Latest Trends in Pyrolysis Gas Chromatography for Analytical and Applied Pyrolysis of Plastics

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Pyrolysis is considered to be a promising method for polymer characterization (in the field of analytical pyrolysis) and for chemical feedstock recovery from plastic wastes (in the field of applied pyrolysis) because it can decompose any polymeric material into smaller molecules by applying heat alone in an inert atmosphere. Pyrolysis-gas chromatography (Py-GC) involves pyrolyzing polymeric materials in a micropyrolyzer and a subsequent direct GC analysis of pyrolyzates. Py-GC has immense potential for applications in the fields of both analytical and applied pyrolysis, as it allows for rapid and accurate analysis of pyrolyzates. This is beneficial for elucidating microstructure and composition of polymers and for a rapid screening of pyrolysis conditions for designing feedstock recycling processes. In this review, we examined the latest research trends in Py-GC applications for polymer characterization, analysis of plastics in the environment, and chemical feedstock recovery from plastics.

Keywords Analytical pyrolysis, applied pyrolysis, gas chromatography, plastics

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1 Latest Trends in Plastic Production and Waste Plastic Recycling

Plastics are widely used in our daily life owing to their light weight and inexpensive features, as well as because of their good processability and ease of functionalization through combination with additives. Global plastic production has increased from 1.5 million tons (Mt) in 1950 to 359 Mt in 2018. Over the last ten years (2008 - 2018), plastic production has increased ~1.5 times.1,2 In the domestic market, over 150 types of resins are being manufactured.3,4 Plastics are classified into thermoplastics and thermosetting types, according to the molecular structure or molding method, and into commodity

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plastics, engineering plastics, and super engineering plastics, according to their heat resistance and application. In general, plastic products contain several additives, such as antioxidants, stabilizers, lubricants, antistatic agents, antifogging agents, plasticizers, nucleating agents, flame retardants, foaming agents, and fillers, to achieve the desired performance. More than 230 types of additives have been manufactured in Japan; therefore, there are uncountable combinations of resins and additives. The rapid and accurate analysis of plastic products, especially identification of the polymer type, polymer composition and microstructure, the additive type, and changes in the polymer structure by deterioration have of late been in high demand in the polymer industry.

The constant growth of waste plastic generation is observed in the data of global primary plastic waste generation. According to a report published by the Ellen Macarthur Foundation, 78 Mt of plastic packaging materials were produced in 2013, of which 40% was treated by landfilling, 32% was leaked into the environment, 14% was incinerated for energy recovery, and only 14% was recycled. Plastic leaked into the environment leads to soil and water pollution, thereby deteriorating the ecosystem. In Japan, 8.9 Mt of waste plastics were generated in 2018, of which 84% was recycled or utilized as an energy source (23% in mechanical recycling, 4% in feedstock recycling, and 56% for energy recovery), and 16% was treated by incineration without energy recovery and landfilling. In Japan, the Fourth Fundamental Plan for Establishing a Sound Material-Cycle Society (2018) proposed establishing the Resource Circulation Strategy for Plastics, which was formulated in May 2019. The strategy has sloganized “3R+Renewable”, which aims to promote the reduction, reuse, recycling, and use of bio-based plastics. Several milestones were established as part of the strategy: a 25% reduction in single-use plastics usage by 2030, 60% reuse/recycling of plastic containers and packaging by 2030, complete utilization of waste plastics via reuse and recycling by 2035, and the introduction of ∼2 Mt of bio-based plastics by 2030. Global trends like the Sustainable Development Goals (SDGs) and circular economy have led to a recent rapid increase in demand for plastic recycling. In addition, a recent focus on ocean plastic pollution and the decision by China to ban waste plastic imports have had significant impacts on several industrial sectors around the world. Therefore, the development of technologies that can significantly increase the amount of recycled plastic waste as well as to improve the quality of recycled products have recently been in high demand.

As described above, pyrolysis is a promising technology that can meet the demands of both the polymer industry and the plastic recycling industry. Pyrolysis involves the decomposition of polymeric materials with low solubility, high molecular mass, and low volatility into smaller molecules by the application of heat alone in an inert atmosphere. Pyrolysis allows the characterization of a polymer structure and composition based on the distribution of pyrolyzates. Particularly, plastic pyrolyzates can be utilized as a monomer, fuel, or a valuable chemical. To harness the immense potential of pyrolysis for a broad range of applications, a high-throughput technology to conduct pyrolysis is crucial. This review presents the latest developments in pyrolysis–gas chromatography (Py-GC) applications for polymer characterization, analysis of plastics in the environment, and chemical feedstock recovery from plastics.

2 Pyrolysis-Gas Chromatography

Pyrolysis-gas chromatography (Py-GC) allows for the pyrolysis of polymeric materials in a micropyrolyzer, followed by GC analysis of the pyrolyzates. Capillary columns and mass spectrometer (MS) have been commonly employed for Py-GC, whereas the detection system should be selected to suit the purpose of pyrolyzate analysis. Prof. Tsuge developed an innovative Py-GC method for the first in-depth microstructural analysis of polymers using analytical pyrolysis. He also developed a vertical furnace-type pyrolyzer that greatly
improves the reproducibility of the observed data by Py-GC. Currently, there are mainly three types of pyrolyzers, viz. filament-type (Fig. 1(A)), Curie-point type (Fig. 1(B)), and micro-furnace-type (Fig. 1(C)), which allow for rapid heating, with accurate and broad temperature control. Basically, Py-GC allows for the investigation of any polymers and additives without any pretreatment, thus providing important compositional and structural information in a simple manner. Analysitcal pyrolysis enables elucidation of the chemical composition and structure of materials in the fields of environmental, biological, medical, forensic, cultural heritage, food, geochemical, polymer, and materials science, involving the use of new instrumentation and new analytical methods based on pyrolysis reactions. On the other hand, applied pyrolysis involves the development of pyrolytic processes for producing valuable chemicals, energy carriers (gas, liquid, and solid), materials from fossils, renewable feedstock or waste, along with the recycling of materials and the disposal of toxic substances. In both categories, Py-GC is a promising technique that allows for the rapid and accurate analysis of pyrolyzates, which is beneficial for elucidating the pyrolysis reaction mechanism and rapid screening of the pyrolysis conditions.

Based on recent (2000 onwards) peer-reviewed international journal publications, in this review, we examine the latest trends and challenges associated with the analytical and applied pyrolysis of plastics by employing Py-GC techniques. Notably, although Py-GC has a very long history (over 60 years),23 and there are many excellent studies that are not summarized in this review. Here, we have focused on the characterization of polymer microstructures and analyses of plastics in the environment using analytical pyrolysis, on Py-GC applications for chemical feedstock recovery from plastics and new instrumentation using applied pyrolysis. This review did not deal with the synthesis of new polymers and additives, nor with any subsequent analysis of pyrolyzates and their combustion behavior. Co-pyrolysis with other feedstocks, such as coal, petroleum fraction, and biomass, was also not reviewed.

3 Py-GC for Analytical Pyrolysis

3-1 Characterization of polymer structure

The characterization of monomer composition and end/side group structure has been in great demand in many industries, including both polymer manufacturers and polymer consumers, for evaluating product quality. Spectroscopic analyses, such as infrared spectroscopy and nuclear magnetic resonance spectroscopy, are common polymer characterization techniques used to identify and quantify functional groups in polymers, while Py-GC is beneficial for detailed elucidation of polymer microstructure. The selected reports on polymer structure characterization by Py-GC are summarized in Table 1. Identification and quantification of monomer composition is a major trend in Py-GC studies (Entries 4, 6, 11, 12, 15, 17, 18).23 Wampler et al.25 (Entry 11) pyrolyzed block (7 – 25 wt% ethylene) and random (40.1 – 78.6 wt% ethylene) copolymers of ethylene and propylene at 650 – 850°C using Py-GC/MS. They reported that the ethylene/propylene ratio in the block and random copolymers are strongly related to the pentadecane (as PE pyrolyze)/PP hexamer ratio and hexene (ethylene trimer)/dimethyl heptene (propylene trimer) ratio, respectively. Wang et al.27 (Entry 15) quantified the ethylene/propylene composition in their copolymers (0 – 100 wt% ethylene) based on trimmer distribution in their pyrolyzates obtained at 700°C by Py-GC/fluence ionization detector (FID). They also suggested that the copolymer microstructure can be inferred based on the trimer distribution. Salinas et al.29 (Entry 18) pyrolyzed physical mixtures of poly(acrylonitrile-co-1,3-butadiene-co-styrene)/polymamide 6 (ABS/PAm) (10 – 80 wt% ABS) by using Py-GC/MS and FID at 700°C and reported a good linearity between caprolactam/main ABS pyrolyzes and the PA6 content in the blends. Ohtani et al. have extensively studied reactive-Py-GC techniques, using tetramethylammonium hydroxide (TMAH) as an organic alkali, for the structural characterization of condensation polymers like poly(aryl ether sulfone) (PES) and polysulfone (PSF) (Entry 4),23 ultraviolet (UV)-curled resins consisting of multi-component acrylic esters (Entry 6),24 and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)) (Entry 12).28 Excess TMAH was added to samples in a sample cup, followed by pyrolysis at appropriate temperatures (depending on the polymer type) for accurate quantification of the monomer composition. Takeuchi et al. (Entry 17)29 reported a two-step reactive-Py-GC method (Fig. 2(a)) for the characterization of styrene-co-butyl acrylate-co-methacrylic acid (St-BA-MAA, St/BA/MAA molar ratio = 30:33:37) terpolymer. The first step involves the conversion of polar MAA units in the terpolymer sample to methyl methacrylate (MMA) units using tetramethylammonium acetate (TMMAc) at 200°C, followed by ready depolymerization into MMA monomers upon pyrolysis (Fig. 2(b)). The converted sample was then pyrolyzed at 600°C to obtain a specific pyrogram, consisting of the characteristic products of each monomer unit, the yields of which were interpreted in terms of the terpolymer composition. The terpolymer composition (mol%) was estimated to be St/BA/MAA = 29.9/33.1/37.1, which was almost identical to the feed composition, with excellent relative standard deviations of < 0.25%.

The application of the Py-GC technique for structural characterization has been widely reported (Entries 1 – 3, 5, 7, 8, 16): identification of end groups in styrene-methyl methacrylate (St-MMA) copolymers synthesized under different conditions30 (Entry 1), tacticity of MMA sequences in the several types of MMA copolymers31 (Entry 2), branching and cross-linking structures in commercial polycarbonate (PC) synthesized by different methods32 (Entry 3), branching type of poly-α-olefins33 (Entry 5), abnormal structures like branching and condensed structures in liquid-crystalline aromatic polymers (LCPs) based on 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (NHA)34 (Entry 7), substituted side chains in poly(p-phenyleneethylenylene) (PPE) with different side chains35 (Entry 8), and cross-linking structure in thermally pretreated poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT)36 (Entry 16). The Py-GC technique can be used for microstructure analysis of thermosetting polymers, such as novolac and resol resins37 (Entry 10) and UV-cured resins38,39 (Entries 6, 9, 13). Fully cured novolac resin mainly produced phenol and its derivatives, as well as a certain amount of less-volatile compounds with two condensed rings, whereas xanthenes and bisphenols were obtained from partially cured novolac (Entry 10). Thus, the extent of curing can be evaluated by using the Py-GC technique. Matsubara and Ohtani28 quantified the molecular weight of original bisphenol A (BPA)-type epoxy acrylate prepolymer in UV-cured resins by ascertaining the relationship between the molecular weight of the prepolymer and the relative yields of specific products during reactive pyrolysis using TMAH (Entry 13). Lizarraga et al.40 (Entry 14) investigated pyrolyzates of polyacrylne with two different forms: fully reduced leucoemeraldine (LE) and immediately oxidized emeraldine (EM), and reported that...
**Table 1** Summary of reports on the use of Py-GC for polymer microstructure analysis

| Entry | Method (Deriv. reagent) | Samples | Major achievements | References |
|-------|--------------------------|---------|--------------------|------------|
| 1     | Py-GC/FID/NPD, FID/MS    | St-MMA copolymers synthesized by different conditions | Identification of end groups in St-MMA copolymers | Ohtani et al.*30 (2000) |
| 2     | Py-GC/MS                 | MMA/MA, MMA/EA, MMA/BA, MMA/2-EHA | Identification of tacticity of MAA sequences in the polymer chains | Kira et al.*31 (2000) |
| 3     | Py-GC/MS (TMAH)          | PC synthesized by different methods | Identification of branching and cross-linking structures | Oba et al.*32 (2000) |
| 4     | Py-GC/MS, FID (TMAH)     | Commercial PES and PSF with different MW | Identification of monomer composition | Ohtani et al.*33 (2001) |
| 5     | Py-GC/MS                 | Poly-alpha-olefins and copolymers | Identification of branching type | Rui et al.*34 (2001) |
| 6     | Py-GC/MS, FID (TMAH)     | UV-cured resins consisting of multi-component acrylic esters | Quantification of the monomer ratio | Matsubara et al.*28 (2002) |
| 7     | Py-GC/MS, FID (TMAH)     | LCP (HBA/HNA = 73/27, molar ratio) | Identification of abnormal structures such as branched structures and condensed structures | Oba et al.*36 (2002) |
| 8     | Py-GC/MS                 | PPE substituted with varying side groups | Identification of substituted side-chains | Setlers et al.*37 (2002) |
| 9     | Py-GC/MS, FID (TMAH)     | UV-cured resin prepared from PEDA (PEDA:MMP = 100:3, molar ratio) | Identification of network structures | Matsubara et al.*38 (2003) |
| 10    | Py-GC/MS                 | Cured novolac and resol resins | Identification of difference in curing progress level | Sobera and Hetter*27 (2003) |
| 11    | Py-GC/MS                 | Block copolymers of ethylene and propylene with different ratios | Quantification of ethylene and propylene ratio | Wampler et al.*29 (2003) |
| 12    | Py-GC/MS, FID (TMAH)     | P3(3HB-co-3HV) with a range of 3HV contents (4 – 23 mol%) | Quantification of copolymer composition | Sato et al.*30 (2005) |
| 13    | Py-GC/MS, FID, FTIR (TMAH) | UV-cured resin prepared from BPA type epoxy acrylate | Quantification of molecular weight of BPA type epoxy acrylate prepolymer | Matsubara et al.*36 (2006) |
| 14    | Py-GC/MS                 | Polyamine forms (leucoemeraldine and emeraldine) | Identification of different oxidation states in aryl amine polymers | Lizarraga et al.*40 (2007) |
| 15    | Py-GC/FID                | Ethylene propylene copolymers with different ratios | Quantification of monomer composition and information on inferring monomer arrangement | Wang et al.*27 (2007) |
| 16    | Py-GC/MS, FID, FTIR (TMAH) | Commercial PET and PBT with and without thermal treatment | Identification of cross-linking structures such as biphenyl type structures | Kawai et al.*36 (2008) |
| 17    | Py-GC/MS, FID (TMAH, TMAAc) | St-BA-MAA terpolymer (St/BA/MAA = 30/33/37, molar ratio) | Precise quantification of monomer composition via two-step reactive Py-GC method | Takeuchi et al.*28 (2015) |
| 18    | Py-GC/MS, FID (TMAH)     | ABS/PA6 blends with different ratio | Quantification of blending ratio | Salinas et al.*35 (2016) |
| 19    | Py-GC/MS, FID (TMAH)     | St-BA copolymer (ST:BA, 80:20 molar ratio) prepared via radical polymerization with various amounts of BPO | Quantification of feed amounts of BPO | Ohtani et al.*40 (2017) |
| 20    | Py-GC/APCI-TOFMS         | MMA-St-BA terpolymer (MMA/St/BA = 40/40/20, weight ratio) synthesized via radical polymerization with AMBN | Identification of all possible pyrolyzates (AMBN fragment, monomer unit) | Harata et al.*42 (2020) |

**[Abbreviations]** Equipment: Py; pyrolysis; GC; gas chromatograph; FID: flame ionization detector; NPD: nitrogen phosphorus detector; MS: mass spectrometer; FTIR: Fourier transform infrared spectroscopy; IRMS: isotope ratio mass spectrometer; APCI: atmospheric pressure chemical ionization; TOFMS: time-of-flight mass spectrometer. Derivatization reagent: TMAH: tetramethyl ammonium hydroxide; TMAAc: tetramethylammonium acetate. Polymer and monomer: St: styrene; MMA: methyl methacrylate; MA: methyl acrylate; EA: ethyl acrylate; BA: n-butyl acrylate; 2-EHA: 2-ethyl hexyl acrylate; PC: polycarbonate; PES: poly(aryl ether sulfone); PFS: polysulfone; LCP: liquid crystalline aromatic polyester; HBA: 4-hydroxybenzoic acid; HNA: 2-hydroxy-6-naphthoic acid; PPE: poly(p-phenyleneethylenylene); PEDA: poly(ethylene glycol) diacrylate; 3HB: 3-hydroxybutyrate; 3HV: 3-hydroxyvalerate; PETA: pentaerythritol triacylate; HDPE: high density polyethylene; LDPE: low density polyethylene; VLDPE: very low density polyethylene; ABS: acrylonitrile-co-1,3-butadiene-co-styrene; PA6: polyamide 6; AMBN: 2,2’-azobis(2-methylbutyronitrile).

different pyrolyzates were obtained from each form. They suggested that Py-GC/MS can be used for identification among different oxidation states in conducting polymers. The quantitative analysis of end groups in copolymer samples is difficult due to the production of complex pyrolyzates that overlap with the key end-group products. However, the initial content of benzyol peroxide (BPO) as a radical polymerization initiator in St-BA copolymers was successfully determined by the quantification of end groups of St-BA copolymers by a two-step reactive-Py-GC method*41 (Entry 19). Benzoyloxy terminal groups were selectively decomposed to produce methyl benzoate in the first step using TMAH at a relatively low temperature (250 °C). The residual polymer sample containing phenyl terminal groups was then subjected to ordinary Py-GC analysis at an elevated temperature (600 °C). Of late, complex end groups in MMA-St-BA terpolymer, which was radically polymerized using 2,2’-azobis(2-methylbutyronitrile) (AMBN), were selectively detected and exclusively identified by a new Py-GC/MS system using an atmospheric-pressure chemical ionization (APCI) source combined with a high-resolution time-of-flight mass spectrometer (TOFMS)*42 (Entry 20).
3-2 Analysis of plastics in the environment

The advanced techniques for polymer microstructure analysis by Py-GC have been validated in the previous section. The excellent performance of Py-GC has often been utilized to analyze environmental plastics in soil and water, which would ultimately help to maintain a healthy ecosystem, as aforementioned. The importance of evaluating the biodegradation performance and elucidating the biodegradation mechanism of biodegradable plastics is also clearly mentioned in the Resource Circulation Strategy for Plastics in Japan.8 Sato et al.43 investigated the degradation of poly(ε-caprolactone) (PCL) containing an α-benzylxylo terminal by an enzyme, cholesterol esterase, using reactive-Py-GC/MS and FID with TMAH and matrix-assisted laser desorption/ionization (MALDI)-MS. The content of the specific terminal units can be estimated using reactive-Py-GC, while any structural changes and the molecular weight of the individual polymer chains in the residual polymer fractions during enzymatic degradation can be determined by MALDI-MS. Baidurah et al.44 quantified butylene adipate (BAd) and butylene succinate (BS) units in poly(butylene succinate-co-butylene adipate) (PBSA) at different biodegradation levels using reactive-Py-GC/MS and FID with TMAH to evaluate the soil burial biodegradation behavior of PBSA. The copolymer composition of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] was also determined by the same technique to evaluate its soil burial biodegradation behavior.

Of late, Py-GC has emerged as the most attractive technique for characterizing microplastics (MPs), which are defined as synthetic solid particles or polymeric matrices of any shape with a size of less than 5 mm. La Nasa et al.45 summarized the main pyrolyzates of the common polymers in MPs, along with their corresponding m/z values; this is shown in Fig. 3. It is worth noting that the best target ions strongly depend on the combination of plastics and matrix. Fabbri et al.46 isolated polyvinyl chloride (PVC) and polystyrene (PS) from core sediments and suspended particulate matter (SPM) collected from the coastal lagoon Pialassa Biona (Italy) and quantified these by pyrolyzing them at 700°C using Py-GC/MS. Fries and co-workers47–48 proposed a two-step MPs separation method, which involves an air-induced overflow using saturated NaCl (fluidization) and subsequent density separation using a NaCl solution. Hydrogen peroxide was used to eliminate the biogenic organics. They investigated organic additives and plastic types of MPs in sediments collected from Norderney island (Germany) using thermal desorption (TD)-GC/MS (heating up to 350°C) and Py-GC/MS (700°C), respectively. Fischer and Scholz-Böttcher49 reported on the simultaneous identification and mass related quantification of MPs in fish samples using reactive Py-GC/MS with TMAH. Biological matrices were eliminated by enzymatic and chemical digestion,51,52 thereby reducing any interference during MP quantification. They compared the performance of a Curie-point pyrolyzer with that of a microfurnace pyrolyzer, which has larger sample cups. Calibration curve (with area) vs. internal pyrolysis process standards (ISTDpy) for the quantification of MPs in some selected environmental samples (sea salt, surface water, and muddy sediment) using the latter is superior in terms of the dynamic range, linearity, process standard deviation, and overall sensitivity. An internal standard mixture is added just before the pyrolysis mimicks the potential interactions between polymer-specific indicator compounds and pyrolytic products of residual organic sample matrices during pyrolysis. Application in selected environmental samples after adequate preconcentration has illustrated the capability and sensitivity of the microfurnace-Py-GC/MS for MP quantification toward the actual analyte concentrations (ppt to ppm) in these samples.53 Zhou et al.54 demonstrated Triton X-45 based cloud-point extraction (CPE) for the first time as a preconcentration method for analyzing trace nanoplastics such as PS and polyethylene methacrylate (PMMA) in environmental water. The CPE-obtained extract was subsequently analyzed by Py-GC/MS, and high sensitivity with detection limits of 11.5 and 2.5 fm for PS and PMMA, respectively, were obtained. Since MP analysis by Py-GC/MS is in high demand, and the common data processing method (manual selection of a set of characteristic pyrolysis products for each polymer) is time-consuming, Matsui et al.55 developed an automated identification algorithm (generation of summed mass spectra) for 11 types of synthetic polymers (PE, PP, PS, PVC, PMMA, nylon6, nylon66, ABS, PET, PC, and polyurethane (PU)) and implemented it in the F-Search software (Frontier Laboratories Ltd.). Harata et al.56 applied Py-GC-APCI-TOFMS for the reliable identification of polymer species in a complex mixture to establish this system as a platform for the analysis of environmental MPs. The unique APCI/fragmentation process and the high mass resolution of TOFMS were exploited to confirm presence of the respective polymer species in the extracted ion chromatograms (EICs) of a mixed sample for the selected key ions. PE and PP were successfully and uniquely identified in a mixed sample by focusing on the specific fragment ions of the pyrolyzates formed during the APCI (m/z 114.093 ± 0.020 and m/z 156.139 ± 0.020,

![Fig. 2](image-url)
respectively). These species could be specifically analyzed from the ElCs, even in the presence of interfering species produced by other polymers.

4 Py-GC for Applied Pyrolysis

4-1 Py-GC for feedstock recycling of plastics

Feedstock recovery from polymeric materials such as plastic wastes by pyrolysis is another important application of Py-GC. Pyrolysis is a promising feedstock recycling technique for the conversion of waste plastics into monomers, fuels, and valuable chemicals through the cleavage of multiple chemical bonds. This is distinctly advantageous for treating heterogeneous plastic wastes consisting of several types of plastics combined with inorganics such as metals and fillers, which are otherwise difficult to recycle using mechanical methods. In this regard, understanding the pyrolyzate evolution behavior and the effects of the pyrolysis conditions on the pyrolyzate distribution is vital. Py-GC requires a small amount of sample, and pyrolyzates are directly introduced into the gas chromatograph, thereby allowing for a rapid screening of the pyrolysis conditions. This feature is extremely beneficial and can aid in the rapid designing of pyrolytic recycling processes and scaling up of the pyrolysis reactors, since pyrolysis in bigger reactors is generally time-consuming.

Recent studies employing Py-GC techniques for considering the chemical feedstock recovery from plastics are summarized in Table 2. This review mainly focuses on the purpose of Py-GC utilization and the analytical methods used in each study.
An evaluation of the significance of the product yield and quality or the catalyst performance is beyond the scope of this review. Blazsó and Czégény62 employed filament-type Py-GC/MS (FT-Py-GCMS) to investigate the effects of the pyrolysis temperature and type of molecular sieves on the degradation of brominated aromatic compounds in tetrabromobisphenol A (TBBPA) blended PC (Entry 21). Brominated flame retardants (BFRs) often deteriorate the quality of the pyrolysis products due to contamination of brominated compounds and thus de-bromination is one of the most challenging factors in feedstock recycling.63 In a pyrolysis test conducted by Blazsó and Czégény,62 a ∼0.2 mg solid sample was sandwiched by a 0.5 mg catalyst bed, wherein the sample and catalyst were separated by quartz wool so as to focus on the catalytic effects on the volatiles. The sample and catalysts were heated in the same quartz wool so as to focus on the catalytic effects on the volatiles. The sample and catalysts were heated in the same quartz wool so as to focus on the catalytic effects on the volatiles.

Table 2  Summary of reports on the use of Py-GC for feedstock recycling of plastics

| Entry | System | Samples | Catalyst | Contact mode | Target of Py-GC employment | References |
|-------|--------|---------|----------|--------------|----------------------------|------------|
| 21    | FT-Py-GC/MS | TBBPA, ALL-TBBPA, PC/TBBPA (4 wt%-TBBPA) | Molecular sieves: 4A, 13X, NaY, Al-MCM-41 | Ex situ | Screening temp. and catal. for effective destruction of brominated aromatic compounds | Blazsó and Czégény62 (2006) |
| 22    | MF-Py-GC/MS | PLLA/LLDPE blend | MgO | In situ | Evaluating effects of MgO on pyrolysis reaction behavior of PLLA/LLDPE blend | Omura et al.64 (2006) |
| 23    | FT-Py-GC/MS | LDPE, recycled PE (AGR and URB) | ZSM-5, n-ZSM-5, Beta, Al-MCM-41, Al-SBA-15, SiO2 | Ex situ | Screening catal. type for effective transformation of PE into hydrocarbons | Aguado et al.60 (2007) |
| 24    | MF-Py-GC/MS | MDI, BD, and PTMGBased PUE with different monomer ratio | None | Ex situ | Evaluating effects of monomer composition on MDI and MDA production selectivity | Kumagai et al.69 (2017) |
| 25    | TR-GCMS/FID/TCD | PE, PP, PS, PET | HZSM-5 | In situ | Evaluating effects of catal. contact mode on products recovery | Xue et al.72 (2017) |
| 26    | TR-GCMS | PET | CaO with different basicity | Ex situ | Monitoring reactions between PET pyrolyzates and CaO | Kumagai et al.79 (2017) |
| 27    | TR-GCMS | PET | CaO with different basicity | Ex situ | Monitoring CaO deactivation and the subsequent change of reaction selectivity | Kumagai et al.77 (2018) |
| 28    | H2-TR-GC/MS | iPrP, IPP (as PC pyrolyzates) | HZSM-5 with different SiO2/Al2O3 ratio, HY, MOR, FER, NiY with different Ni amount | Ex situ | Screening catal. for simultaneous hydrogenation and dealkylation of IPP for selective phenol production | Siddiqui et al.71 (2019) |
| 29    | TR-GCMS | Aluminum plastic laminate | HZSM-5, HY, Al-MCM-41 | Ex situ | Screening catalyst for effective aromatic oil production | Park et al.78 (2019) |
| 30    | TR-GCMS | PPCB (3.0 wt%-Br) | Natural clays (olivin, bentonite, dolomite), HY | In situ | Screening catalyst type and contact mode for effective de-bromination | Kumagai et al.77 (2019) |
| 31    | H2/steam-TR-GC/FID | iPrP, IPP, BPA (as PC pyrolyzates) | NiY-Y-zeolite | In situ | Evaluating effects of steam on enhanced phenol recovery | Nishiyama et al.49 (2020) |
| 32    | MF-Py-GC/MS | MDI, BD, and PTMGBased PUE with different monomer ratio | None | Ex situ | Evaluating effects of hard- and soft-segments on MDI and MDA production selectivity | Kumagai et al.79 (2019) |
| 33    | MF-Py-GC/MSTR-GC/MS | Epoxy-based CFRP | SiO2, zeolite catalysts (MOR-10, MFI-12, BEA-12, BEA-18.5, BEA-92.5, FAU-2.8) | In situ | Screening catalyst type and contact mode for effective phenol recovery | Oshima et al.79 (2020) |
| 34    | TR-GCMS | PET | ZnO, MgO, TiO2, ZrO2 | Ex situ | Screening catalyst for effective aromatic oil recovery | Kumagai et al.79 (2020) |

[Abbreviations] Equipment: FT-Py: filament type pyrolyzer; MF-Py: micro-furnace type pyrolyzer; GC: gas chromatograph; MS: mass spectrometer; TR: tandem micro-reactor; FID: flame ionization detector; TCD: thermal conductivity detector; H2-TR: TR equipped with H2 generator; H2/steam-TR: TR equipped with H2 generator and steam injection port. Samples: TBBPA: tetrabromobisphenol A; Al11-TBBPA: TBBPA diallyl ether; PC: polycarbonate; PLLA: poly(l-lactic acid); LLDPE: linear low-density polyethylene; AGR: PE pellet from recycled municipal plastic waste; URB: PE pellet from agriculture green house film; MDI: 4,4′-diphenylmethane diisocyanate; BD: 1,4-butandiol; PTMG: poly(oxytetramethylene glycol); PUE: polyurethane elastomer; MDA: 4,4′-diphenylmethanediamine; IPP: isopropylphenol; IPB: isopropylphenol; PC: polycarbonate; BPA: bisphenol A; PPCB: phenolic printed circuit board; CFRP: carbon fiber reinforced plastics. Catalysts: ASR: automotive shredder dust; 4A: Union Carbide Type A4 (Fluka); 13X: molecular sieves 13X (Linde); NaY: sodium form Y zeolite (Alrdich); Al-MCM-41: aluminum-doped mesoporous silica; n-ZSM5: nanocrystalline ZSM-5; Beta: beta type zeolite; Al-SBA-15: aluminum-doped mesoporous silica; Y: Y-zeolite; MOR: Mordenite; FER: Ferrierite. Contact mode: In situ: plastic and catalyst are mixed and then the mixture is pyrolyzed; Ex situ: pyrolysis of plastic and the volatile is subsequently reacted with catalyst.
mechanism: random session and an unzipping reaction in the absence and presence of MgO, respectively. Aguado et al. evaluated the performance of several types of zeolites (standard ZSM-5, nanocrystalline ZSM-5 (n-ZSM-5), and Beta) and mesostructured solids (Al-MCM-41 and Al-SBA-15) for recovering hydrocarbons from waste PEs such as AGR (granular material from agriculture greenhouse film) and URB (pelletized high density PE (HDPE) from recycled municipal plastic waste) (Entry 23). Each combination of the catalyst and PE sample mixture was screened by FT-Py-GC/MS. Rapid screening revealed that zeolite catalysts could completely eliminate heavy linear products, resulting in an increased light hydrocarbon fraction and a marked selectivity toward the formation of single-ring aromatic species, particularly benzene, toluene, and xylene (BTX). The formation of aromatics was particularly notable with n-ZSM-5. Mesostructured catalysts such as Al-MCM-41 and Al-SBA-15 favored the production of light C2–C5 hydrocarbons, while the formation of aromatic products was significantly less with zeolitic materials.

In recent years, the recovery of isocyanate monomers such as 4,4′-diphenylmethane diisocyanate (MDI) and amines such as 4,4′-diphenylmethanediamine (MDA) through pyrolysis of waste PUs and their further gasification into syngas are challenging in the feedstock recycling of PUs by pyrolysis. Therefore, evaluating the selectivity to MDI and MDA during pyrolysis is important. Kumagai et al. investigated the pyrolysis behavior of MDI-1,4-butanediol (BD)-poly(oxytetramethylene glycol) (PTMG)-based polyurethane elastomer (PUE) with different monomer ratios (i.e., different hard-segment (HS) and soft-segment (SS) ratios) through online evolved gas analysis (EGA) by employing MF-Py-GC/MS (Entries 24 and 32). In the EGA-MS method, pyrolyzates generated in the MF-Py are directly introduced into the MS through a deactivated metal capillary tube. Therefore, this method allows for monitoring of the time- and temperature-dependent pyrolyzates emission behavior. They particularly focused on the effects of the HS and SS compositions on the reaction selectivity to MDI via a 4-membered-ring transition state (Scheme 1(a)) and MDA via a 6-membered-ring transition state (Scheme 1(b)). The temperature-dependent EICs of MDI (m/z 198 (MDA−), 224 (4-amino-4′-isocyanate diphenyl methane ion (MAI−)), and 250 (MDI−)) obtained by the slow pyrolysis of PUEs at a heating rate of 10°C/min are shown in Fig. 4 (the full information is available in Ref. 69; a detailed discussion is avoided here). EGA revealed that the emission behavior of the target ions was strongly influenced by the PUE composition.
It was also confirmed that the production temperature of each target compound was different, suggesting the potential of the selective recovery of each target ion by controlling the pyrolysis temperature.

4-2 Tandem micro-reactor-GC for feedstock recycling of plastics

As discussed in the previous section, online product analysis is the most suitable method for investigating the dynamic pyrolysis reaction behavior. During catalytic pyrolysis, understanding the dynamic reaction behavior between the pyrolyzates and the catalyst is vital. The conventional TG-MS, TG-Fourier transform infrared spectrometer (TG-FTIR), and Py-GC are often used to evaluate the catalytic performance of solid catalysts by mixing them with plastics. However, plastics and mixed solids are heated using the same temperature program, while the optimum temperature for the pyrolysis of plastics and the optimum temperature for reactions with solids are different in most cases. To overcome this limitation and to evaluate the pyrolysis of plastics and the catalyst performance under the best conditions, a tandem micro-reactor (TR), in which the first micro-reactor is used for the pyrolysis or volatilization of the substances and the second micro-reactor is used for catalytic reactions, was developed.\(^{60,71}\)

Xue et al.\(^{72}\) investigated the catalytic effect of HZSM-5 on the recovery of hydrocarbons from PE, PP, PS, and PET using TR-GC/MS (Entry 25). They tested two different configurations, in situ (plastic and catalyst are mixed and then the mixture is pyrolyzed) and ex situ (pyrolysis of plastic and the volatile is subsequently reacted with catalyst), at 600 °C for both the first and the second reactor. Interestingly, a different mechanism of catalysis was observed for each plastic in the in situ and ex situ contact. Siddiqui et al.\(^{73}\) investigated the performance of zeolite catalysts on aluminum-plastic laminate pyrolyzates using TR-GC/MS, where the first and second reactors were maintained at 600 and 320 °C, respectively (Entry 29), and observed an increased production of aromatic hydrocarbons. TR-GC/MS allows one to simultaneously combine the in situ and ex situ contact modes. Thus, Park et al.\(^{74}\) used this technique to investigate the two-step catalytic pyrolysis of a phenolic-printed circuit board (PPCB) over natural clays. PPCB and natural clays (dolomite, bentonite, and olivine) were mixed together in the first reactor (in situ mode), while on H-form Y zeolite (HY) was set to the second reactor (ex situ mode); both of the reactors were maintained at 600 °C (Entry 30). The combination of in situ dolomite and ex situ HY resulted in the highest quality of oil production (high aromatics with low Br concentration) and longer catalyst lifetimes compared to those with the simple ex situ HY mode. Oshima et al.\(^{75}\) achieved a phenol recovery from carbon-fiber-reinforced plastic (CFRP) by zeolite catalysts screening using TR-GC/MS (Entry 33). TR-GC/MS allowed for conducting the catalyst stability test by multiple introductions of CFRP without any catalyst exchange and regeneration, revealing the product distribution change during 12 times of CFRP introduction and the necessity of catalyst regeneration in the actual application.

Kumagai et al.\(^{76-78}\) extensively investigated the catalytic pyrolysis of PET using TR-GC/MS (Entries 26, 27, 34). Pyrolysis of PET produces significant amounts of high-boiling point terephthalic acid (TPA; b.p. ~400 °C),\(^{79,80}\) which causes the corrosion and clogging of pipes.\(^{81,82}\) Therefore, they developed a process for the simultaneous recovery of benzene-rich aromatic oils and the complete suppression of TPA formation by using CaO.\(^{83,84}\) The emission behavior of the time- and temperature-dependent products from the CaO fixed bed (Fig. 5) was monitored online to investigate the reaction between PET pyrolyzates and CaO with different basicities. The PET pyrolyzates produced at 450 °C in the first micro-reactor were carried to the CaO bed that was heated to 450 °C to form a CaO-PET pyrolyzate complex as an intermediate. Next, the intermediate was gradually degraded by heating at a rate of 10 °C/min. Products generated from the CaO fixed-bed were monitored by online GC/MS (Figs. 5(a) – 5(d); full information is available in Ref. 76).\(^{76}\) The target compounds were monitored simultaneously with the intermediate decomposition, which significantly improved the understanding of the catalytic reactions between PET pyrolyzates and CaO and the role of CaO basicity on the product selectivity. However, a detailed discussion on the mechanism has been avoided here. This approach has been extensively applied to study the catalytic effects of other metal oxide catalysts such as ZnO, MgO, TiO₂, and ZrO₂ (Entry 34), and changes in the product selectivity.
Fig. 6 H₂/steam-TR-GC/FID and the corresponding experimental scheme: (a) initial setup, (b) naphthalene evaporation and trapping, (c) initiation of reaction and trapping of products, and (d) GC/FID analysis.  

Table 3 Definition of abbreviations used in the main sentence

| Abbreviation | Definition | Abbreviation | Definition |
|--------------|------------|--------------|------------|
| ABS          | Acrylonitrile-co-1,3-butadiene-co-styrene | MPs         | Microplastics |
| AGR          | Granular material from agriculture greenhouse film | MS           | Mass spectrometer |
| AMBN         | 2,2'-Azobis(2-methylbutyronitrile) | NaY         | Sodium form Y zeolite |
| APCI         | Atmospheric-pressure chemical ionization | NHA         | 2-Hydroxy-6-naphthoic acid |
| BA           | Butyl acrylate | Ni/Y        | Ni-loaded Y-zeolite |
| BAd          | Butylene adipate | n-ZSM-5     | Nanocrystalline ZSM-5 |
| BD           | 1,4-Butanediol | PA6         | Polyamide 6 |
| BFRs         | Brominated flame retardants | PBSA        | Poly(butylene succinate-co-butylene adipate) |
| BPA          | Bisphenol A | PBT         | Poly(butylene terephthalate) |
| BPO          | Benzoyl peroxide | PC         | Polycarbonate |
| BS           | Butylene succinate | PCL        | Poly(ε-caprolactone) |
| BTX          | Benzene, toluene, xylene | PE         | Polyethylene |
| CFRP         | Carbon-fiber-reinforced plastic | PES        | Poly(aryl ether sulfone) |
| CPE          | Cloud-point extraction | PET        | Poly(ethylene terephthalate) |
| EGA          | Evolved gas analysis | PLLA       | Poly(lactic acid) |
| EICs         | Extracted ion chromatograms | PMMA       | Poly(methyl methacrylate) |
| EM           | Emeraldine | PP           | Polypropylene |
| FID          | Flame ionization detector | PPCB       | Phenolic-printed circuit board |
| FT           | Filament-type | PPE        | Poly(p-phenylenenylene) |
| FTIR         | Fourier transform infrared spectrometer | PS         | Polyurethane |
| GC           | Gas chromatography | PSF        | Polysulfone |
| GC × GC      | Two-dimensional GC | PTMG       | Poly(oxytetramethylene glycol) |
| 3HB          | 3-Hydroxybutyrate | PU         | Polyurethane |
| HBA          | 4-Hydroxybenzoic acid | PUE        | Polyurethane elastomer |
| HDPE         | High density polyethylene | PVC       | Polyvinyl chloride |
| HS           | Hard-segment | Py         | Pyrolysis |
| 3HV          | 3-Hydroxyvalerate | SDGs       | Sustainable Development Goals |
| HY           | H form Y zeolite | SPM        | Suspended particulate matter |
| IPP          | Isopropenyl phenol | SS         | Soft-segment |
| iPnP         | Isopropyl phenol | St         | Styrene |
| ISTDpy       | Internal pyrolysis process standards | TBBPA      | Tetra bromobisphenol A |
| LE           | Leucoemeraldine | TD         | Thermal desorption |
| LCP          | Liquid-crystalline aromatic polyester | TG         | Thermogravimetry |
| LLDPE        | Linear low density polyethylene | TMAAc      | Tetramethylammonium acetate |
| MAA          | Methacrylic acid | TMAH       | Tetramethylammonium hydroxide |
| MAI          | 4-Amino-4’-isocyanate diphenyl methane | TOFMS      | Time-of-flight mass spectrometer |
| MALDI        | Matrix assisted laser desorption/ionization | TPA        | Terephthalic acid |
| MDA          | 4,4’-Di phenylmethanedi amine | TR         | Tandem micro-reactor |
| MDI          | 4,4’-Diphenylmethane diisocyanate | URB        | Pelletized HDPE from recycled municipal plastic waste |
| MF           | Micro-furnace type | UV         | Ultraviolet |
| MMA          | Methyl methacrylate |  | |
due to CaO deactivation were monitored by TR-GC/MS (Entry 27).

Kumagai et al. combined a H2 generator (H2 generated from 
water electrolysis) with TR-GC/MS (H2-TR-GC/MS) for 
evaluating the selective phenol recovery through simultaneous 
hydrogenation/dealkylation of isopropylphenol (iPrP) and 
isopropenylphenol (IPP) as the major PC pyrolyzates85 using 
Ni-loaded zeolite (Ni/Y)86 (Entry 28). The catalyst was filled 
in the second micro-reactor, in which H2 was supplied from the 
H2 generator. The H2 concentration in the carrier gas was 
adjustable. In addition, catalyst stability tests could be 
conveniently conducted under He/H2 flow by multiple sample 
introduction. Furthermore, they developed simultaneous H2 and 
steam injection TR (H2/steam-TR) for the first time. Injection 
ports for H2 and the steam were introduced in the TR and 
connected to a H2 generator, in which H2 was generated from 
water electrolysis, and a micro-syringe, respectively82 (Entry 
31). Generally, the pyrolysis of plastic produces a wide variety 
of pyrolyzates; hence, the construction of absolute calibration 
curves for all of the pyrolyzates for the purpose of quantification 
is unrealistic. Therefore, to directly quantify the product yields, 
the TR system was combined with a GC/FID, and naphthalene 
since an internal standard was set in the second micro-reactor 
(Fig. 6(a)). When the second micro-reactor was heated up, 
naphthalene was evaporated and captured in the column and 
cooled by the cooling traps (Fig. 6(b)). Subsequently, the 
sample holder was dropped into the heating zone of the first 
reactor, where the sample was rapidly pyrolyzed and carried 
into the second reactor. During the same time when the sample 
holder was dropped, steam was injected through the micro-
syringe. The products generated from the TR and injected 
steam were collected in the column cooled by the cooling traps 
for 5 min (Fig. 6(c)). Next, the cooling traps were removed, 
and the GC oven program was started (Fig. 6(d)). Thus, this 
system allowed for a high-throughput quantitative evaluation of 
phenol recovery from BPA, isopropyl phenol (IPP), and 
isopropyl phenol (iPrP) pyrolysis under H2 and steam flow.

5 Conclusions and Perspective

This review summarizes the latest global trends in plastic 
production and waste-plastic recycling, as well as technologies 
involving pyrolysis that are in high demand in this regard. 
Specifically, the latest trends in Py-GC for characterizing 
polymer structure, the analysis of plastics in the environment, 
and the feedstock recycling of plastics have been discussed. 
It is concluded that Py-GC is a promising technique that allows 
for the rapid and accurate analyses of pyrolyzates and the time- 
and temperature-dependent pyrolyzate emission behaviors. 
A review of studies related to Py-GC in the analytical pyrolysis 
of plastics revealed an increased variation and accuracy in 
methods for the identification and quantification of polymer 
types, composition, and microstructure year by year, which are 
otherwise difficult to determine using conventional spectroscopic 
analyses. A review of studies related to Py-GC in the feedstock 
recycling of plastics revealed that modified Py-GC systems such 
as TR-GC allowed for the rapid screening of both the catalysts 
and reaction conditions, thereby accelerating the designing of 
pyrolytic feedstock recycling processes.

Thus, the latest research trend implies that analytical pyrolysis 
demands more accurate pyrolyzate identification and 
quantification approaches and expanding the target polymers in 
the future, which can be achieved by developing new reactive-
Py-GC techniques and the combination of a micro pyrolyzer 
with a high-performance apparatus such as two-dimensional 
GC-TOFMS (GC × GC-TOFMS) and GC/APCI-TOFMS. 
Applied pyrolysis will require the development of evolved Py-
GC systems, which will allow to control more variable reaction 
parameters, such as the type of gases including steam, pressure, 
and residence time in the reactor, for evaluating more advanced 
catalytic pyrolysis processes in the future. Thus, Py-GC is 
expected to emerge as a more powerful technology that will 
continue to evolve in various industries.

6 Abbreviations

Definition of the abbreviations used in the main sentence was 
summarized in Table 3.

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8 References

1. The Compelling Facts About Plastics, Plastics Europe, The 
Compelling Facts About Plastics 2009, https://www.
plasticseurope.org/en/resources/publications/180-
compelling-facts-about-plastics-2009
2. Plastics—The Facts 2019, Plastics Europe, https://www.
plasticseurope.org/en/resources/publications/1804-plastics-
facts-2019
3. The Chemical Daily Co., Ltd., “16918 of Chemical Goods 
in 2018”, 2018, The Chemical Daily Co., Ltd., Tokyo, 
1073
4. S. Kumagai and T. Yoshioka, Mater. Cycles Waste Manag. 
Res., 2014, 25, 124
5. R. Geyer, J. R. Jambeck, and K. L. Law, Sci. Adv., 2017, 3, 
e1700782/1
6. The New Plastics Economy: Rethinking the Future of 
Plastics, Ellen MacArthur Foundation, https://www.
ellenmacarthurfoundation.org/publications/the-new-plastics-
economy-rethinking-the-future-of-plastics.
7. Plastic Waste Management Institute, PWMI News-letter, 
2020, 49
8. The Resource Circula-tion Strategy for Plastics, Ministry of 
The Environment, https://www.env.go.jp/press/files/jp/111747.
pdf
9. Transforming Our World: The 2030 Agenda for Sustainable 
Development, United Nations, https://sustainabledevelop
ment.un.org/post2015/transformingourworld
10. Closing the Loop: An EU Ac-tion Plan for a Circular 
Economy, European Commission, https://ec.europa.eu/
environment/circular-economy/index_en.htm
11. Group of Seven, Ocean plas-tics charter, Global Affairs 
Canada, http://publications.gc.ca/pub?id=9.859436&sl=0
12. P. G. Ryan, B. J. Dilley, R. A. Ronconi, and M. Connan, 
Proc. Natl. Acad. Sci. U. S. A., 2019, 116, 20892
13. D. Kawecki and B. Nowack, Environ. Sci. Technol., 2019, 
53, 9664
14. D. Xanthos and T. R. Walker, Mar. Pollut. Bull., 2017, 118, 
17
15. J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. 
Perryman, A. Andrade, R. Narayan, and K. L. Law, Science, 
2015, 347, 768.
78. S. Kumagai, R. Yamasaki, T. Kameda, Y. Saito, A. Watanabe, C. Watanabe, N. Teramae, and T. Yoshioka, *Energy Fuels*, 2020, 34, 2492.
79. M. Dzieciol and J. Trzeszczynski, *J. Appl. Polym. Sci.*, 2001, 81, 3064.
80. T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, and A. Okuwaki, *Polym. Degrad. Stab.*, 2004, 86, 499.
81. M. Fukushima, M. Shioya, K. Wakai, and H. Ibe, *J. Mater. Cycles Waste Manag.*, 2009, 11, 11.
82. M. Fukushima, B. Wu, H. Ibe, K. Wakai, E. Sugiyama, H. Abe, K. Kitagawa, S. Tsuruga, K. Shimura, and E. Ono, *J. Mater. Cycles Waste Manag.*, 2010, 12, 108.
83. S. Kumagai, G. Grause, T. Kameda, and T. Yoshioka, *Chem. Lett.*, 2014, 43, 637.
84. T. Yoshioka, E. Kitagawa, T. Mizoguchi, and A. Okuwaki, *Chem. Lett.*, 2004, 33, 282.
85. S. Kumagai, S. Ono, S. Yokoyama, T. Kameda, and T. Yoshioka, *J. Anal. Appl. Pyrolysis*, 2017, 125, 193.
86. S. Kumagai, M. Asakawa, T. Kameda, Y. Saito, A. Watanabe, C. Watanabe, N. Teramae, and T. Yoshioka, *Sci. Rep.*, 2018, 8, 1.
87. S. Kumagai, M. Asakawa, T. Kameda, Y. Saito, A. Watanabe, C. Watanabe, N. Teramae, and T. Yoshioka, *React. Chem. Eng.*, 2019, 4, 2099.