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A novel analytical pyrolysis device applicable for measurements of less volatile pyrolyzates

Hirohisa Kano[a], Takahiro Okamoto[a], Shinya Kitagawa[a], Yoshinori Iiguni[a], Hajime Ohtani[a,*], Hiroshi Ito[b], Koichiro Iwai[a,b], Minoru Kuno[c]

[a] *Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

[b] *Toyota Central R&D Labs., Inc., Nagakute, Aichi, 480-1192, Japan*

[c] *GL Science Inc., 237-2, Sayamagahara, Iruma, Saitama, 358-0032, Japan*

ABSTRACT

A novel analytical pyrolysis device suitable for the measurements of the less volatile pyrolyzates was developed. This device is comprised of a pyrolysis unit based on the vertical microfurnace pyrolyzer and a movable pyrolysis tube made of stainless steel. The upper side of the pyrolysis tube is first set at the heated center of the pyrolysis unit. A polymer sample in a sample cup is introduced into the heated center and pyrolyzed under the flow of nitrogen carrier gas. The pyrolyzates are then transferred to the bottom side of the pyrolysis tube which is cooled down by air blow and the less volatile pyrolyzates are condensed. After that the pyrolysis tube is moved down out of the pyrolysis unit and blocked from the hot zone by moving the three port valve. Finally the trapped pyrolyzates are flushed by an appropriate solvent into a collection vial. The recovered pyrolyzates in the solution can be then subjected to the measurements suitable for less volatile products such as matrix-assisted laser desorption/ionization mass spectrometry. Moreover, this device is also on-line connected to the injection port of a high performance liquid chromatographic system, which is also appropriate for the measurements of oligomeric products. The basic performance of the developed device was tested by using some polymer samples forming less volatile pyrolyzates such as ~~poly(methyl acrylate), Nylon 11,~~ poly(butylene terephthalate) and poly(2,6-dimethyl-1,4-phenylene ether). In addition, the usefulness of this method was demonstrated through the characterization of the crosslinking

sequences in a photocured resin combined with the thermally-assisted hydrolysis and methylation reaction.

Keywords: Less volatile pyrolyzate, HPLC, MALDI-MS, Pyrolysis device, Analytical pyrolysis, Polymer characterization

1. Introduction

Recently, modern p~~P~~yrolysis-gas chromatography (Py-GC) is widely utilized ~~for~~ in the field of polymer characterization not only for simple "fingerprint" identification and compositional analysis, but also for the detailed structural analysis such as copolymer sequences, region- and stereoregularities, end groups, and branching and cross-linking structures ~~of various polymeric materials~~ [1-3]. For such advanced objectives, it is often demanded to inspect a wide range of pyrolyzates including large molar mass (oligomeric) products and/or highly polar compounds. This technique, however, is inherently inapplicable for the measurements of such less volatile pyrolyzates ~~such as large molar mass (oligomeric) products and highly polar compounds~~ due to the use of GC separation, even if they possesses useful information for the characterization of the sample materials. Therefore, an analytical pyrolysis technique suitable for such intractable pyrolyzates has been required.

A possible approach to overcome this issue ~~should be~~ is the combination of pyrolysis and high performance liquid chromatographic (HPLC) separation ~~applicable even for less volatile products~~. Stepwise (off-line) analyses of collected pyrolyzates by solvent-trap or extraction have been reported by using HPLC (or supercritical fluid chromatography (SFC)) for polymeric samples such as polystyrene [4, 5] and latex containing polar vinyl acid components [6]. In 1996 van der Hage and Boon [7] proposed an on-line Curie-point pyrolysis-HPLC-mass spectrometry (MS) system. In this ~~system~~ method, by controlled solvent flow with appropriate valve switching, condensed pyrolyzates in the pyrolysis chamber were washed out into a precolumn for trapping. The collected products were then flushed into the separation column of HPLC by switching the solvent and its flowing path with the valve control. The feasibility and the potential of this ~~system~~ technique were demonstrated through the analysis of high molar mass pyrolysis

products of lignin polymers. Recently, a generic pyrolysis interface called “PyroVial” was presented [8]. The sample in the closed vial was electrically heated up to 1000 °C on the dedicated socket. Combined with a sophisticated syringe manipulation, the vial containing the pyrolyzates can be hyphenated to any chromatographic methods including GC, HPLC and SFC.

Alternative measure for this subject would be the direct combination between pyrolysis and MS without separation. In the conventional pyrolysis-MS technique, however, vaporized pyrolyzates have been predominantly measured using electron ionization (EI), chemical ionization (CI) and field ionization (FI) sources [9]. Less volatile pyrolyzates, therefore, cannot be analyzed and considerable fragmentation sometimes makes the observed mass spectra too complicate to interpret especially for EI source. Meanwhile, matrix assisted laser desorption/ionization (MALDI)-MS and electrospray ionization (ESI)-MS are widely utilized in recent years for the characterization of ~~oligomeric and polymeric~~ large molar mass compounds especially for oligomeric components~~in recent years~~ [10, 11]. Thus the combination between pyrolysis and MALDI- and/or ESI-MS ~~must be~~ is also a promising approach to obtain the information of less volatile pyrolyzates.

In this work, a novel pyrolysis device suitable for the analysis of the less volatile pyrolyzates was developed on the basis of a microfurnace pyrolyzer which is one of the representative pyrolyzers used for analytical purpose [3]. Pyrolysis reaction is achieved basically under the same conditions for conventional Py-GC measurements. The device can trap the less volatile pyrolyzates in a movable pyrolysis tube and flush the trapped components with an appropriate solvent. The recovered pyrolyzates in the solvent are readily analyzed by MALDI- and ESI-MS. Furthermore, this device can be also on-line connected to the injection port of HPLC. The basic performance and applicability of the device was tested by using some polymer samples forming less volatile pyrolyzates.

2. Experimental

2.1. Construction and operation of pyrolysis device

Fig. 1 shows the schematic diagram and the operation of the developed pyrolysis device. ~~The~~

~~operation of the device was shown in Fig. 2.~~ This device is comprised of a pyrolysis unit based on a vertical microfurnace pyrolyzer [3], of which temperature is controlled by a PID controller (EC5530, Ohkura) and a movable pyrolysis tube (5) made of stainless steel (190 mm long x 4 mm o.d. x 2 mm i.d.) set inside of an outer tube (1/4 inch o.d. x 4.35 mm i.d.). The upper side of the pyrolysis tube is first positioned at the heated center of the pyrolysis unit (Fig. 2(a)). A polymer sample weighed about 1 mg in a surface deactivated stainless steel sample cup (6) (Eco cup, Frontier Lab) is introduced into the heated center at 500 or 550 °C and pyrolyzed under the flow of nitrogen carrier gas (70 mL min^{-1}). As for thermally-assisted hydrolysis and methylation (THM) of a photocured resin sample, 3 mg of the resin mixed with 5 μL of a 25 wt% of tetramethylammonium hydroxide (TMAH) (Aldrich) in the sample cup was introduced into the pyrolysis unit set at 400 °C. The pyrolyzates are then transferred to the bottom side of the pyrolysis tube which is cooled down by cooling fans (4) and the less volatile pyrolyzates are condensed. To increase the trapping efficiency, the connecting union at the bottom of the pyrolysis tube is packed with quarts wool (10) (3 mg). During this step nitrogen seal gas (10 mL min^{-1}) (3) flows to prevent the leakage of pyrolysis products outside of the pyrolysis (inner) tube. After that the pyrolysis tube is moved down out of the pyrolysis unit sealed with a tough O-ring (9) (Kalrez S004, 3.5 mm x 1.5 mm, DuPont) and blocked from the hot zone by switching the three port valve (8) (Fig. 2(b)).

Fig. 1. Schematic diagram and operation of pyrolysis unit with movable trapping tube for pyrolyzates.

~~**Fig. 2.** Operation of the pyrolysis unit.~~

Finally the trapped pyrolyzates are flushed by an appropriate solvent (7) into a collection vial (5 mL volume) (11). The flushing solvent (1 mL THF; HPLC grade; Tokyo Chemical Industry) is pushed out to the pyrolysis tube with the seal gas by rotating another 3-port switching valve (8) for the seal gas. The recovered pyrolyzates in the solution ~~can be~~ are readily subjected to the measurements for less volatile products such as MALDI- and ESI-MS. Moreover, this ~~system~~ device can be also on-line connected to the injection port of HPLC. After the PTFE 3-port valve (15) is switched and the position of the collection vial

is adjusted, the solution of the recovered pyrolyzates is transferred to the sample loop (2 µL volume) of the injector (Rheodyne 7725i) with the pressure of the seal gas. ~~(A photograph of the system and the detailed operation are given as supplementary data.)~~

2.2. Conditions for on-line HPLC

On-line HPLC measurements of the collected pyrolyzates were carried out with an LC-VP HPLC system (Shimadzu) consisting of dual solvent delivery pumps (LC-10ADvp; Shimadzu), a degasser (DGU-12A, Shimadzu), a column oven (CO-10ADvp, Shimadzu), a photodiode array UV-visible detector (SPD-M10A, Shimadzu), and a system controller (SCL-10A, Shimadzu). The separation column was Chemcobond 3.5-ODS-H (Chemco, 150 mm x 1.0 mm, 3.5 µm particles) connected with a guard column of the same packings (Chemco, 35 mm x 1.0 mm). A mixed solvent of water and THF was adopted as the mobile phase for a gradient elution. The gradient conditions were programmed from 30 (for PBT) or 20% (for PPE) THF (10 min hold) to 100% THF (for 60 min), occasionally added with 0.1% (v/v) trifluoroacetic acid mainly for polar products from PBT. The column oven was set at 40 °C. The UV detection was carried out either at 240 (for PBT) or 280 (for PPE) nm.

2.3. Conditions for MALDI-MS

~~MALDI-MS measurements of the collected pyrolyzates were performed to confirm the high molar mass oligomeric and polar products that cannot be detected by Py-GC.~~ In this work, either high resolution spiral time-of-flight (TOF)-MS (JMS-S3000, JEOL) or conventional TOF-MS (AXIMA-CFRplus, Shimadzu Kratos) was used. The spiral TOF-MS was equipped with Nd:YLF laser (349 nm) and performed with 0.5 ns pulse width and 250 Hz frequency, while the conventional TOF-MS was with nitrogen laser (337 nm), operated in 3 ns pulse width and 10 Hz frequency. Ions generated by the laser desorption were introduced into the flight tube with an accelerating voltage of 20 kV and separated in a positive spiral mode (JMS-S3000) and a linear mode (AXIMA-CFR plus). The mass spectra were acquired by averaging 30-100 and 100 individual laser shots, with the delay time set at 150 and 80 ns, respectively for the spiral and the

conventional TOF. Mass calibration was accomplished either by using poly(ethylene glycol) (average molecular weight 400 - 2000) as external standard or a hindered amine light stabilizer (Chimassorb 119FL, Ciba Specialty Chemicals, *m/z* 2285.61 for the monoisotopic ion) as the internal standard. As for the matrix reagent, 2-(4-hydroxyphenylazobenzoic acid) (HABA; Sigma-Aldrich), 4-hydroxybenzylidene malononitrile (HBMN; Alfa Aesar) and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB; Tokyo Chemical Industry) were used. Each matrix solution (10 mg mL^{-1}) was prepared by dissolving 1 mg of the matrix reagent in 0.1 mL of THF (HPLC grade; Tokyo Chemical Industry), then 10 μL each of the matrix and the sample solutions were mixed, and an aliquot (1 μL) of the mixed solution dropped on the sample plate was subjected to MALDI-MS measurement. In the case of internal calibration, 1 μL of the calibrant solution (1 mg mL^{-1} in THF) was also added to the sample/matrix mixed solution. The ions observed in the MALDI mass spectra were predominantly sodium-cationized molecules of the products under the conditions in this work.

2.4. Conditions for HPLC-ESI-MS

In order to identify the collected pyrolyzates of poly(phenylene ether) (PPE) subjected to HPLC measurements, a HPLC-MS system consisting of UPLC ~~system~~ (Acuity, Waters) and TOF-MS (SYNAPT G2, Waters) was used. MS was operated in the positive ESI mode under the conditions of source temperature 120 ºC, desolvation N_2 gas temperature 350 ºC, desolvation gas flow 800 L h^{-1}, capillary voltage of 3.0 kV, and cone voltage 40 V. The separation column and the conditions for measurements were basically the same as those for the on-line HPLC-UV detection (section 2.2).

2.5. Conditions for Py-GC-MS

Py-GC-MS measurements of the polymer samples were also performed for comparison. A vertical microfurnace pyrolyzer (PY-2020iD, Frontier Lab) was attached to the injection port of a GC-MS system (GCMS-QP2010 Plus, Shimadzu). About 0.1 mg of a polymer sample weighed in a deactivated stainless

steel sample cup was pyrolyzed at 500 or 550 °C under the flow of helium carrier gas. The flow rate of 50 mL min^{-1} of carrier gas at pyrolyzer was reduced to 1.0 mL min^{-1} at a metal capillary separation column (Ultra-Alloy 5 MS, 30 m x 0.25 mm i.d., coated with 0.25 μm of 5% diphenyl-95% dimethyl-polysiloxane, Frontier Lab) by means of a splitter. The temperature both of PY/GC interface and the GC injection port was set at 320 °C. The column oven temperature was first held at 40 °C for 2 min, then programmed to 320 °C at a rate of 10 °C min^{-1} and finally held at 320 °C for 30 min. The separated components were introduced into the ionization source of a quadrupole MS through a GC/MS interface held at 320 °C. The ionization was achieved with electron ionization at 70 eV. The mass scan range was *m/z* 29 - 600.

2.6. Polymer samples

Poly(methyl acrylate) (PMA) sample was radically polymerized in a standard procedure. Industrially available pelletized samples were used for Nylon 11 (polyundecanoamide) and poly(butylene terephthalate) (PBT). Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) sample obtained using Mn-based catalyst was the same as that used in previous work [12]. The results for PMA and Nylon 11 are discussed as supplementary information. ~~The chemical structure of the polymer samples are shown in Fig. 3.~~

The photocured acrylic resin sample was prepared with neopentyl glycol diacrylate through photopolymerization in the presence of 7 wt% 2,2'-dimethoxy-2-phenylacetophenone as a photoinitiator using the UV-cured equipment consisting of a conveyor and a medium-pressure mercury lamp.

~~**Fig. 3.** Polymer samples.~~

3. Results and discussion

~~*3.1. Poly(methyl acrylate) (PMA)*~~

~~The basic performance of the pyrolysis device was tested for PMA sample. PMA generally decomposes into a series of MA oligomers through the random chain scission accompanied by radical transfer reactions at elevated temperature [13, 14]. Fig. 4 shows a typical pyrogram of PMA observed by~~

conventional Py-GC-MS at 550 °C. In this case MA monomer and oligomers up to heptamer (n = 7) can be observed [3]. Recently, by using a special Py-high temperature-GC equipped with a septum-free injector [15] and a thermally stable short capillary column coated with carborane-siloxane stationary phase, it was reported that the larger oligomers up to 16-mer were detected in the pyrogram of PMA under the conditions for the GC system around 400 °C [16].

Fig. 4. Pyrogram of PMA observed by Py-GC-MS at 550 °C.

PMA sample was then subjected to the developed pyrolysis device. An aliquot of the collected pyrolyzates (at 550 °C) dissolved in THF was measured by MALDI-spiral-TOF-MS using HABA as a matrix reagent. The observed mass spectrum is shown in Fig. 5. A series of MA oligomers are observed at least up to 26-mer, and each n-mer contains three types of products as shown in Fig. 5(b). These results demonstrate that high molar mass pyrolyzates unobservable by Py-GC are successfully recovered by the pyrolyisis device.

Fig. 5. MALDI mass spectrum of pyrolysis products at 550 °C of PMA collected in THF

3.2. Nylon 11

Aliphatic polyamides (Nylon) are known to be pyrolyzed mainly into various sizes of cyclic amides (lactams) and linear products having nitrile, alkyl and/or olefinic terminals formed through *cis*-elimination reactions along with random chain scissions. As for Nylon 11, therefore, the pyrolysis products listed in Table 1 should be yielded. Fig. 6 shows a typical pyrogram of Nylon 11 obtained by Py-GC-MS at 550 °C. Although various pyrolyzates listed in Table 1 are observed [3, 17], the assigned products are mostly those having only one or no amide group such as L_1, L_2 and $D_{0\text{-}10}$. Even the largest pyrolyzate, $A_{1\text{-}20}$, of which molecular weight is *ca.* 508, contains merely two amide groups.

Table 1 Representative pyrolyzates of Nylon 11.

Fig. 6. Pyrogram of Nylon11 observed by Py-GC-MS at 550 ºC.

Nylon 11 was then pyrolyzed at 550 °C in the pyrolysis device and the pyrolyzates were collected with THF. The recovered solution was sampled to be measured directly by MALDI-MS. Fig. 7 shows the observed mass spectra for the pyrolyzates of Nylon 11 obtained by MALDI-spiral-TOF-MS with HABA matrix. In the oligomer range larger than *m/z* 500, which cannot be detected by Py-GC-MS, a number of products are detected. Among these, trimeric and tetrameric lactams (L_3 and L_4) are distinctly observed. As shown in the expanded spectrum in Fig. 7(b), various linear products containing three amide groups were identified in the *m/z* range between 620 and 645. (The observed peak splitting should be caused by the overlapping of possible isotopic ions for individual pyrolyzates.) Moreover, although with small intensities, ions for the pyrolyzates were clearly observed even in the region around 1400, which corresponding to the octameric products with seven amide groups. These observations indicated that not only large molar mass but also polar pyrolyzates originated from polar polymers such as Nylons should be able to be analyzed by using the developed pyrolysis device.

Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of Nylon11 collected in THF.

3.1 Basic performance of the developed pyrolysis device

3.1.1. Poly(butylene terephthalate) (PBT)

The basic performance of the developed pyrolysis device including on-line HPLC measurements of the pyrolyzates obtained by this device was ~~then performed~~ evaluated using PBT, which is widely utilized as one of typical engineering plastics and contains aromatic moieties suitable for UV detection. In general, polyesters like PBT thermally decompose into oligomeric products primarily through *cis*-elimination at the ester linkages followed by partial decarboxylation. It has been reported for PBT, therefore, several types of products listed in Table 1 should be formed by pyrolysis reactions ~~initiated chiefly with the cis-elimination shown in Fig. 8~~ [12-14].

Table 1 Possible pyrolyzates of PBT.

~~**Fig. 8.** Pyrolysis pathway of PBT.~~

Fig. 2 shows a pyrogram of PBT obtained by Py-GC-MS at 500 °C. The main pyrolyzates observed are 1,3-butadiene and A_n, B_n and C_n with degree of polymerization (n) of 0 or 1 [3, 12]. The yields of E_n and F_n products having phenyl terminal(s) were fairly small, probably because the contribution of decarboxylation to form phenyl terminals would be minor under the conditions of relatively low pyrolysis temperature at around 500 °C. Meanwhile highly polar decarboxylic acid products (D_n) only shows a broad hump around 20 min for terephthalic acid (D_0). At least the larger pyrolyzates than C_1, or the products with molar mass > 500, were not able to be observed by conventional Py-GC-MS at all.

Fig. 2. Pyrogram of PBT observed by Py-GC-MS at 500 ºC.

Next PBT was pyrolyzed at 500 °C in the pyrolysis device, and the pyrolyzates were collected in THF. The obtained THF solution was first measured directly by conventional MALDI-MS with HBMN as a matrix reagent. Fig. 3 shows the MALDI mass spectrum of the recovered pyrolyzates of PBT. The pyrolyzates observed in the pyrogram by Py-GC-MS (Fig. 2) such as B_0, A_1-C_1 and E_1 were also observed, although smaller products (A_0, E_0, etc) might evaporate during MALDI process and not be detected in the mass spectrum. In addition, the pyrolyzates that could be hardly detected by Py-GC-MS, *e. g.* D_1, F_1 and the products with greater degrees of polymerization (n = 2, 3), were also clearly confirmed in the MALDI mass spectrum (Fig. 3). These observations prove that such larger pyrolyzates from PBT can be sufficiently recovered by the pyrolysis device.

Fig. 3. MALDI mass spectrum of pyrolysis products at 500 ºC of PBT collected with THF.

The solution of the collected pyrolyzates was then subjected to on-line HPLC measurements. Fig. 4

shows the UV-detected chromatogram of the recovered pyrolyzates of PBT. In this chromatogram, several peaks were clearly observed. In order to identify the peak components, the eluents around the main peaks (26 - 29, 34 - 37, 42 - 44, and 46 - 48 min) were fractionated (5 times for accumulation) and subjected to MALDI-MS measurements. As the results, the pyrolysis products designated in Fig. 4 were at least assigned. Among these, the highly polar and/or large molar mass components, which cannot be detected by Py-GC-MS, were included (A_2, B_2, C_2, D_2, E_2, etc). This result demonstrates that on-line HPLC measurements of less volatile pyrolyzates are able to be performed by using the analytical pyrolysis system developed.

Fig. 4. On-line Py-HPLC-UV chromatogram of collected pyrolysis products of PBT at 500 ºC.

3.1.2. Poly(2,6-dimethyl-1,4-phenylene ether) (PPE)

~~Finally~~ The pyrolysis device was then applied to the characterization of PPE. It has been reported that PPE thermally decompose into various oligomers in a unique manner with the major contribution of Fries rearrangement reaction to form C-C bondings along with the simple cleavages of the main chains as shown in Fig. 5 [15, 16]. Fig. 6 shows a typical pyrogram of PPE obtained by Py-GC-MS at 550 °C. Although a wide range of oligomeric products should be formed, observed pyrolyzates by Py-GC-MS were limited to mainly monomers, dimers and trimers together with minor amounts of tetramers. Table 2 summarizes the peak assignments of major pyrolyzates in dimeric and trimeric regions. Reflecting the considerable contribution of Fries arrangement, various types of products containing some isomers with methylene and/or ether linkage(s) can be formed [3, 15, 16].

Fig. 5. Typical pyrolysis pathway of PPE .

Fig. 6. Pyrogram of PPE observed by Py-GC-MS at 550 ºC.

Table 2 Peak assignment of PPE pyrolyzates observed in dimer and trimer regions in the pyrogram.

The PPE sample was also pyrolyzed in the new pyrolysis devices at 550 °C. The recovered solution ~~in~~

~~THF~~ of the pyrolyzates in THF was first analyzed by MALDI-spiral-TOF-MS using DCTB as the matrix reagent. The observed mass spectrum is shown in Fig. 7. In addition to the pyrolyzates up to tetramers (n = 4) observed by Py-GC-MS, higher molar mass oligomers are clearly detected at least up to heptamers (n = 7). This fact shows the less volatile pyrolyzates of PPE can be successfully recovered by the pyrolysis device.

Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of PPE collected in THF.

~~Here it should be noted that a number of clusters were observed for oligomers of each degree of polymerization (n). Hence the peaks in the pentamer region (n = 5) were examined in detail. A representative formation pathway of a pentameric (n = 5) product is shown in Fig. 15, provided that the Fries rearrangement would completely proceed during pyrolysis pathway. The resultant pyrolyzate shown in Fig. 15 should be possibly the largest pentamer, and is abbreviated to 5-0. Depending on the cleavage position, the smaller pentamers by one or two CH_2 unit(s) could be also produced, which are abbreviated 5-1 and 5-2, respectively. These three types of products, 5-0 ~ 5-2, would be thus the most probable pentameric pyrolyzates. In fact, as for the dimeric and trimeric pyrolyzates of PPE observed by Py-GC-MS, the corresponding products were confirmed to be predominant as shown in Fig. 13 and Table 3. In the observed MALDI mass spectrum of the PPE pyrolyzates, however, 5-0 ~ 5-2 were not the main products in pentamer region as shown in the expanded view in Fig. 14. Smaller components corresponding to 5-3 ~ 5-6 appeared rather abundantly. Moreover, the larger *m/z* ions by 2 for 5-0 ~ 5-6, which might be attributed to a hydrogenated ($+H_2$) or an oxidized ($+O - CH_2$) product of 5-0 ~ 5-6, were detected in higher intensities than those for 5-0 ~ 5-6. These observations suggest that the undesirable degradations and/or secondary reactions might fairly take place for PPE pyrolyzates during MALDI process [23].~~

~~**Fig. 15.** Pyrolysis pathway of PPE to form pentamer (n = 5) with maximum numbers of substitution (5-0).~~

The recovered solution of the PPE pyrolyzates was then subjected to on-line HPLC measurements. Fig. 8 shows the chromatogram of the collected PPE pyrolyzates observed in UV detection at 280 nm. The fact that a number of separated peaks were clearly observed suggest that the analysis of the less volatile pyrolyzates for PPE can be achieved by on-line HPLC measurement. In the case of the PPE pyrolyzates, however, the correct identification of each eluent should be difficult by the fractionation-MALDI-MS technique because of possible decomposition and secondary reaction during laser irradiation as mentioned in supplementary information. Therefore, HPLC-ESI-MS measurements were carried out for the appropriate identification of the PPE pyrolyzates, in which an aliquot of the collected PPE pyrolyzate solution was sampled and introduced separately (off-line) into ~~the~~ HPLC-ESI-MS ~~system~~.

Fig. 8. On-line HPLC chromatograms of collected pyrolysis products of PPE at 550 ºC by UV detection.

~~Fig. 17 shows the observed total ion chromatogram (TIC) of the collected pyrolyzates of PPE. Since the separation conditions have not been optimized, the observed peak separation is far from sufficient. The eluted components, however, can be identified on the basis of the accumulated ESI mass spectrum for the whole range of the chromatogram. Fig. 18 shows the expanded region for the pentamers in the accumulated ESI mass spectrum in the range between 10 and 50 min. It is interesting to note that the observed main pentamers (5-0 - 5-2) are those expected to form by pyrolysis as shown in Fig. 15. This result indicates even the PPE pyrolyzates can be observed in the original form by ESI-MS, unlike MALDI-MS. Moreover, the fact that the ions for pentamers are clearly detected suggests the less volatile pyrolyzates of PPE should be analyzed by HPLC combined with the developed pyrolysis device.~~

~~**Fig. 17.** Total ion chromatograms of collected pyrolysis products of PPE obtained by HPLC-ESI-MS.~~

~~**Fig. 18.** Accumulated ESI mass spectrum of collected pyrolysis products of PPE at 550 ºC.~~

~~Finally,~~ The elution behaviors of individual pyrolyzates were examined in detail based on the

corresponding selected ion chromatograms (SIMs) obtained by HPLC-ESI-MS. Fig. 9 shows the SIMs of some PPE pyrolyzates for the largest components of individual oligomers (tetramers to hexamers). Not only the elution times of the products shifted depending on their molecular size, but also the number of the observed peaks for the individual oligomers increased with increase in *m/z*. The latter multiple peaks should be attributed to the possible formation of the isomeric pyrolyzates. As for pentamers (*m/z* 639), at least five separated peaks are observed. If the pyrolysis of PPE proceeds with the complete Fries rearrangement, the formed pentamer ~~(5-0)~~ must be that containing 5 OH groups ~~alone as shown in~~ (Fig. S5). However, considerable amounts of dimeric and trimeric pyrolyzates containing ether linkage(s) were also confirmed in the pyrogram of PPE obtained by Py-GC-MS as shown in Fig. 6 and Table 2. This fact suggests that various isomeric products containing ether linkage(s) should be also formed in the pentamer region. Even for the pentameric products with the same ~~molecular weight as (5-0) (~~*m/z* 639~~)~~, various isomeric forms can be considered as shown in Table 3. (Further isomeric products should be produced depending on the difference in the distributions of OH groups.) Since these pentamers contain various numbers of OH groups (1 - 5), there polarity should be different from each other which in turn causes the peak separation in the chromatogram. This result demonstrated that even the isomeric products in less volatile pyrolyzates can be separated by HPLC measurements which could not be differentiated by MS analyses alone.

Fig. 9. Extracted ion chromatograms of oligomeric pyrolysis products of PPE at 550 ºC.

Table 3 Possible isomeric pyrolyzates for pentamer (5-0) of PPE observed in extracted ion chromatogram.

3.2 Application to elucidate crosslinking sequences in photocured resin using THM

Photocurable acrylic esters are utilized for many industrial materials. Characterization of the network structures in the cured resins has been requested to correlate it with various properties of the resins. It has been demonstrated that THM-GC often brings us valuable clues on the chemical structure in the photocured acrylic resins. In this technique, the ester linkages in the cured resin samples selectively decomposed into

methyl derivatives which provide various information such as conversion, copolymer composition and average molar mass of prepolymers [2]. As for the cross-linking sequences, it was reported that the chain length distribution of the network junctions composed of up to six acryloyl units in the photocured acrylic resin sample could be estimated from the peak intensities of the characteristic methyl acrylate (MA) oligomers (up to hexamer) reflecting cross-linking sequence structure [17]. However, the network junctions containing longer sequence comprised of more than seven acryloyl units were not elucidated because the corresponding higher MA oligomers were not observed in the pyrogram due to their low volatility.

In this case, the developed pyrolysis device could provide the information of the longer cross-linking sequences in the cured acrylic resins through the THM reaction in the presence of TMAH. Fig. 10 presents possible THM reactions in the photocured resin sample formed from neopentylglycol diacrylate, in which two types of MA oligomers might be produced. The cured resin sample mixed with TMAH was introduced into the pyrolysis device at 400 ºC. The collected products in THF were then analyzed by conventional MALDI-MS with HABA as a matrix reagent and NaI as a cationization agent. Fig. 11 shows the MALDI mass spectrum of the THM products of the cured acrylic resin sample. Two series of the MA oligomers were observed at least up to 18-mers. This result demonstrates that the developed pyrolysis device can provide us the information of the chain length distribution of the network junctions in cured resins even for the longer sequences which cannot be evaluated by THM-GC measurements.

Fig. 10. Thermally-assisted hydrolysis and methylation pathway of photo cured acrylic resin sample.

Fig. 11. MALDI mass spectrum of THM products of photocured acrylic resin sample collected in THF.

4. Conclusion

A novel pyrolysis device suitable for analysis of the less volatile pyrolyzates was developed using a microfurnace type pyrolysis unit combined with a movable pyrolysis tube (made of stainless steel). The less volatile pyrolyzates of polymer samples were trapped on the inner wall of the pyrolysis tube by air

cooling, and then solvent-flushed into a collection vial. The recovered solution containing less volatile pyrolyzates can be directly analyzed by MALDI-MS. The on-line HPLC analyses of the solutions were also possible. In the present state, however, only the HPLC-UV detection system has been on-line connected with the pyrolysis device. The more powerful combination~~, however,~~ could be that between pyrolysis and HPLC-MS. The development of on-line connection of ~~a~~ HPLC-ESI-MS ~~system~~ with the pyrolysis device is currently in progress along with the optimization of the operating conditions.

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Figure captions:

Fig. 1. Schematic diagram and operation of pyrolysis unit with movable trapping tube for pyrolyzates. (a) Pyrolysis and trapping of pyrolyzates. (b) Collection of pyrolyzates by solvent flushing. (1) heating block, (2) carrier gas, (3) seal gas, (4) cooling fan, (5) movable pyrolysis tube, (6) sample cup, (7) flushing solvent, (8) 3-port switching valve, (9) Kalrez O-ring (10) quartz wool, (11) solvent collection vial, (12) PTFE tube, (13) stainless steel filter, (14) gas outlet, and (15) PTFE 3-port valve.

~~**Fig. 2.** Operation of the pyrolysis unit. (a) Pyrolysis and trapping of pyrolyzates. (b) Collection of pyrolyzates by solvent flushing.~~

~~**Fig. 3.** Polymer samples.~~

~~**Fig. 4.** Pyrogram of PMA observed by Py-GC-MS at 550 ºC.~~

~~**Fig. 5.** MALDI mass spectrum of pyrolysis products at 550 ºC of PMA collected in THF. (a) overall spectrum. (b) its expended view between *m/z* = 1550 and 1600.~~

~~**Fig. 6.** Pyrogram of Nylon11 observed by Py-GC-MS at 550 ºC.~~

~~**Fig. 7.** MALDI mass spectrum of pyrolysis products at 550 ºC of Nylon11 collected in THF. (a) overall spectrum. (b) its expended view between *m/z* = 620 and 645.~~

~~**Fig. 8.** Pyrolysis pathway of PBT.~~

Fig. 2. Pyrogram of PBT observed by Py-GC-MS at 500 ºC.

Fig. 3. MALDI mass spectrum of pyrolysis products at 500 ºC of PBT collected with THF.

Fig. 4. On-line Py-HPLC-UV chromatogram of collected pyrolysis products of PBT at 500 ºC.

Fig. 5. Typical pyrolysis pathway of PPE .

Fig. 6. Pyrogram of PPE observed by Py-GC-MS at 550 ºC.

Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of PPE collected in THF.

~~**Fig. 15.** Pyrolysis pathway of PPE to form pentamer (n = 5) with maximum numbers of substitution (5-0) through complete Fries rearrangement.~~

Fig. 8. On-line HPLC chromatogram of collected pyrolysis products of PPE at 550 ºC by UV detection.

~~**Fig. 17.** Total ion chromatogram of collected pyrolysis products of PPE at 550 ºC obtained by HPLC-ESI-MS~~.

~~**Fig. 18.** Accumulated ESI mass spectrum of collected pyrolysis products of PPE at 550 ºC. (Partial view around pentamer)~~

Fig. 9. Extracted ion chromatograms of oligomeric pyrolysis products of PPE at 550 ºC for various degrees of polymerization (n = 4-6)~~ with maximum numbers of substitution (n - 0)~~.

Fig. 10. Thermally-assisted hydrolysis and methylation pathway of photocured acrylic resin sample.

Fig. 11. MALDI mass spectrum of THM products of photocured acrylic resin sample collected in THF.

~~Table 1~~

~~Representative pyrolyzates of Nylon 11.~~

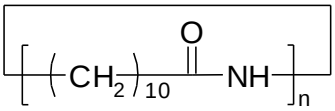
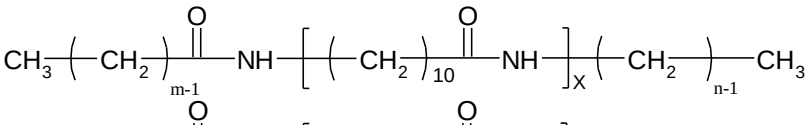
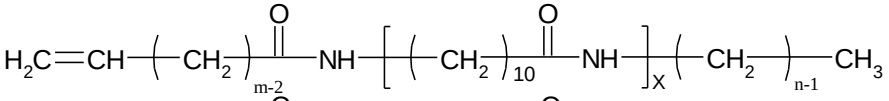
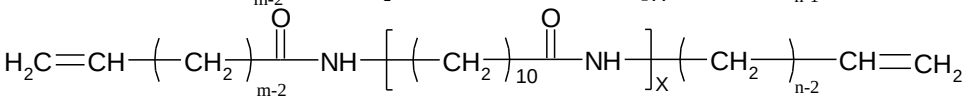
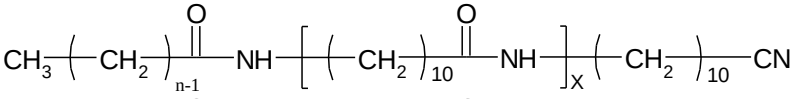
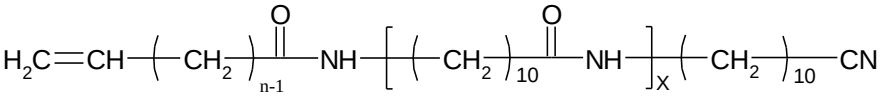
peak code	chemical structure
L_n	
$A_{X-(m+n)}$	
$B_{X-(m+n)}$	
$C_{X-(m+n)}$	 m+n≤20, m≤10, n≤10
D_{X-n}	
E_{X-n}	 n≤10

Table 1

Possible pyrolyzates of PBT.

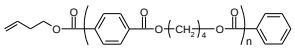
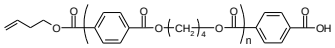
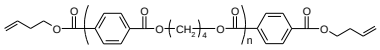
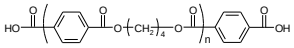
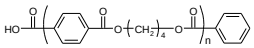
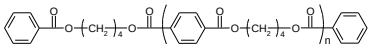
peak code	chemical structure	MW
A_n		176+220n
B_n		220+220n
C_n		274+220n
D_n		166+220n
E_n		122+220n
F_n		298+220n

Table 2

Peak assignment of PPE pyrolyzates observed in dimer and trimer regions in the pyrogram.

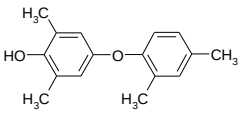
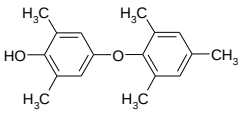
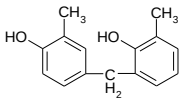
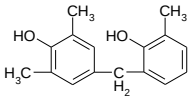
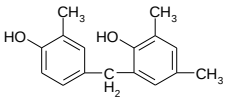
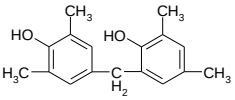
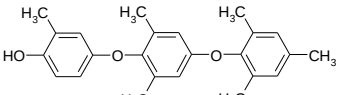
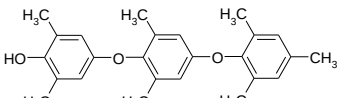
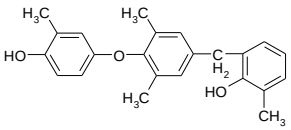
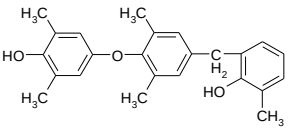
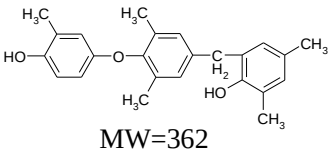
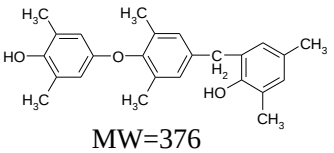
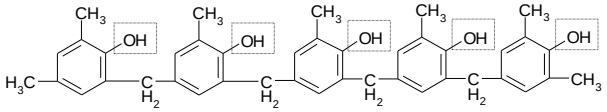
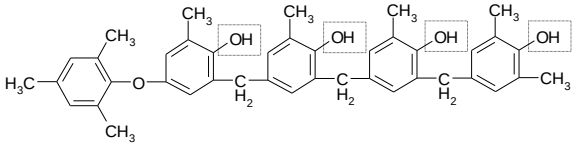
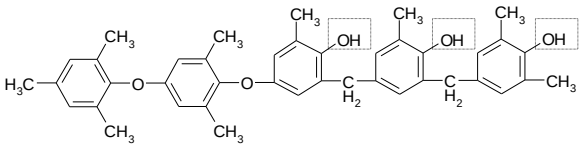
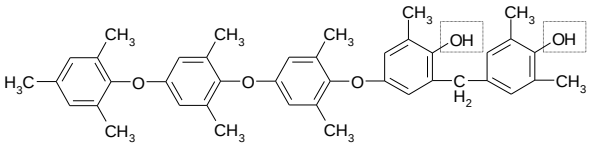
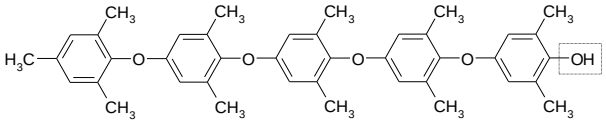
	chemical structure		
n=2	 MW=242	 MW=256	 MW=228
	 MW=242	 MW=242	 MW=256
n=3	 MW=362	 MW=376	
	 MW=348	 MW=362	
	 MW=362	 MW=376	

Table 3

Possible isomeric pyrolyzates for pentamer ~~(5-0)~~ of PPE observed in extracted ion chromatogram at *m/z* 639.

polarity	Structure of the pyrolyzates of PPE
high	
	
middle	
	
low	

*Manuscript (unmarked)
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A novel analytical pyrolysis device applicable for measurements of less volatile pyrolyzates

Hirohisa Kano[a], Takahiro Okamoto[a], Shinya Kitagawa[a], Yoshinori Iiguni[a], Hajime Ohtani[a,*], Hiroshi Ito[b], Koichiro Iwai[a,b], Minoru Kuno[c]

[a] *Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

[b] *Toyota Central R&D Labs., Inc., Nagakute, Aichi, 480-1192, Japan*

[c] *GL Science Inc., 237-2, Sayamagahara, Iruma, Saitama, 358-0032, Japan*

ABSTRACT

A novel analytical pyrolysis device suitable for the measurements of the less volatile pyrolyzates was developed. This device is comprised of a pyrolysis unit based on the vertical microfurnace pyrolyzer and a movable pyrolysis tube made of stainless steel. The upper side of the pyrolysis tube is first set at the heated center of the pyrolysis unit. A polymer sample in a sample cup is introduced into the heated center and pyrolyzed under the flow of nitrogen carrier gas. The pyrolyzates are then transferred to the bottom side of the pyrolysis tube which is cooled down by air blow and the less volatile pyrolyzates are condensed. After that the pyrolysis tube is moved down out of the pyrolysis unit and blocked from the hot zone by moving the three port valve. Finally the trapped pyrolyzates are flushed by an appropriate solvent into a collection vial. The recovered pyrolyzates in the solution can be then subjected to the measurements suitable for less volatile products such as matrix-assisted laser desorption/ionization mass spectrometry. Moreover, this device is also on-line connected to the injection port of a high performance liquid chromatographic system, which is also appropriate for the measurements of oligomeric products. The basic performance of the developed device was tested by using some polymer samples forming less volatile pyrolyzates such as poly(butylene terephthalate) and poly(2,6-dimethyl-1,4-phenylene ether). In addition, the usefulness of this method was demonstrated through the characterization of the crosslinking sequences in a photocured resin

combined with the thermally-assisted hydrolysis and methylation reaction.

Keywords: Less volatile pyrolyzate, HPLC, MALDI-MS, Pyrolysis device, Analytical pyrolysis, Polymer characterization

1. Introduction

Recently, modern pyrolysis-gas chromatography (Py-GC) is widely utilized in the field of polymer characterization not only for simple "fingerprint" identification and compositional analysis, but also for the detailed structural analysis such as copolymer sequences, region- and stereoregularities, end groups, and branching and cross-linking structures [1-3]. For such advanced objectives, it is often demanded to inspect a wide range of pyrolyzates including large molar mass (oligomeric) products and/or highly polar compounds. This technique, however, is inherently inapplicable for the measurements of such less volatile pyrolyzates due to the use of GC separation, even if they possesses useful information for the characterization of the sample materials. Therefore, an analytical pyrolysis technique suitable for such intractable pyrolyzates has been required.

A possible approach to overcome this issue is the combination of pyrolysis and high performance liquid chromatographic (HPLC) separation. Stepwise (off-line) analyses of collected pyrolyzates by solvent-trap or extraction have been reported by using HPLC (or supercritical fluid chromatography (SFC)) for polymeric samples such as polystyrene [4, 5] and latex containing polar vinyl acid components [6]. In 1996 van der Hage and Boon [7] proposed an on-line Curie-point pyrolysis-HPLC-mass spectrometry (MS) system. In this method, by controlled solvent flow with appropriate valve switching, condensed pyrolyzates in the pyrolysis chamber were washed out into a precolumn for trapping. The collected products were then flushed into the separation column of HPLC by switching the solvent and its flowing path with the valve control. The feasibility and the potential of this technique were demonstrated through the analysis of high molar mass pyrolysis products of lignin polymers. Recently, a generic pyrolysis interface called "PyroVial" was presented [8]. The sample in the closed vial was electrically heated up to 1000 °C on the dedicated

socket. Combined with a sophisticated syringe manipulation, the vial containing the pyrolyzates can be hyphenated to any chromatographic methods including GC, HPLC and SFC.

Alternative measure for this subject would be the direct combination between pyrolysis and MS without separation. In the conventional pyrolysis-MS technique, however, vaporized pyrolyzates have been predominantly measured using electron ionization (EI), chemical ionization (CI) and field ionization (FI) sources [9]. Less volatile pyrolyzates, therefore, cannot be analyzed and considerable fragmentation sometimes makes the observed mass spectra too complicate to interpret especially for EI source. Meanwhile, matrix assisted laser desorption/ionization (MALDI)-MS and electrospray ionization (ESI)-MS are widely utilized in recent years for the characterization of large molar mass compounds especially for oligomeric component [10, 11]. Thus the combination between pyrolysis and MALDI- and/or ESI-MS is also a promising approach to obtain the information of less volatile pyrolyzates.

In this work, a novel pyrolysis device suitable for the analysis of the less volatile pyrolyzates was developed on the basis of a microfurnace pyrolyzer which is one of the representative pyrolyzers used for analytical purpose [3]. Pyrolysis reaction is achieved basically under the same conditions for conventional Py-GC measurements. The device can trap the less volatile pyrolyzates in a movable pyrolysis tube and flush the trapped components with an appropriate solvent. The recovered pyrolyzates in the solvent are readily analyzed by MALDI- and ESI-MS. Furthermore, this device can be also on-line connected to the injection port of HPLC. The basic performance and applicability of the device was tested by using some polymer samples forming less volatile pyrolyzates.

2. Experimental

2.1. Construction and operation of pyrolysis device

Fig. 1 shows the schematic diagram and the operation of the developed pyrolysis device. This device is comprised of a pyrolysis unit based on a vertical microfurnace pyrolyzer [3], of which temperature is controlled by a PID controller (EC5530, Ohkura) and a movable pyrolysis tube (5) made of stainless steel (190 mm long x 4 mm o.d. x 2 mm i.d.) set inside of an outer tube (1/4 inch o.d. x 4.35 mm i.d.). The upper

side of the pyrolysis tube is first positioned at the heated center of the pyrolysis unit (Fig. 2(a)). A polymer sample weighed about 1 mg in a surface deactivated stainless steel sample cup (6) (Eco cup, Frontier Lab) is introduced into the heated center at 500 or 550 °C and pyrolyzed under the flow of nitrogen carrier gas (70 mL min^{-1}). As for thermally-assisted hydrolysis and methylation (THM) of a photocured resin sample, 3 mg of the resin mixed with 5 μL of a 25 wt% of tetramethylammonium hydroxide (TMAH) (Aldrich) in the sample cup was introduced into the pyrolysis unit set at 400 °C. The pyrolyzates are then transferred to the bottom side of the pyrolysis tube which is cooled down by cooling fans (4) and the less volatile pyrolyzates are condensed. To increase the trapping efficiency, the connecting union at the bottom of the pyrolysis tube is packed with quarts wool (10) (3 mg). During this step nitrogen seal gas (10 mL min^{-1}) (3) flows to prevent the leakage of pyrolysis products outside of the pyrolysis (inner) tube. After that the pyrolysis tube is moved down out of the pyrolysis unit sealed with a tough O-ring (9) (Kalrez S004, 3.5 mm x 1.5 mm, DuPont) and blocked from the hot zone by switching the three port valve (8) (Fig. 2(b)).

Fig. 1. Schematic diagram and operation of pyrolysis unit with movable trapping tube for pyrolyzates.

Finally the trapped pyrolyzates are flushed by an appropriate solvent (7) into a collection vial (5 mL volume) (11). The flushing solvent (1 mL THF; HPLC grade; Tokyo Chemical Industry) is pushed out to the pyrolysis tube with the seal gas by rotating another 3-port switching valve (8) for the seal gas. The recovered pyrolyzates in the solution are readily subjected to the measurements for less volatile products such as MALDI- and ESI-MS. Moreover, this device can be also on-line connected to the injection port of HPLC. After the PTFE 3-port valve (15) is switched and the position of the collection vial is adjusted, the solution of the recovered pyrolyzates is transferred to the sample loop (2 μL volume) of the injector (Rheodyne 7725i) with the pressure of the seal gas.

2.2. Conditions for on-line HPLC

On-line HPLC measurements of the collected pyrolyzates were carried out with an LC-VP HPLC

system (Shimadzu) consisting of dual solvent delivery pumps (LC-10ADvp; Shimadzu), a degasser (DGU-12A, Shimadzu), a column oven (CO-10ADvp, Shimadzu), a photodiode array UV-visible detector (SPD-M10A, Shimadzu), and a system controller (SCL-10A, Shimadzu). The separation column was Chemcobond 3.5-ODS-H (Chemco, 150 mm x 1.0 mm, 3.5 μm particles) connected with a guard column of the same packings (Chemco, 35 mm x 1.0 mm). A mixed solvent of water and THF was adopted as the mobile phase for a gradient elution. The gradient conditions were programmed from 30 (for PBT) or 20% (for PPE) THF (10 min hold) to 100% THF (for 60 min), occasionally added with 0.1% (v/v) trifluoroacetic acid mainly for polar products from PBT. The column oven was set at 40 °C. The UV detection was carried out either at 240 (for PBT) or 280 (for PPE) nm.

2.3. Conditions for MALDI-MS

In this work, either high resolution spiral time-of-flight (TOF)-MS (JMS-S3000, JEOL) or conventional TOF-MS (AXIMA-CFRplus, Shimadzu Kratos) was used. The spiral TOF-MS was equipped with Nd:YLF laser (349 nm) and performed with 0.5 ns pulse width and 250 Hz frequency, while the conventional TOF-MS was with nitrogen laser (337 nm), operated in 3 ns pulse width and 10 Hz frequency. Ions generated by the laser desorption were introduced into the flight tube with an accelerating voltage of 20 kV and separated in a positive spiral mode (JMS-S3000) and a linear mode (AXIMA-CFR plus). The mass spectra were acquired by averaging 30-100 and 100 individual laser shots, with the delay time set at 150 and 80 ns, respectively for the spiral and the conventional TOF. Mass calibration was accomplished either by using poly(ethylene glycol) (average molecular weight 400 - 2000) as external standard or a hindered amine light stabilizer (Chimassorb 119FL, Ciba Specialty Chemicals, *m/z* 2285.61 for the monoisotopic ion) as the internal standard. As for the matrix reagent, 2-(4-hydroxyphenylazobenzoic acid) (HABA; Sigma-Aldrich), 4-hydroxybenzylidene malononitrile (HBMN; Alfa Aesar) and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB; Tokyo Chemical Industry) were used. Each matrix solution (10 mg mL^{-1}) was prepared by dissolving 1 mg of the matrix reagent in 0.1 mL of THF (HPLC grade; Tokyo Chemical Industry), then 10 μL each of the matrix and the sample

solutions were mixed, and an aliquot (1 μL) of the mixed solution dropped on the sample plate was subjected to MALDI-MS measurement. In the case of internal calibration, 1 μL of the calibrant solution (1 mg mL^{-1} in THF) was also added to the sample/matrix mixed solution. The ions observed in the MALDI mass spectra were predominantly sodium-cationized molecules of the products under the conditions in this work.

2.4. Conditions for HPLC-ESI-MS

In order to identify the collected pyrolyzates of poly(phenylene ether) (PPE) subjected to HPLC measurements, a HPLC-MS system consisting of UPLC (Acuity, Waters) and TOF-MS (SYNAPT G2, Waters) was used. MS was operated in the positive ESI mode under the conditions of source temperature 120 ºC, desolvation N_2 gas temperature 350 ºC, desolvation gas flow 800 L h^{-1}, capillary voltage of 3.0 kV, and cone voltage 40 V. The separation column and the conditions for measurements were basically the same as those for the on-line HPLC-UV detection (section 2.2).

2.5. Conditions for Py-GC-MS

Py-GC-MS measurements of the polymer samples were also performed for comparison. A vertical microfurnace pyrolyzer (PY-2020iD, Frontier Lab) was attached to the injection port of a GC-MS system (GCMS-QP2010 Plus, Shimadzu). About 0.1 mg of a polymer sample weighed in a deactivated stainless steel sample cup was pyrolyzed at 500 or 550 °C under the flow of helium carrier gas. The flow rate of 50 mL min^{-1} of carrier gas at pyrolyzer was reduced to 1.0 mL min^{-1} at a metal capillary separation column (Ultra-Alloy 5 MS, 30 m x 0.25 mm i.d., coated with 0.25 μm of 5% diphenyl-95% dimethyl-polysiloxane, Frontier Lab) by means of a splitter. The temperature both of PY/GC interface and the GC injection port was set at 320 °C. The column oven temperature was first held at 40 °C for 2 min, then programmed to 320 °C at a rate of 10 °C min^{-1} and finally held at 320 °C for 30 min. The separated components were introduced into the ionization source of a quadrupole MS through a GC/MS interface held at 320 °C. The ionization was achieved with electron ionization at 70 eV. The mass scan range was *m/z* 29 - 600.

2.6. Polymer samples

Poly(methyl acrylate) (PMA) sample was radically polymerized in a standard procedure. Industrially available pelletized samples were used for Nylon 11 (polyundecanoamide) and poly(butylene terephthalate) (PBT). Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) sample obtained using Mn-based catalyst was the same as that used in previous work [12]. The results for PMA and Nylon 11 are discussed as supplementary information.

The photocured acrylic resin sample was prepared with neopentyl glycol diacrylate through photopolymerization in the presence of 7 wt% 2,2'-dimethoxy-2-phenylacetophenone as a photoinitiator using the UV-cured equipment consisting of a conveyor and a medium-pressure mercury lamp.

3. Results and discussion

3.1 Basic performance of the developed pyrolysis device

3.1.1. Poly(butylene terephthalate) (PBT)

The basic performance of the developed pyrolysis device including on-line HPLC measurements of the pyrolyzates obtained by this device was evaluated using PBT, which is widely utilized as one of typical engineering plastics and contains aromatic moieties suitable for UV detection. In general, polyesters like PBT thermally decompose into oligomeric products primarily through *cis*-elimination at the ester linkages followed by partial decarboxylation. It has been reported for PBT, therefore, several types of products listed in Table 1 should be formed by pyrolysis reactions [12-14].

Table 1 Possible pyrolyzates of PBT.

Fig. 2 shows a pyrogram of PBT obtained by Py-GC-MS at 500 °C. The main pyrolyzates observed are 1,3-butadiene and A_n, B_n and C_n with degree of polymerization (n) of 0 or 1 [3, 12]. The yields of E_n and F_n products having phenyl terminal(s) were fairly small, probably because the contribution of

decarboxylation to form phenyl terminals would be minor under the conditions of relatively low pyrolysis temperature at around 500 °C. Meanwhile highly polar decarboxylic acid products (D_n) only shows a broad hump around 20 min for terephthalic acid (D_0). At least the larger pyrolyzates than C_1, or the products with molar mass > 500, were not able to be observed by conventional Py-GC-MS at all.

Fig. 2. Pyrogram of PBT observed by Py-GC-MS at 500 ºC.

Next PBT was pyrolyzed at 500 °C in the pyrolysis device, and the pyrolyzates were collected in THF. The obtained THF solution was first measured directly by conventional MALDI-MS with HBMN as a matrix reagent. Fig. 3 shows the MALDI mass spectrum of the recovered pyrolyzates of PBT. The pyrolyzates observed in the pyrogram by Py-GC-MS (Fig. 2) such as B_0, A_1-C_1 and E_1 were also observed, although smaller products (A_0, E_0, etc) might evaporate during MALDI process and not be detected in the mass spectrum. In addition, the pyrolyzates that could be hardly detected by Py-GC-MS, *e. g.* D_1, F_1 and the products with greater degrees of polymerization (n = 2, 3), were also clearly confirmed in the MALDI mass spectrum (Fig. 3). These observations prove that such larger pyrolyzates from PBT can be sufficiently recovered by the pyrolysis device.

Fig. 3. MALDI mass spectrum of pyrolysis products at 500 ºC of PBT collected with THF.

The solution of the collected pyrolyzates was then subjected to on-line HPLC measurements. Fig. 4 shows the UV-detected chromatogram of the recovered pyrolyzates of PBT. In this chromatogram, several peaks were clearly observed. In order to identify the peak components, the eluents around the main peaks (26 - 29, 34 - 37, 42 - 44, and 46 - 48 min) were fractionated (5 times for accumulation) and subjected to MALDI-MS measurements. As the results, the pyrolysis products designated in Fig. 4 were at least assigned. Among these, the highly polar and/or large molar mass components, which cannot be detected by Py-GC-MS, were included (A_2, B_2, C_2, D_2, E_2, etc). This result demonstrates that on-line HPLC

measurements of less volatile pyrolyzates are able to be performed by using the analytical pyrolysis system developed.

Fig. 4. On-line Py-HPLC-UV chromatogram of collected pyrolysis products of PBT at 500 ºC.

3.1.2. Poly(2,6-dimethyl-1,4-phenylene ether) (PPE)

The pyrolysis device was then applied to the characterization of PPE. It has been reported that PPE thermally decompose into various oligomers in a unique manner with the major contribution of Fries rearrangement reaction to form C-C bondings along with the simple cleavages of the main chains as shown in Fig. 5 [15, 16]. Fig. 6 shows a typical pyrogram of PPE obtained by Py-GC-MS at 550 °C. Although a wide range of oligomeric products should be formed, observed pyrolyzates by Py-GC-MS were limited to mainly monomers, dimers and trimers together with minor amounts of tetramers. Table 2 summarizes the peak assignments of major pyrolyzates in dimeric and trimeric regions. Reflecting the considerable contribution of Fries arrangement, various types of products containing some isomers with methylene and/or ether linkage(s) can be formed [3, 15, 16].

Fig. 5. Typical pyrolysis pathway of PPE .

Fig. 6. Pyrogram of PPE observed by Py-GC-MS at 550 ºC.

Table 2 Peak assignment of PPE pyrolyzates observed in dimer and trimer regions in the pyrogram.

The PPE sample was also pyrolyzed in the new pyrolysis devices at 550 °C. The recovered solution of the pyrolyzates in THF was first analyzed by MALDI-spiral-TOF-MS using DCTB as the matrix reagent. The observed mass spectrum is shown in Fig. 7. In addition to the pyrolyzates up to tetramers (n = 4) observed by Py-GC-MS, higher molar mass oligomers are clearly detected at least up to heptamers (n = 7). This fact shows the less volatile pyrolyzates of PPE can be successfully recovered by the pyrolysis device.

Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of PPE collected in THF.

The recovered solution of the PPE pyrolyzates was then subjected to on-line HPLC measurements. Fig. 8 shows the chromatogram of the collected PPE pyrolyzates observed in UV detection at 280 nm. The fact that a number of separated peaks were clearly observed suggest that the analysis of the less volatile pyrolyzates for PPE can be achieved by on-line HPLC measurement. In the case of the PPE pyrolyzates, however, the correct identification of each eluent should be difficult by the fractionation-MALDI-MS technique because of possible decomposition and secondary reaction during laser irradiation as mentioned in supplementary information. Therefore, HPLC-ESI-MS measurements were carried out for the appropriate identification of the PPE pyrolyzates, in which an aliquot of the collected PPE pyrolyzate solution was sampled and introduced separately (off-line) into HPLC-ESI-MS.

Fig. 8. On-line HPLC chromatograms of collected pyrolysis products of PPE at 550 ºC by UV detection.

The elution behaviors of individual pyrolyzates were examined in detail based on the corresponding selected ion chromatograms (SIMs) obtained by HPLC-ESI-MS. Fig. 9 shows the SIMs of some PPE pyrolyzates for the largest components of individual oligomers (tetramers to hexamers). Not only the elution times of the products shifted depending on their molecular size, but also the number of the observed peaks for the individual oligomers increased with increase in *m/z*. The latter multiple peaks should be attributed to the possible formation of the isomeric pyrolyzates. As for pentamers (*m/z* 639), at least five separated peaks are observed. If the pyrolysis of PPE proceeds with the complete Fries rearrangement, the formed pentamer must be that containing 5 OH groups (Fig. S5). However, considerable amounts of dimeric and trimeric pyrolyzates containing ether linkage(s) were also confirmed in the pyrogram of PPE obtained by Py-GC-MS as shown in Fig. 6 and Table 2. This fact suggests that various isomeric products containing ether linkage(s) should be also formed in the pentamer region. Even for the pentameric products with the same *m/z* 639, various isomeric forms can be considered as shown in Table 3. (Further isomeric products should be produced depending on the difference in the distributions of OH groups.) Since these

pentamers contain various numbers of OH groups (1 - 5), there polarity should be different from each other which in turn causes the peak separation in the chromatogram. This result demonstrated that even the isomeric products in less volatile pyrolyzates can be separated by HPLC measurements which could not be differentiated by MS analyses alone.

Fig. 9. Extracted ion chromatograms of oligomeric pyrolysis products of PPE at 550 ºC.

Table 3 Possible isomeric pyrolyzates for pentamer of PPE observed in extracted ion chromatogram.

3.2 Application to elucidate crosslinking sequences in photocured resin using THM

Photocurable acrylic esters are utilized for many industrial materials. Characterization of the network structures in the cured resins has been requested to correlate it with various properties of the resins. It has been demonstrated that THM-GC often brings us valuable clues on the chemical structure in the photocured acrylic resins. In this technique, the ester linkages in the cured resin samples selectively decomposed into methyl derivatives which provide various information such as conversion, copolymer composition and average molar mass of prepolymers [2]. As for the cross-linking sequences, it was reported that the chain length distribution of the network junctions composed of up to six acryloyl units in the photocured acrylic resin sample could be estimated from the peak intensities of the characteristic methyl acrylate (MA) oligomers (up to hexamer) reflecting cross-linking sequence structure [17]. However, the network junctions containing longer sequence comprised of more than seven acryloyl units were not elucidated because the corresponding higher MA oligomers were not observed in the pyrogram due to their low volatility.

In this case, the developed pyrolysis device could provide the information of the longer cross-linking sequences in the cured acrylic resins through the THM reaction in the presence of TMAH. Fig. 10 presents possible THM reactions in the photocured resin sample formed from neopentylglycol diacrylate, in which two types of MA oligomers might be produced. The cured resin sample mixed with TMAH was introduced into the pyrolysis device at 400 ºC. The collected products in THF were then analyzed by conventional MALDI-MS with HABA as a matrix reagent and NaI as a cationization agent. Fig. 11 shows the MALDI

mass spectrum of the THM products of the cured acrylic resin sample. Two series of the MA oligomers were observed at least up to 18-mers. This result demonstrates that the developed pyrolysis device can provide us the information of the chain length distribution of the network junctions in cured resins even for the longer sequences which cannot be evaluated by THM-GC measurements.

Fig. 10. Thermally-assisted hydrolysis and methylation pathway of photo cured acrylic resin sample.

Fig. 11. MALDI mass spectrum of THM products of photocured acrylic resin sample collected in THF.

4. Conclusion

A novel pyrolysis device suitable for analysis of the less volatile pyrolyzates was developed using a microfurnace type pyrolysis unit combined with a movable pyrolysis tube (made of stainless steel). The less volatile pyrolyzates of polymer samples were trapped on the inner wall of the pyrolysis tube by air cooling, and then solvent-flushed into a collection vial. The recovered solution containing less volatile pyrolyzates can be directly analyzed by MALDI-MS. The on-line HPLC analyses of the solutions were also possible. In the present state, however, only the HPLC-UV detection system has been on-line connected with the pyrolysis device. The more powerful combination could be that between pyrolysis and HPLC-MS. The development of on-line connection of HPLC-ESI-MS with the pyrolysis device is currently in progress along with the optimization of the operating conditions.

Acknowledgments

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Figure captions:

Fig. 1. Schematic diagram and operation of pyrolysis unit with movable trapping tube for pyrolyzates. (a) Pyrolysis and trapping of pyrolyzates. (b) Collection of pyrolyzates by solvent flushing. (1) heating block, (2) carrier gas, (3) seal gas, (4) cooling fan, (5) movable pyrolysis tube, (6) sample cup, (7) flushing solvent, (8) 3-port switching valve, (9) Kalrez O-ring (10) quartz wool, (11) solvent collection vial, (12) PTFE tube, (13) stainless steel filter, (14) gas outlet, and (15) PTFE 3-port valve.

Fig. 2. Pyrogram of PBT observed by Py-GC-MS at 500 ºC.

Fig. 3. MALDI mass spectrum of pyrolysis products at 500 ºC of PBT collected with THF.

Fig. 4. On-line Py-HPLC-UV chromatogram of collected pyrolysis products of PBT at 500 ºC.

Fig. 5. Typical pyrolysis pathway of PPE .

Fig. 6. Pyrogram of PPE observed by Py-GC-MS at 550 ºC.

Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of PPE collected in THF.

Fig. 8. On-line HPLC chromatogram of collected pyrolysis products of PPE at 550 ºC by UV detection.

Fig. 9. Extracted ion chromatograms of oligomeric pyrolysis products of PPE at 550 ºC for various degrees of polymerization (n = 4-6).

Fig. 10. Thermally-assisted hydrolysis and methylation pathway of photocured acrylic resin sample.

Fig. 11. MALDI mass spectrum of THM products of photocured acrylic resin sample collected in THF.

Table 1

Possible pyrolyzates of PBT.

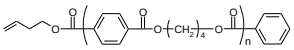
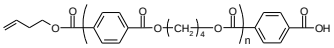
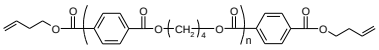
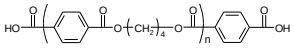
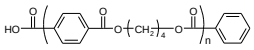
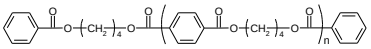
peak code	chemical structure	MW
A_n		176+220n
B_n		220+220n
C_n		274+220n
D_n		166+220n
E_n		122+220n
F_n		298+220n

Table 2

Peak assignment of PPE pyrolyzates observed in dimer and trimer regions in the pyrogram.

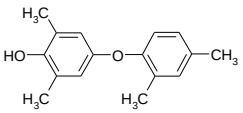
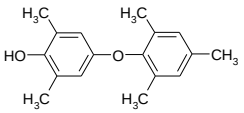
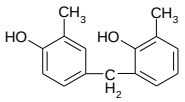
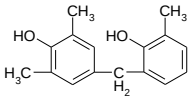
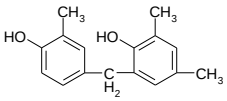
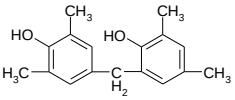
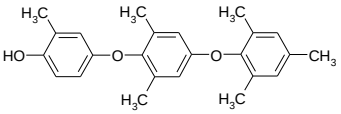
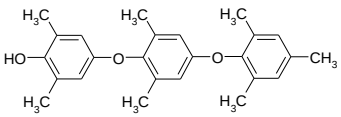
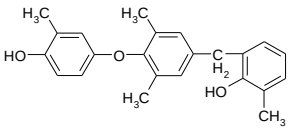
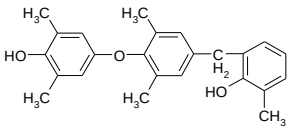
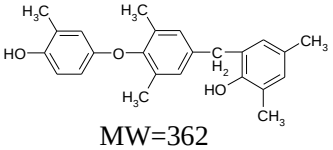
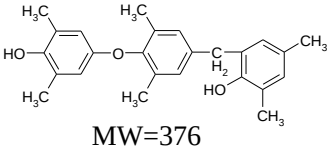
	chemical structure		
n=2	 MW=242	 MW=256	 MW=228
	 MW=242	 MW=242	 MW=256
n=3	 MW=362	 MW=376	
	 MW=348	 MW=362	
	 MW=362	 MW=376	

Table 3

Possible isomeric pyrolyzates for pentamer of PPE observed in extracted ion chromatogram at *m/z* 639.

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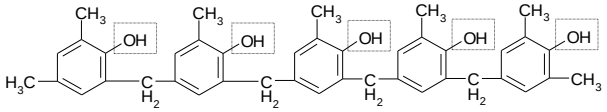
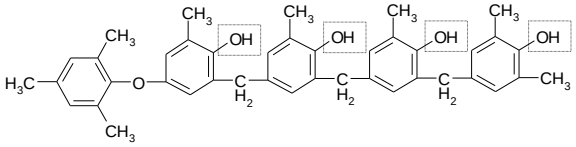
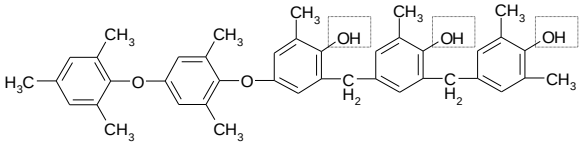
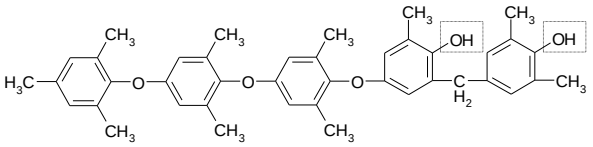
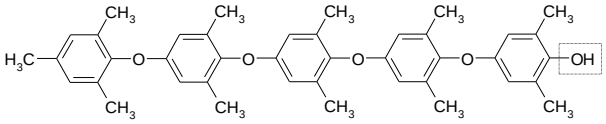
high	
	
middle	
	
low	

Fig. 1

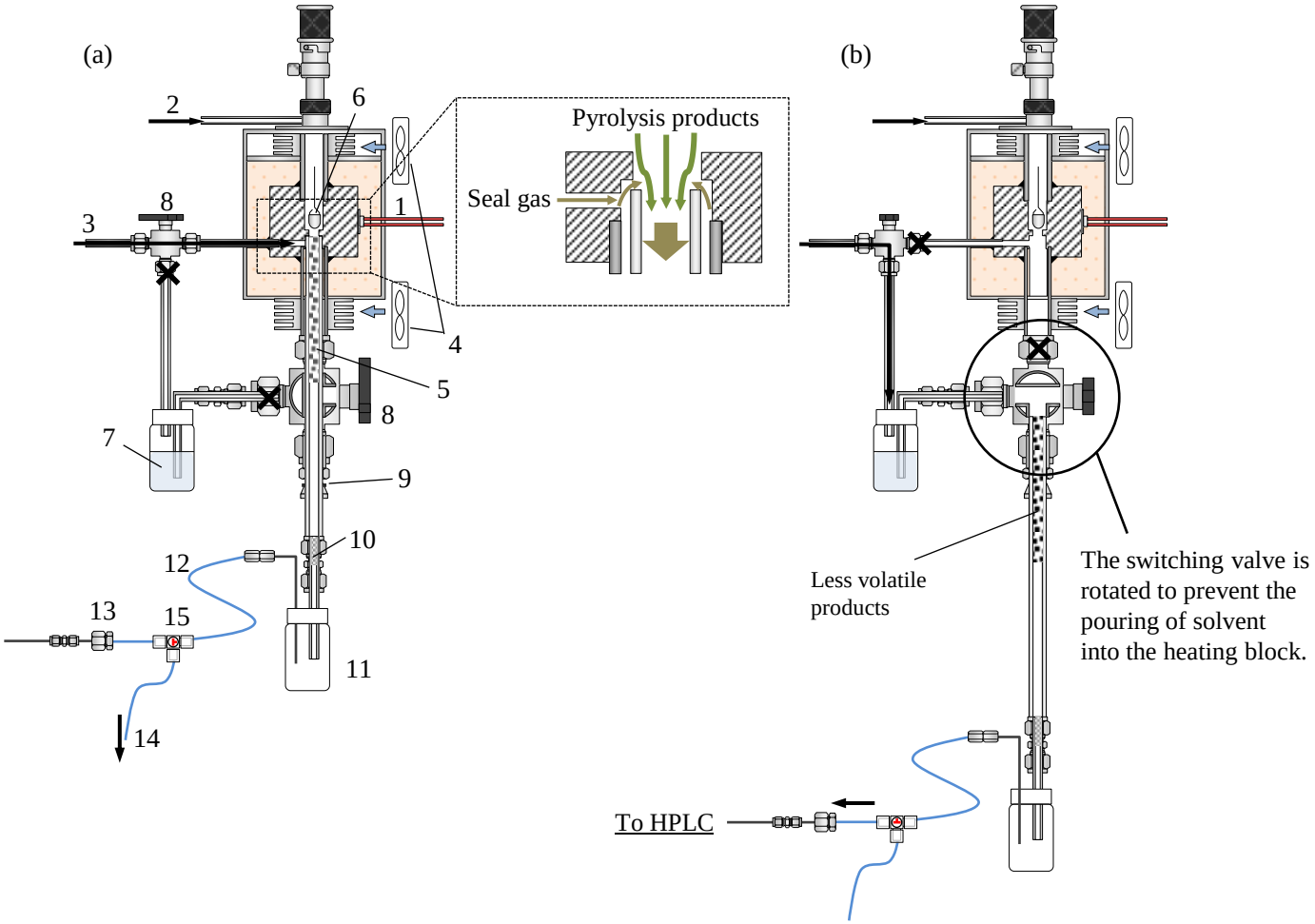


Fig. 1. Schematic diagram and operation of pyrolysis unit with movable trapping tube for pyrolyzates

Fig. 2

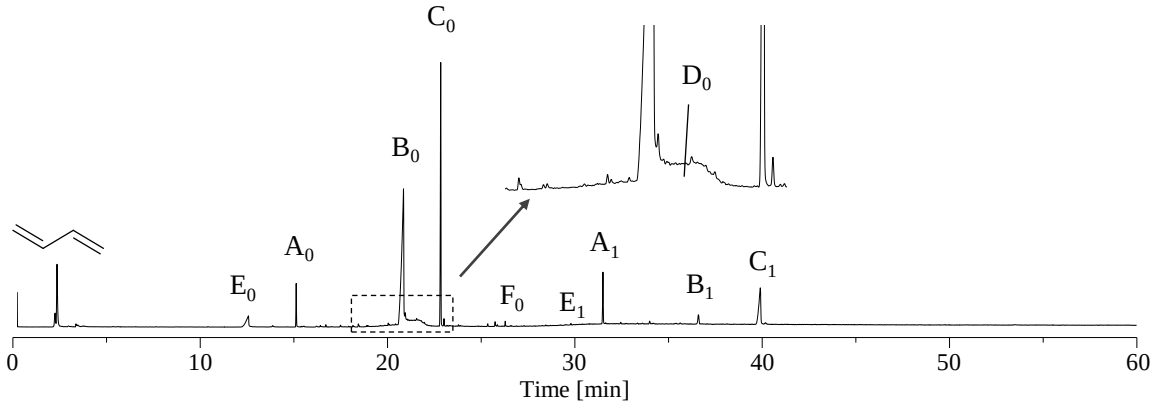


Fig. 2. Pyrogram of PBT observed by Py-GC-MS at 500 ºC.

Fig. 3

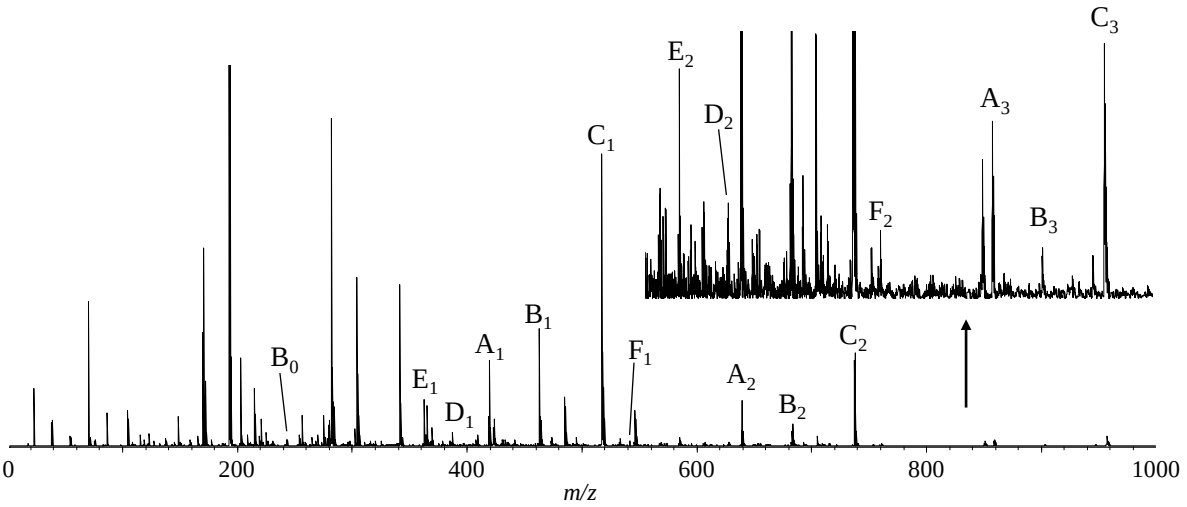


Fig. 3. MALDI mass spectrum of pyrolysis products at 500 ºC of PBT collected with THF.

Fig. 4

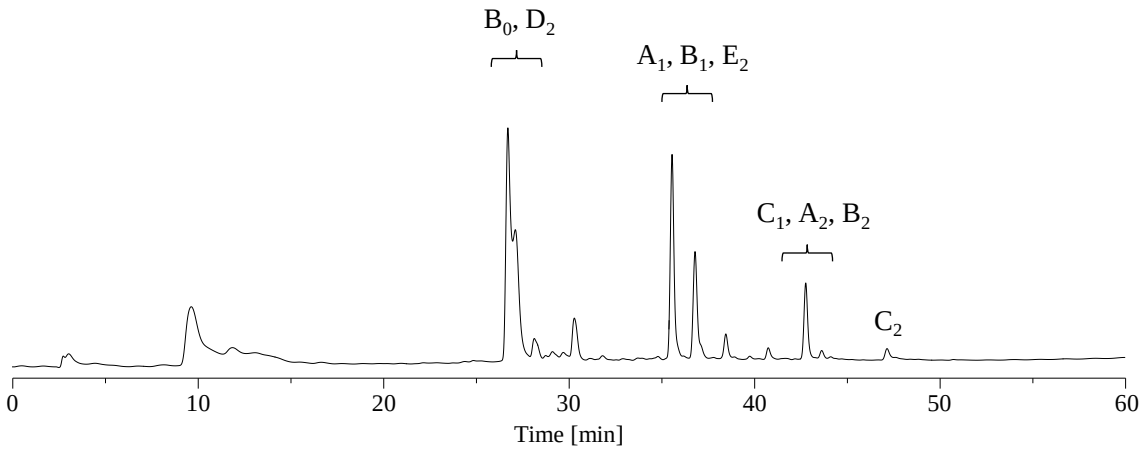


Fig. 4. On-line Py-HPLC-UV chromatogram of collected pyrolysis products of PBT at 500 ºC.

Fig. 5

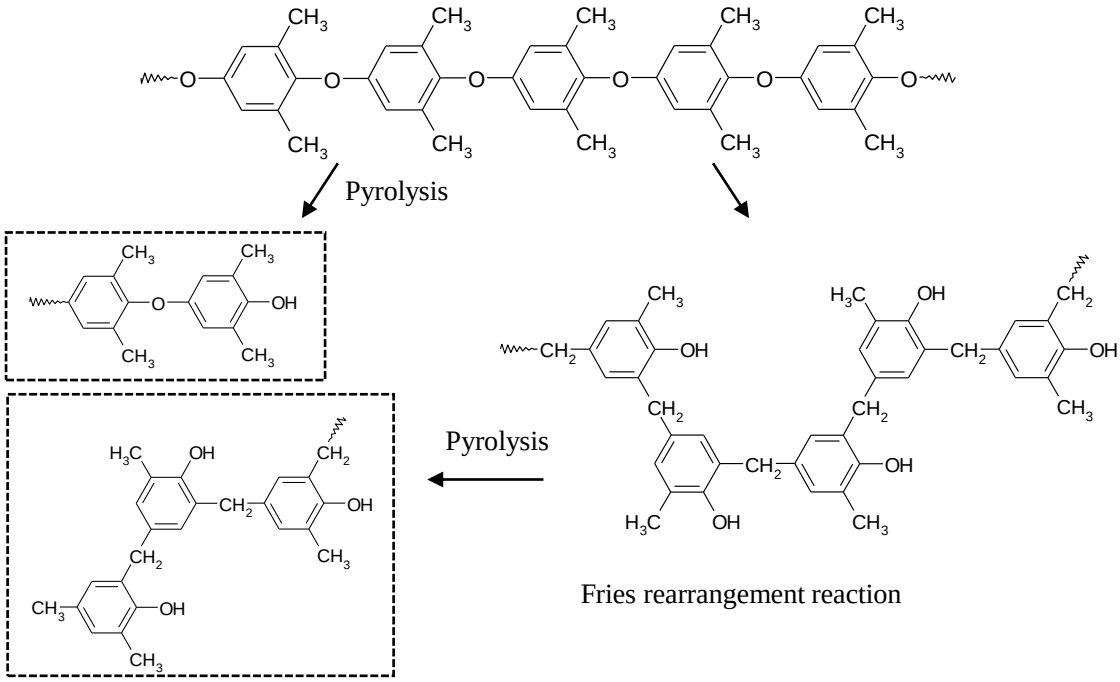


Fig. 5. Typical pyrolysis pathway of PPE .

Fig. 6

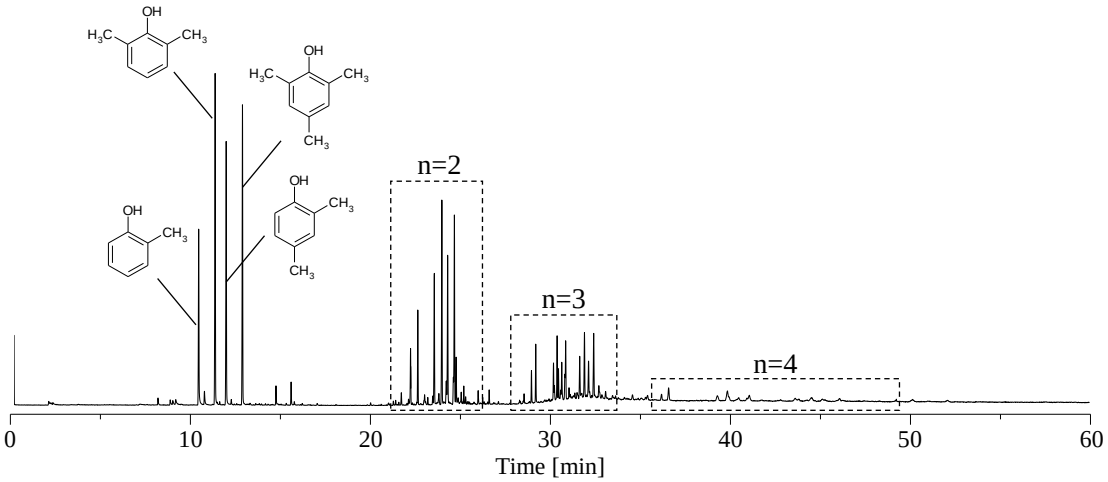


Fig. 6. Pyrogram of PPE observed by Py-GC-MS at 550 ºC

Fig. 7

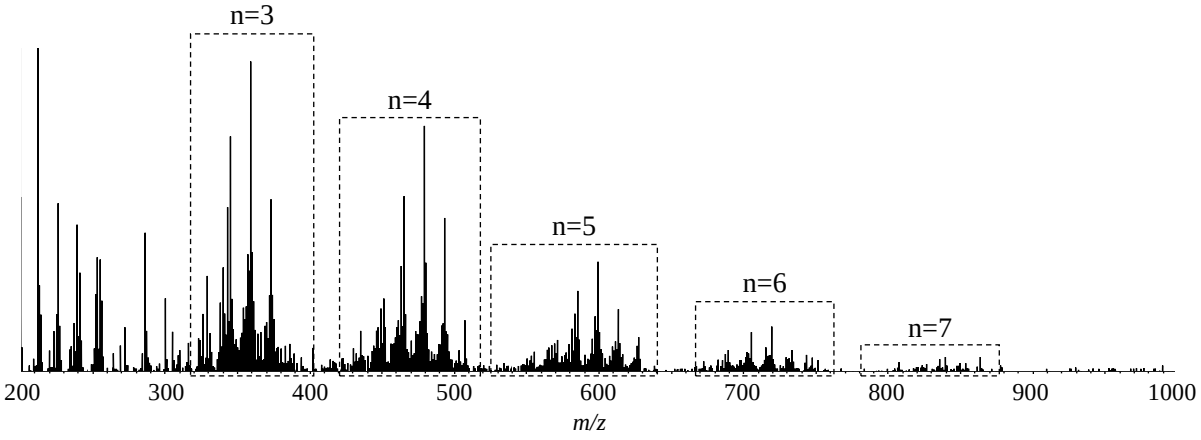


Fig. 7. MALDI mass spectrum of pyrolysis products at 550 ºC of PPE collected in THF.

Fig. 8

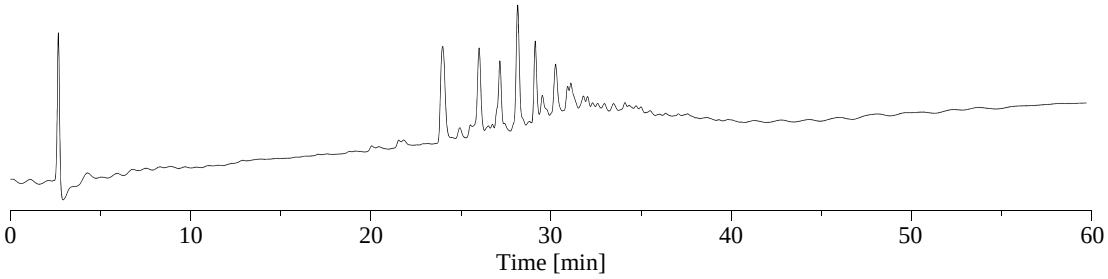


Fig. 8. On-line HPLC chromatogram of collected pyrolysis products of PPE at 550 ºC by UV detection.

Fig. 9

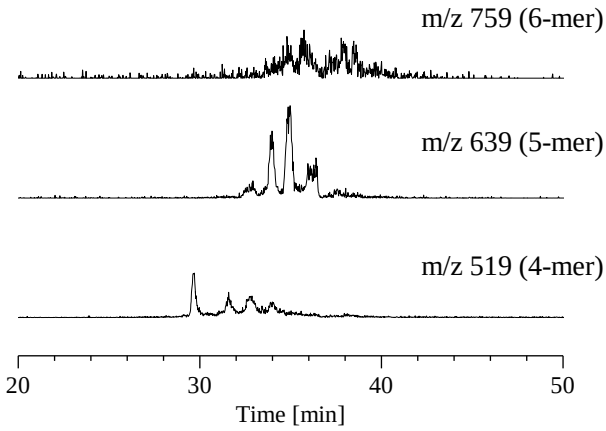


Fig. 9. Extracted ion chromatograms of oligomeric pyrolysis products of PPE at 550 ºC.

Fig. 10

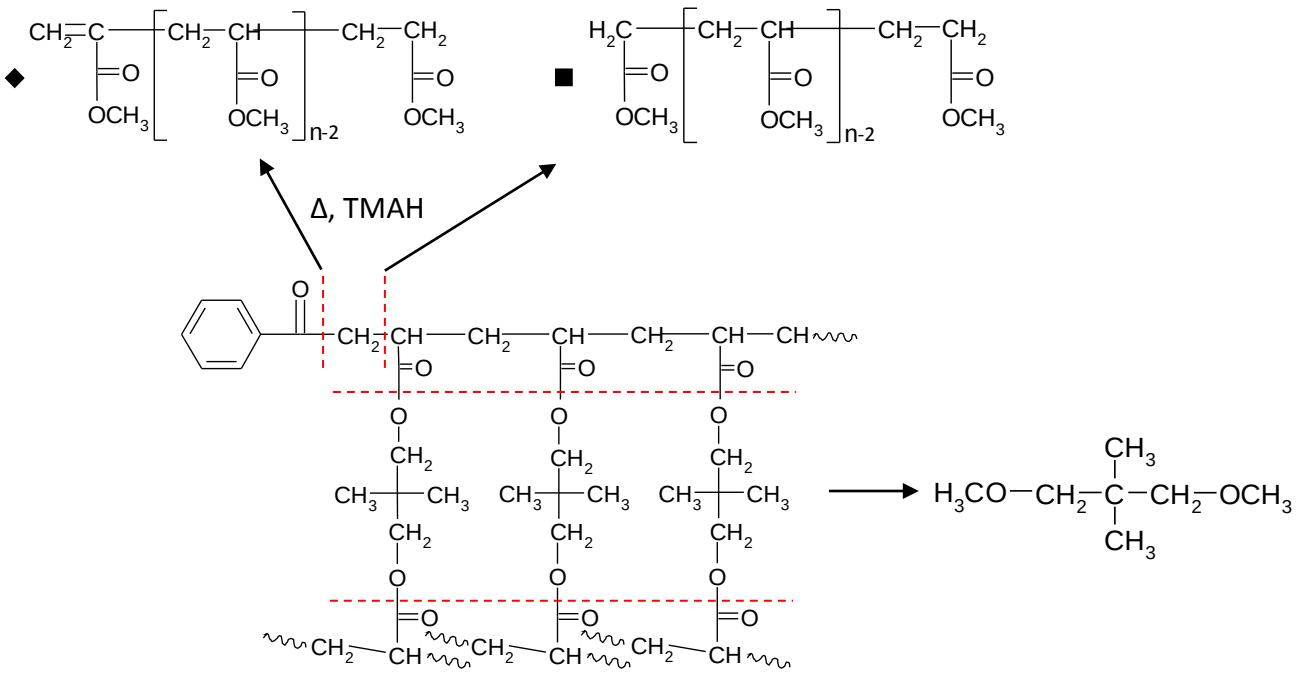


Fig. 10. Thermally-assisted hydrolysis and methylation pathway of photocured acrylic resin sample.

Fig. 11

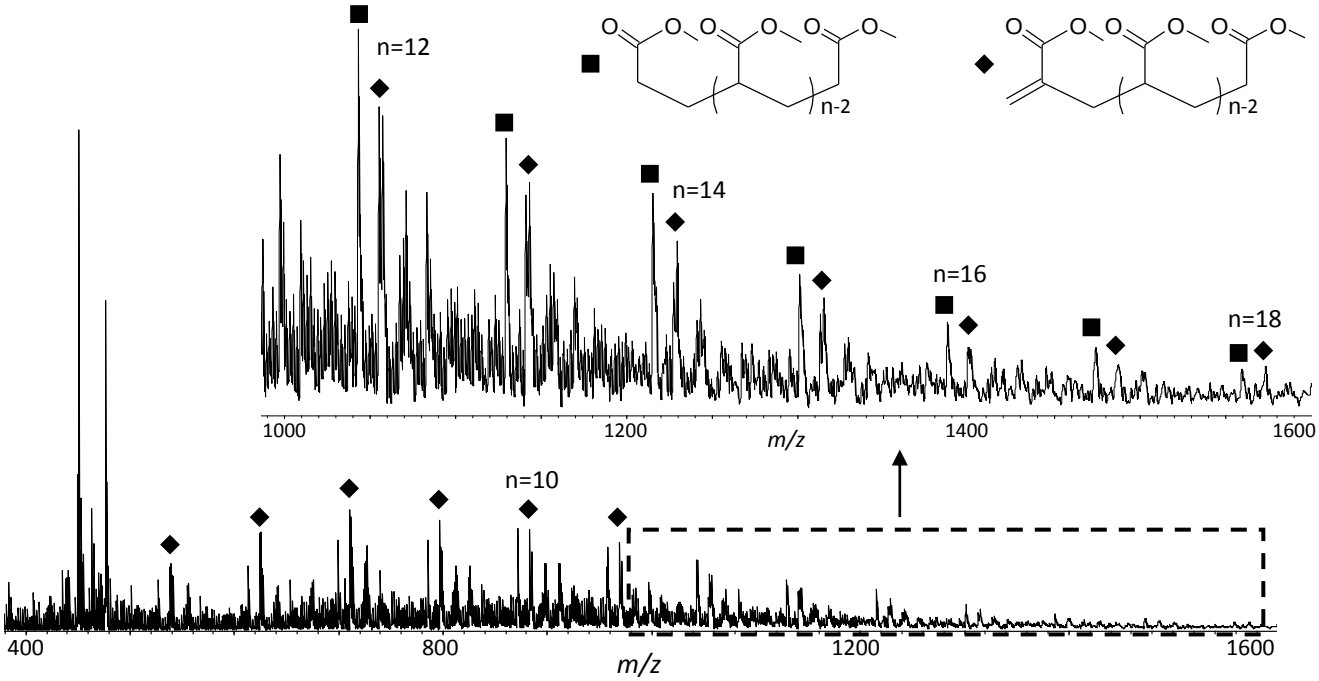


Fig. 11. MALDI mass spectrum of THM products of photocured acrylic resin sample collected in THF.

S1. Results for poly(methyl acrylate) (PMA)

PMA generally decomposes into a series of MA oligomers through the random chain scission accompanied by radical transfer reactions at elevated temperature [S1, S2]. Fig. S1 shows a typical pyrogram of PMA observed by conventional Py-GC-MS at 550 °C. In this case MA monomer and oligomers up to heptamer (n = 7) can be observed [S3].

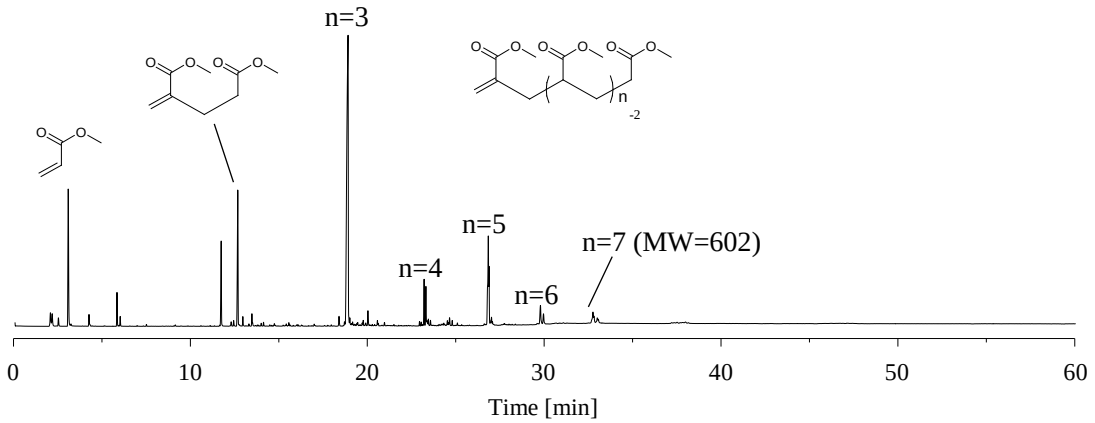


Fig. S1. Pyrogram of PMA observed by Py-GC-MS at 550 ºC.

PMA sample was then subjected to the developed pyrolysis device. An aliquot of the collected pyrolyzates (at 550 °C) dissolved in THF was measured by MALDI-spiral-TOF-MS using HABA as a matrix reagent. The observed mass spectrum is shown in Fig. S2. A series of MA oligomers are observed at least up to 26-mer, and each n-mer contains three types of products as shown in Fig. S2(b). These results demonstrate that high molar mass pyrolyzates unobservable by Py-GC are successfully recovered by the pyrolyisis device.

S2. Results for Nylon 11

Aliphatic polyamides (Nylon) are known to be pyrolyzed mainly into various sizes of cyclic amides (lactams) and linear products having nitrile, alkyl and/or olefinic terminals formed through *cis*-elimination reactions along with random chain scissions. As for Nylon 11, therefore, the pyrolysis products listed in Table S1 should be yielded. Fig. S3 shows a typical pyrogram of Nylon 11 obtained by Py-GC-MS at 550 °C. Although various pyrolyzates listed in Table S1 are observed [S3, S4], the assigned products are mostly those having only one or no amide group such as L_1, L_2 and $D_{0\text{-}10}$. Even the largest pyrolyzate, $A_{1\text{-}20}$, of which molecular weight is *ca.* 508, contains merely two amide groups.

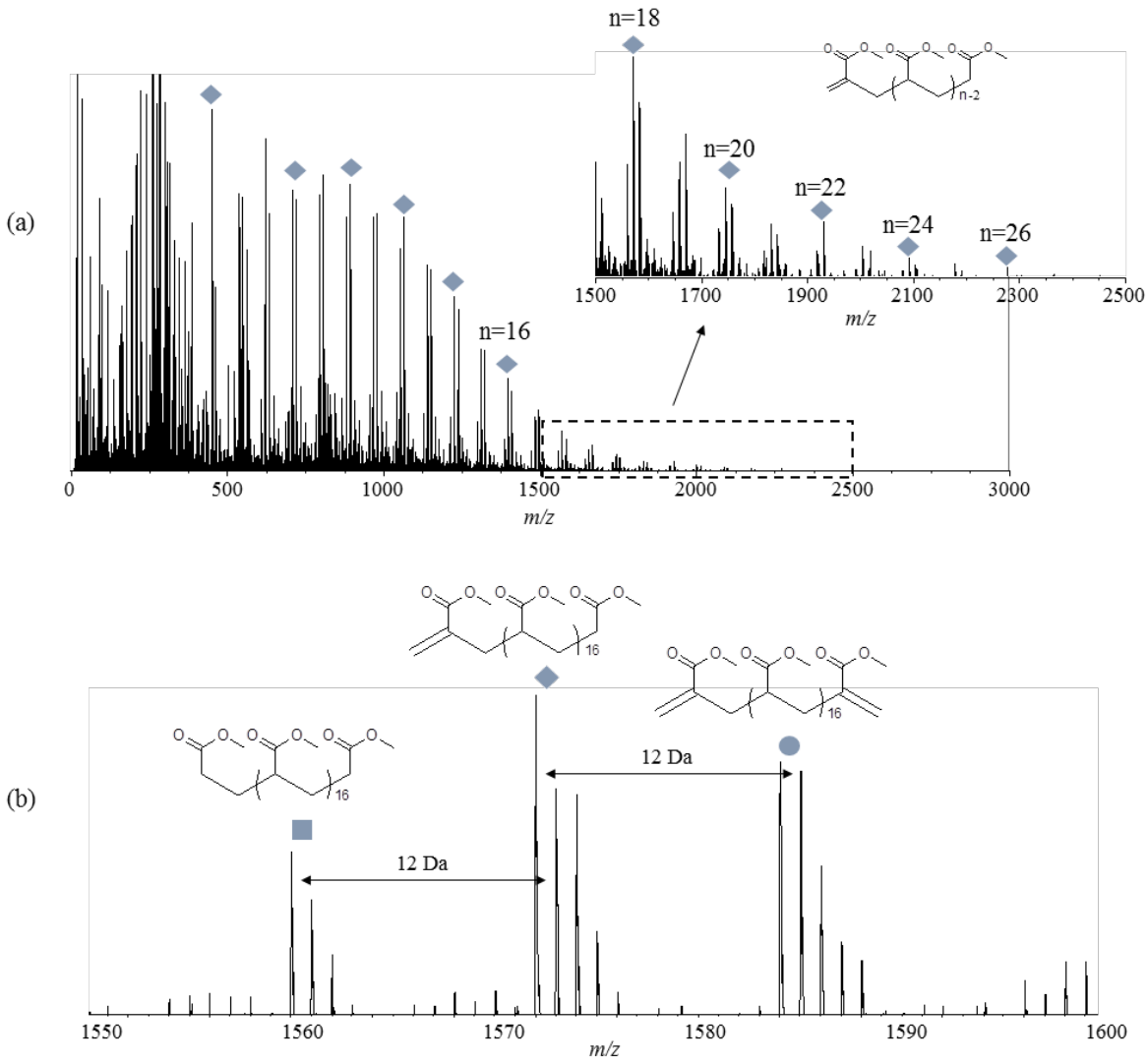
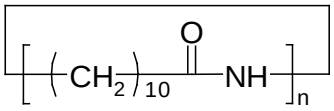
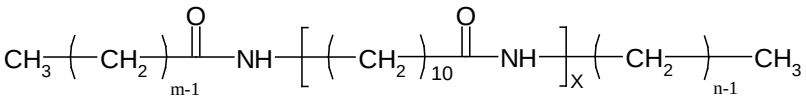
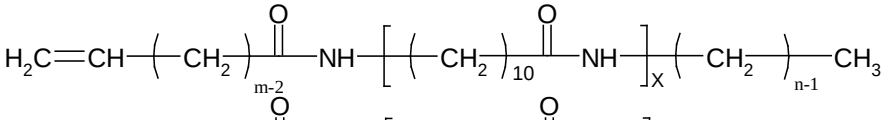
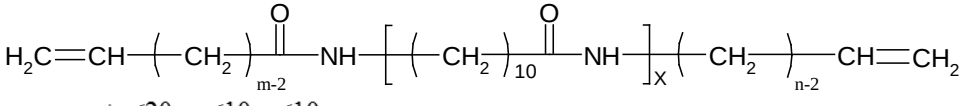
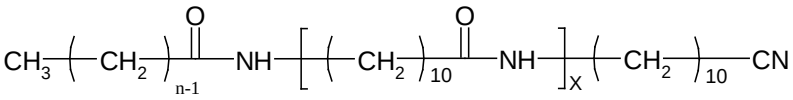
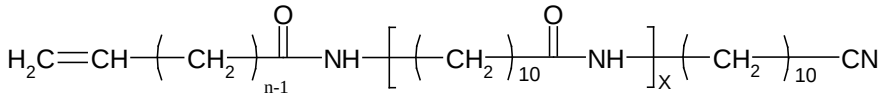


Fig. S2. MALDI mass spectrum of pyrolysis products at 550 ºC of PMA collected in THF. (a) overall spectrum. (b) its expended view between *m/z* = 1550 and 1600.

Nylon 11 was then pyrolyzed at 550 °C in the pyrolysis device and the pyrolyzates were collected with THF. The recovered solution was sampled to be measured directly by MALDI-MS. Fig. S4 shows the observed mass spectra for the pyrolyzates of Nylon 11 obtained by MALDI-spiral-TOF-MS with HABA matrix. In the oligomer range larger than *m/z* 500, which cannot be detected by Py-GC-MS, a number of products are detected. Among these, trimeric and tetrameric lactams (L_3 and L_4) are distinctly observed. As shown in the expanded spectrum in Fig. S4(b), various linear products containing three amide groups were identified in the *m/z* range between 620 and 645. (The observed peak splitting should be caused by the overlapping of possible isotopic ions for individual pyrolyzates.) Moreover, although with small intensities, ions for the pyrolyzates were clearly observed even in the region around 1400, which corresponding to the octameric products with seven amide groups. These observations indicated that not only large molar mass but also polar pyrolyzates originated from polar polymers such as Nylons should be able to be analyzed by using the developed pyrolysis device.

Table S1 Representative pyrolyzates of Nylon 11.

peak code	chemical structure
L_n	
$A_{X-(m+n)}$	
$B_{X-(m+n)}$	
$C_{X-(m+n)}$	 $m+n \leq 20,\ m \leq 10,\ n \leq 10$
D_{X-n}	
E_{X-n}	 $n \leq 10$

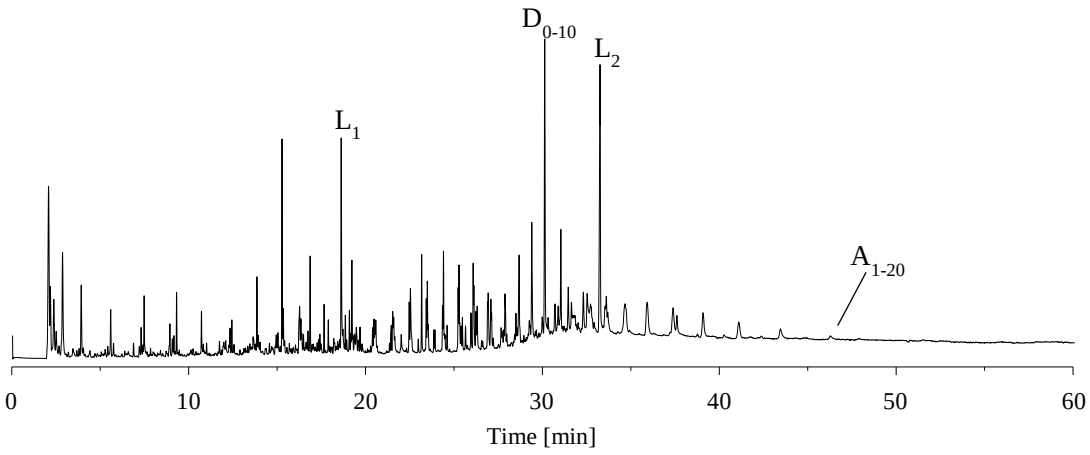


Fig. S3. Pyrogram of Nylon11 observed by Py-GC-MS at 550 ºC.

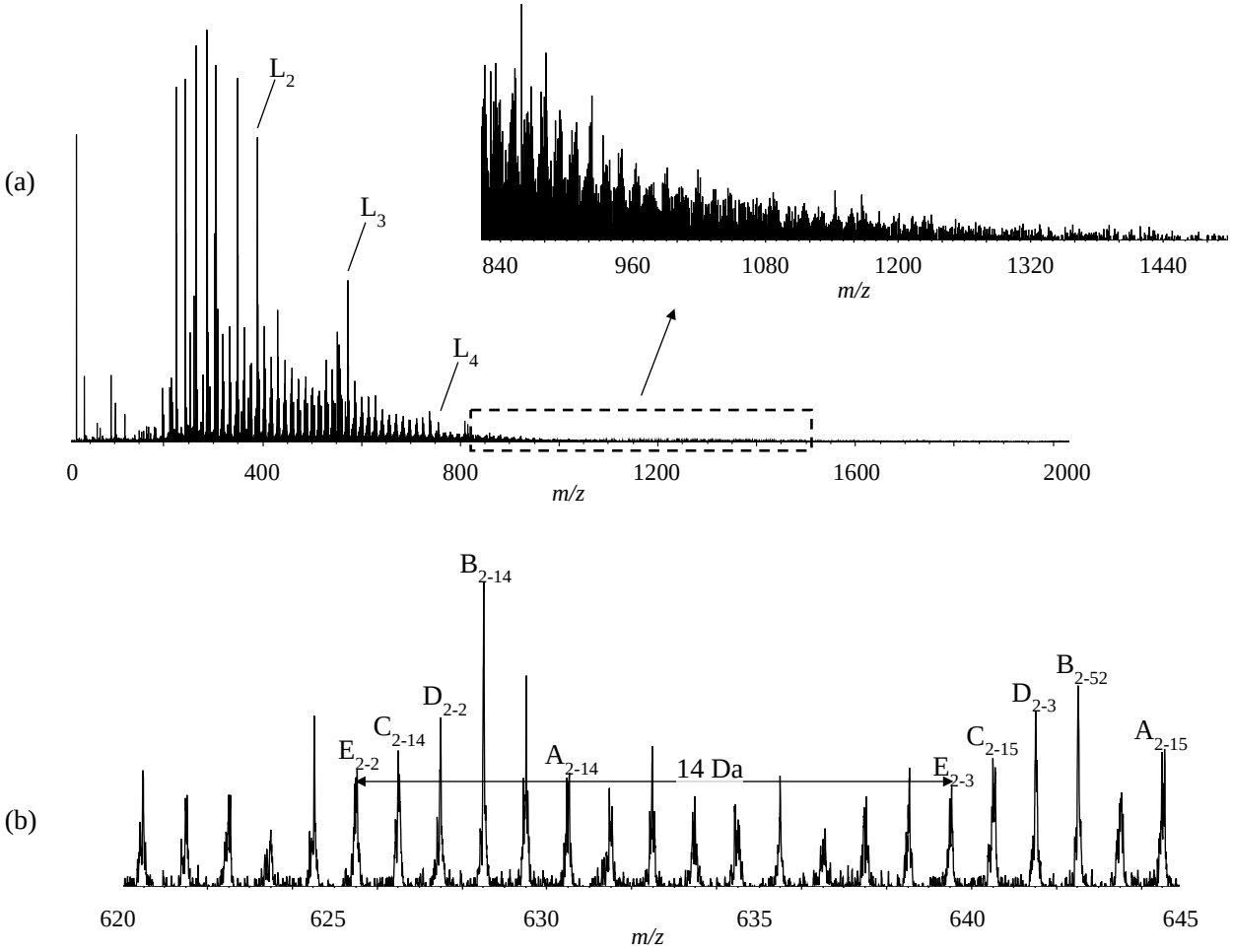


Fig. S4. MALDI mass spectrum of pyrolysis products at 550 ºC of Nylon11 collected in THF. (a) overall spectrum. (b) its expended view between *m/z* = 620 and 645.

S3. Secondary reactions in MALDI process of PPE pyrolyzates

A number of clusters were observed in the MALDI mass spectrum of the PPE pyrolyzates for oligomers of each degree of polymerization (n) (Fig. 7). Here the peaks in the pentamer region (n = 5) were examined in detail. A representative formation pathway of a pentameric (n = 5) product is shown in Fig. S5, provided that the Fries rearrangement would completely proceed during pyrolysis pathway. The resultant pyrolyzate shown in Fig. S5 should be possibly the largest pentamer, and is abbreviated to 5-0. Depending on the cleavage position, the smaller pentamers by one or two CH_2 unit(s) could be also produced, which are abbreviated 5-1 and 5-2, respectively. These three types of products, 5-0 - 5-2, would be thus the most probable pentameric pyrolyzates. In fact, as for the dimeric and trimeric pyrolyzates of PPE observed by Py-GC-MS, the corresponding products were confirmed to be predominant as shown in Fig. S6 and Table 3. In the observed MALDI mass spectrum of the PPE pyrolyzates, however, 5-0 - 5-2 were not the main products in pentamer region as shown in the expanded view in Fig. S6. Smaller components corresponding to 5-3 - 5-6 appeared rather abundantly. Moreover, the larger *m/z* ions by 2 for 5-0 - 5-6, which might be attributed to a hydrogenated ($+H_2$) or an oxidized ($+O - CH_2$) product of 5-0 - 5-6, were detected in higher intensities than those for 5-0 - 5-6. These observations suggest that the undesirable degradations and/or

secondary reactions might fairly occur for PPE pyrolyzates during MALDI process [S5].

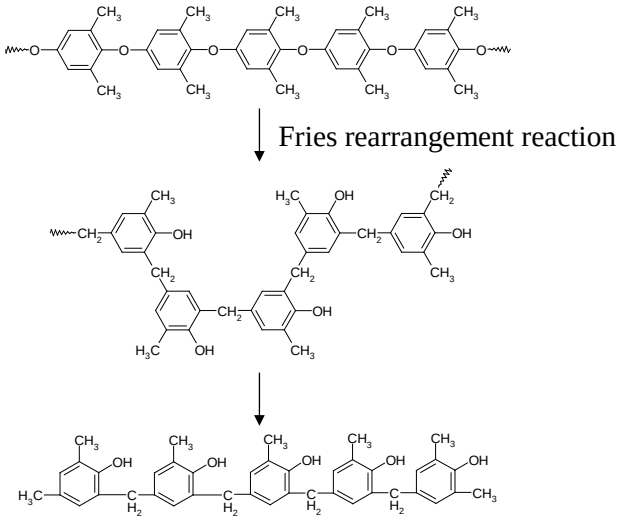


Fig. S5. Pyrolysis pathway of PPE to form pentamer (n = 5) with maximum numbers of substitution (5-0) through complete Fries rearrangement.

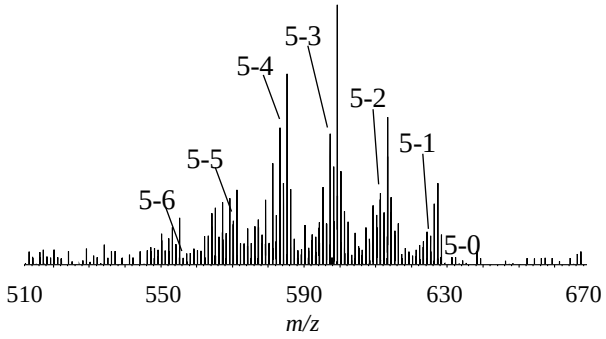


Fig. S6. Expanded MALDI mass spectrum for pentamer region of pyrolysis products at 550 ºC of PPE collected in THF

Fig. S7 shows the observed total ion chromatogram (TIC) of the collected pyrolyzates of PPE observed by HPLC-ESI-MS. Since the separation conditions have not been optimized, the observed peak separation is far from sufficient. The eluted components, however, can be identified on the basis of the accumulated ESI mass spectrum for the whole range of the chromatogram. Fig. S8 shows the expanded region for the pentamers in the accumulated ESI mass spectrum in the range between 10 and 50 min. It is interesting to note that the observed main pentamers (5-0 - 5-2) are those expected to form by pyrolysis as shown in Fig. S5. This result indicates the PPE pyrolyzates can be observed in the original form by ESI-MS, unlike MALDI-MS.

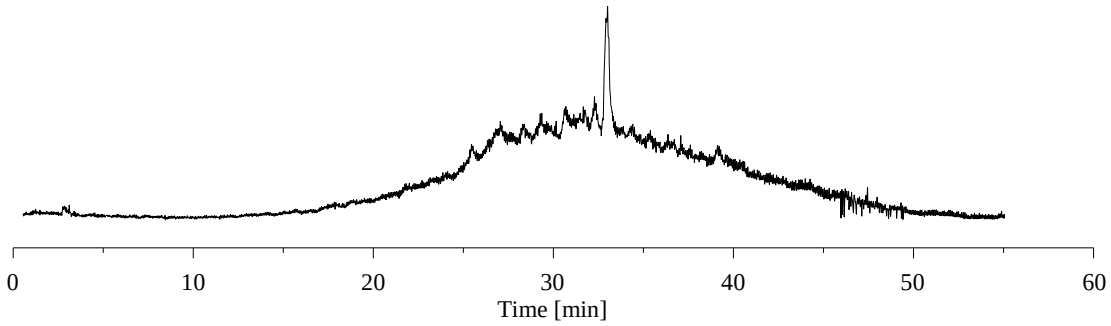


Fig. S7. Total ion chromatograms of collected pyrolysis products of PPE obtained by HPLC-ESI-MS.

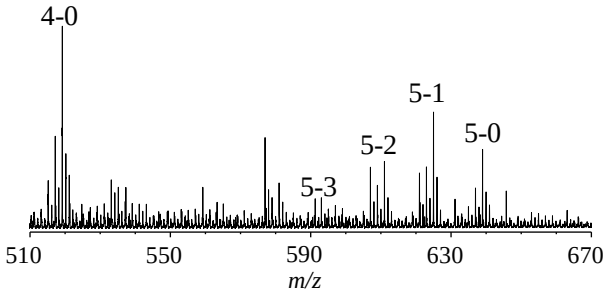


Fig. S8. Accumulated ESI mass spectrum of collected pyrolysis products of PPE at 550 ºC.

References

[S1] R. S. Lehrle, E. J. Place, Polym. Degrad. Stab., 56 (1997) 215-219; 221-226.

[S2] F. Bertini, G. Audisio, V. V. Zuev, Polym. Degrad. Stab., 89 (2005) 233-239.

[S3] S. Tsuge, H. Ohtani, C. Watanabe, Pyrolysis-GC/MS Data Book of Synthetic Polymers -Pyrograms, Thermograms and MS of Pyrolyzates-, Elsevier, 2011.

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