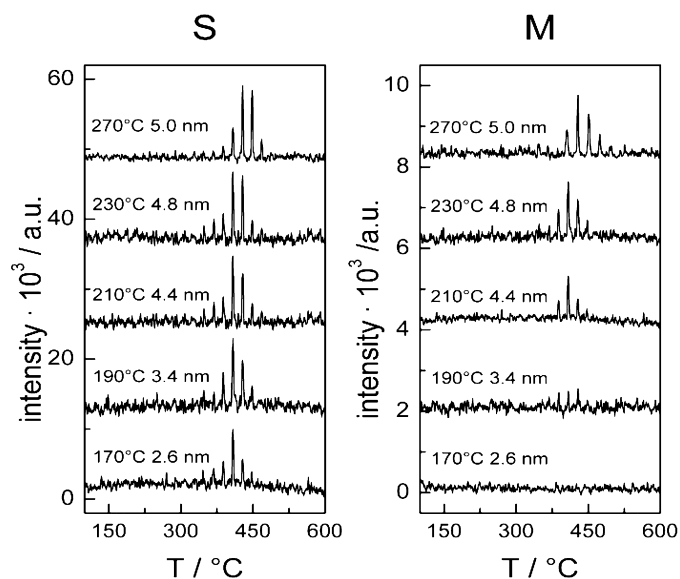

Fig. 7. S (left side) and M (right side) chromatograms obtained from R58 copolymer samples with different thickness.
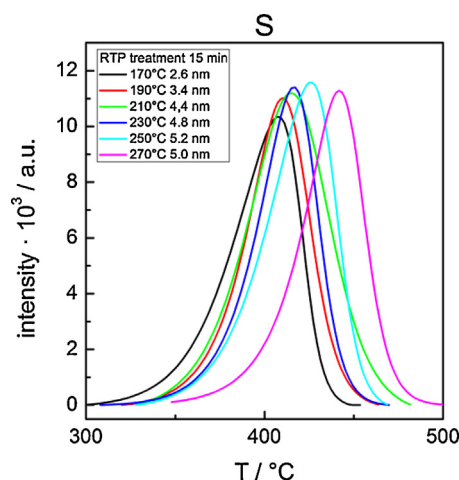

Fig. 8. Normalized S evolution profiles obtained from R58 copolymer samples with different thickness.

mainly unaltered. In this case the standard deviations that affect the determination of the maximum of the degradation profiles is $\pm 5\,^\circ$C.

4. Conclusions

The optimised TGA-GC-MS method allows a deep investigation of the thermal behaviour of P(S-r-MMA) copolymer materials to be performed either in bulk or in film form. A complete validation procedure was carried out and significant differences among the samples differing in their thickness and thermal history were noticed. The described method was demonstrated to be highly effective in the analysis of thin films without requiring any complex or time-consuming sample pretreatments. The interface between TGA and MS results highly versatile since many instrumental parameters (i.e. loop volumes, pulsed sampling frequencies, acquisition modalities, carrier gases, flow rates) can be easily tuned and materials can be analyzed on substantially different scales (bulk materials, thick, thin, and ultrathin films) without any instrumental modification. Moreover the TGA-GC-MS analysis was demonstrated to effectively highlight subtle differences in the thermal behavior of the samples even in the case of ultrathin films. In particular these results indicate that this technology could be widely adopted to systematically investigate the thermal characteristics of ultrathin films, representing an extremely powerful tool that allows correlating their thermal evolution with the specific morphological state and/or with the peculiar preparative conditions.

Acknowledgment

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