

Probing the microwave degradation mechanism of phenol-containing polymeric compounds by sample pretreatment and GC–MS analysis

Yu-Cheng Chang^{a,b}, Fu-Hsiang Ko^{a,b,*}, Chu-Jung Ko^{a,b}, Tieh-Chi Chu^c

^a National Nano Device Laboratories, 1001-1 Ta-Hsueh Road, Hsinchu 300, Taiwan

^b Institute of Nanotechnology, National Chiao Tung University, Hsinchu 300, Taiwan

^c Department of Radiological Technology, Yuanpei University of Science and Technology, Hsinchu 300, Taiwan

Received 2 August 2004; received in revised form 29 September 2004; accepted 29 September 2004

Abstract

We have detected the volatile organic species obtained after microwave digestion of poly(hydroxystyrene) with nitric acid in closed vessels at various reaction temperatures by using headspace solid-phase microextraction (HS–SPME) and gas chromatography/mass spectrometry (GC–MS). We probed the digestion reaction by measuring the response of the detectable species – we detected a total of 20 volatile organic compounds – with respect to the temperature over the range from room temperature to 80 °C. These compounds can be classified into alkane, alkanol, and aromatic species. The alkane species decreased monotonically, whereas the alkanol and aromatic compounds first increased and then decreased, as the digestion temperature increased. We have established the degradation mechanisms, which involve bond scission, recombination, adduct formation, and ring opening, on the basis of product analyses and bond length simulations.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Microwave digestion; Volatile organic species; Digestion reaction; Degradation mechanisms

1. Introduction

The semiconductor industry is an important component of the electronics industry, whose global market yield already exceeds that of the automobile industry [1]. The semiconductor manufacturing process, which evolves continually, involves a wide variety of distinct unit procedures [1,2]. The issue of quality control of any incoming material of interest in the manufacturing process is very crucial [3] because advancing technologies produce semiconductor devices whose physical dimensions continue to decrease [1,3]. Poly(4-hydroxystyrene) is one of the most important raw materials for preparing chemically amplified resists for the manufacture of semiconductors [4,5]. This polymer is the main constituent of resist materials and must be used at a high degree of purity (i.e., <10 ppb of metal contaminants) [6].

During the past few years, we had developed a series of methods [4,7–9] for analyzing lithographic materials such as resists and antireflective coatings. These methods use either closed or open-focused vessels that are subjected to microwave digestion and instrumental analysis. Poly(hydroxystyrene) (PHS) in resist materials is very inert and it is resistant to acid dissolution at room temperature. The material is also thermally stable; from thermogravimetric analysis, it is found to exist at ca. 24% residual mass at up to 900 °C in an ambient environment [4]. The fact that a refractory material forms indicates that the total dissolution of the polymer in an oxidant acid is not easy to achieve. Prior to analysis of the metal concentration, digestion recipes that reach at least 95% digestion efficiency are necessary to minimize spectroscopic interference from the polymer.

Kingston and Jassie evaluated the completeness of dissolution by measuring the free amino acid content resulting from protein hydrolysis in the samples [10]. In some other studies [11,12], the total residual carbon in the digested samples has been measured and used as a relative measure of the

* Corresponding author. Tel.: +886 35726100x7618; fax: +886 35722715.

E-mail address: fhko@ndl.gov.tw (F.-H. Ko).

efficiency of the various digestion schemes. Evaluation of the peak shape and background behavior of voltammograms also has been used to judge the quality of the digestion procedure [13]. Yang et al. have developed a method combining radio-tracer techniques with paper electrophoresis to investigate the effectiveness of the decomposition process of ^{65}Zn -labelled liver samples [14]. In a previous report [7], we proposed that gravimetric methods can be used to evaluate the digestion efficiency and kinetics of polymeric materials; we were able to evaluate digestion kinetics by weighing samples before and after digestion [15]. More conclusive and direct evidence, however, of the presence and identity of the residual matter that remains after acid dissolution is certainly desirable, especially if such matter interferes in any of the subsequent measurements.

Probing the residual organic compounds in digested solutions of poly(hydroxystyrene) is very difficult because of the high acidity of this matrix, the unknown polymeric distribution, and the unclear set of reactions that occur during digestion. Numerous studies using many detection systems [16–24] have focused on investigating the oxidation pathways of phenol-related molecules subjected to wet oxygen, supercritical water, or photooxidation. Prior to instrumental analysis (GC–TCD, GC–FID, HPLC–UV, HPLC–MS, GC–MS, and UV), aliquots of the samples are pretreated by liquid–liquid extraction to separate the compounds of interest. The phenol ($\text{C}_6\text{H}_5\text{OH}$) itself is oxidized into ring-opened (e.g., CO_2 , CO, ethylenedicarboxylic acid, and hexadienedioic acid), single-ring (e.g., catechol, benzenetriol, hydroquinone, and benzoquinone), and multiple-ring (e.g., phenoxyphehol, dibenzofuran, indanone, and dibenzofuranol) compounds; 4-ethylphenol becomes oxidized into ring-opening products, 4-vinylphenol, phenol, etc. Despite the versatility of the methods available to determine the compounds derived when oxidizing phenols, to the best of our knowledge, the oxidation products and pathways followed during the microwave-assisted decomposition (digestion) of phenol-containing molecules and polymeric compounds have yet to be reported. The high nitric acid content present in the digestive solution makes the analysis of organic species more of a challenge and, hence, the reaction mechanisms and degradation kinetics remain unknown. If a database of reaction mechanisms can be established and the kinetics of these processes can be understood then selecting digestion recipes will become more systematic and scientifically proven.

There are the two plausible means of removing interference from the high acid concentration when studying the microwave degradation of polymeric materials: liquid–liquid extraction (LLE) and solid-phase microextraction (SPME) [25–27]. These pretreatment methods present some barriers, however, that need to be overcome. For example, nitric acid in the digestive solution can react with the extraction solvent when using the LLE method, which can limit the phase separation. The direct immersion (DI) SPME method may suffer from fouling of the fiber surface with the dissolved polymer

or corrosion of the fiber coating by the action of the strong acid. Consequently, the analytical results may not be reliable.

In this study, we have evaluated the efficiency of microwave digestion of PHS, in the presence of nitric acid, at various temperatures using the gravimetric method. We have studied the extent of the reaction and the ability to effect phase separation using various liquid–liquid extraction solvents. We propose that using a method of HS–SPME pretreatment and GC–MS analysis is effective for determining the volatile species in the digestion solution. Furthermore, we have characterized the degradation mechanisms of PHS under these conditions.

2. Experimental

2.1. Reagents and materials

Nitric acid (69.5%) and dichloromethane (99%) of pro-analytical grade were obtained from Merck (Darmstadt, Germany). Deionized water ($18.3 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout all the experiments. The PHS (average $M_w = \text{ca. } 20,000$; $T_g = \text{ca. } 130\text{--}185^\circ\text{C}$; density = ca. 1.16 g/mL) used in this study was purchased from Aldrich (Steinheim, Germany). 4-Ethylphenol (>97%), phenol (>99.5%), and sodium hydroxide (95%) were purchased from Chem Service (West Chester, PA).

2.2. Microwave digestion procedures

Microwave digestion of PHS was accomplished by placing closed vessels inside a commercial oven. The microwave system (Model MARS-5, CEM, Matthews, NC, USA) was equipped with a Teflon-coated cavity and a removable 12-position sample carousel. The oven had a variable power range (up to 1200 W) that was adjustable in 1% increments. A pressure sensor (ESP-1500 Plus) could provide “in vessel” pressure measurements of up to 1500 psi; the pressure limit was set at 350 psi. An optical fiber was used to monitor and control the digestion temperature up to 300°C by the use of a feedback system (EST-300 Plus). The dual seal, in conjunction with the frame architecture, of the XP-1500 Plus provides a completely sealed vessel that can handle temperatures of up to 300°C and pressures up to 1500 psi.

A sample of interest (0.1 g) and HNO_3 (3 mL) were mixed in the reaction vessel and digested at various temperatures. The operating parameters of the microwave system were set as follows: microwave power, 450 W; digestion time, 30 min; cooling time, 30 min. To evaluate the residual weight, the digest was transferred to a 10 mL beaker and evaporated to dryness.

2.3. Liquid–liquid extraction

The digestion solution was transferred into a glassy extraction tube. Dichloromethane was added into the tube up to

a total of 10 mL. The extraction tube was shaken vigorously for 10 min, left to stand for 3 h, and then a 0.3 μ L aliquot of the solution in the organic phase was withdrawn and injected into the GC–MS system.

2.4. Solid-phase microextraction

We used manual SPME holders having a 65 μ m polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber assembly (Supelco, Bellefonte, PA). The fibers were conditioned as recommended by the manufacturer.

The acidic solution obtained after digestion was neutralized with 5 M NaOH solution to a value of pH 6–8 and then an aliquot (2 mL) of this solution was transferred into a headspace vial. The vial was sealed with a headspace aluminum cap furnished with a Teflon-faced septum. Prior to HS–SPME, the vial was immersed in a water bath maintained at 50 °C and equilibrated for 5 min. The fiber was exposed to the headspace over the solution for 1 h. The fiber was immediately inserted into the GC injector and the chromatographic analysis was performed. The extracted compounds were desorbed by inserting the fiber into the GC injector for 30 min at 240 °C.

2.5. Chromatographic conditions

The desorption species from the fiber were separated using a GC–MS analyzer (GC: PE AutoSystem XL Model; MS: PE TurboMass, Perkin-Elmer, Norwalk, CT, USA). These species were separated on an RTX-5 column (Supelco, Bellefonte, PA, USA) that had a length of 30 m and an i.d. of 0.25 mm and was coated with a crosslink of 5% diphenyl and 95% dimethylpolysiloxane (minimal bleed at 330 °C). The GC oven temperature program for liquid–liquid extraction was the following: 50 °C, hold 1 min, ramp rate of 10 °C/min to a final temperature of 320 °C, and then hold for 3 min. The GC oven temperature program for HS–SPME of poly(4-hydroxystyrene) was as follows: 40 °C, hold 1 min, ramp rate 2 °C/min to a final temperature of 260 °C, and then hold for 3 min. The GC oven temperature program for the HS–SPME of phenol and 4-ethylphenol was the following: 40 °C, hold 1 min, ramp rate 2 °C/min to 120 °C, hold for 3 min, ramp rate 10 °C/min to a final temperature of 260 °C, hold for 5 min.

3. Results and discussion

3.1. Evaluation of digestion efficiency with gravimetric method

In general, a basic microwave digestion process aims to achieve a high dissolution efficiency by means of adding a digestion acid (e.g., HNO₃) into the closed vessel and reacting the mixture under a high temperature. Table 1 illustrates the digestion efficiency measured by the gravimetric method

Table 1
Digestion efficiency (%) and pressure accumulated during the digestion of PHS at various temperatures

Temperature (°C)	Digestion efficiency (%)	Accumulated pressure (psi)
25	5.00	1
50	10.23	5
80	21.13	14
100	30.74	42
120	47.72	85
140	84.80	120
160	95.20	172
180	98.81	221

and the accumulated pressure of PHS under various digestion temperatures (25, 50, 80, 100, 120, 140, 160, and 180 °C). We found that the digestion efficiency basically increases as the reaction temperature increases and that it has a positive relationship with the accumulating pressure. This observation suggests that the polymer readily decomposes under high oxidation temperatures and that the oxidation by-products cause the rise in pressure. In addition, PHS can react with nitric acid at room temperature, but the digestion efficiency is very low (5%). It is interesting that the digestion efficiency at 140 °C is about twice that at 120 °C. We attribute this finding to the fact that the boiling point of 69.5% nitric acid is 122 °C. The nitric acid vaporizes and refluxes in the closed vessel when the digestion temperature is elevated above the boiling point. Therefore, the digestion efficiency is significantly enhanced at 140 °C; in contrast, most of the nitric acid exists in the liquid state below 120 °C and so digestion is limited at these temperatures.

3.2. Evaluation of extraction solvent for matrix separation

The species resulting from PHS decomposition in solution after microwave degradation are very complicated, but current analytical instrumentation, such as GC–MS, does not allow direct analysis. Conventionally, solvent extraction is used to separate the matrix, but extraction is limited to mild systems. For a degradation system involving strong acid, we need to search for a suitable solvent to separate the products from the matrix. Table 2 lists the reactions of nitric acid with a series of solvents, such as ethanol, isopropanol, octanol, propylene glycol monomethyl ether acetate (PGMEA), *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), cyclohexane, benzene, methylbenzene, and dichloromethane. The reactions in Table 2 can be divided to three groups: (1) the extraction solvent has a very violent reaction with nitric acid, (2) the extraction solvent is miscible with the nitric acid phase and has small exothermic reaction, and (3) the extraction solvent is phase separated from the nitric acid phase and has no exothermic reaction.

The first group, comprising alkanols, such as ethanol, isopropanol, and octanol, react vigorously with the extraction solvent and lead to a serious degree of spraying. This group

Table 2
Effects observed when mixing the extraction solvents with nitric acid

Extraction solvent	Rigorous reaction	Exothermic reaction	Phase separation
Ethanol	Yes	Yes	No
Isopropyl alcohol	Yes	Yes	No
1-Octanol	Yes	Yes	No
PGMEA	No	Yes	No
NMP	No	Yes	No
THF	No	Yes	No
Cyclohexane	No	No	Yes
Benzene	No	No	Yes
Methyl benzene	No	No	Yes
Dichloromethane	No	No	Yes

of solvents clearly cannot be used to extract the digestion species. The second group solvents (PGMEA, NMP and THF) are readily miscible with nitric acid and, hence, they are also unfavorable for matrix separation. The most suitable solvents for separating the nitric acid matrix are cyclohexane, benzene, methylbenzene, and dichloromethane; these organic solvents demonstrate good phase separation with nitric acid solution and, furthermore, no exothermic reaction occurs upon shaking the mixture. Although these solvents are candidates for matrix separation after PHS polymer digestion, we need to consider the effect of interference by the solvent in the GC–MS detection. Because benzene and methylbenzene moieties are subunits of PHS and the digestion solution may contain these compounds, we would be unable to differentiate these signals in the chromatogram as arising from either the extraction solvent or the digestion species. In addition, benzene or methylbenzene might react with the degradation species of the PHS polymer. For these reasons, we do not believe that these solvents are suitable extractants. Dichloromethane seems more appropriate than cyclohexane because the presence of its Cl atoms. By GC–MS detection, we can infer the stability of dichloromethane with the nitric acid. If the extraction species from the digested PHS polymer can be identified as Cl-containing molecules, we would know that the solvent reacts with the digestion products. As a result, dichloromethane is a candidate solvent for both dissolving the digestion species and separating them from the nitric acid matrix. Fig. 1 illustrates the GC–MS chromatograms for PHS after microwave digestion at various digestion temperatures and extraction with dichloromethane. It is interesting that the species signals are very weak for the nitric acid digestion at 25, 80, and 140 °C. As indicated in Table 1, the digestion efficiencies are 5, 21, and 85%, respectively. The degradable species after microwave digestion do exist in the nitric acid solution, but the process of solvent extraction and GC–MS analysis does not indicate their presence. We attribute this contradictory result to the low extraction efficiency, the low concentration of the products, or their non-volatile nature. Clearly, to probe the degradation products of PHS after digestion with nitric acid, we must adopt a different analytical method.

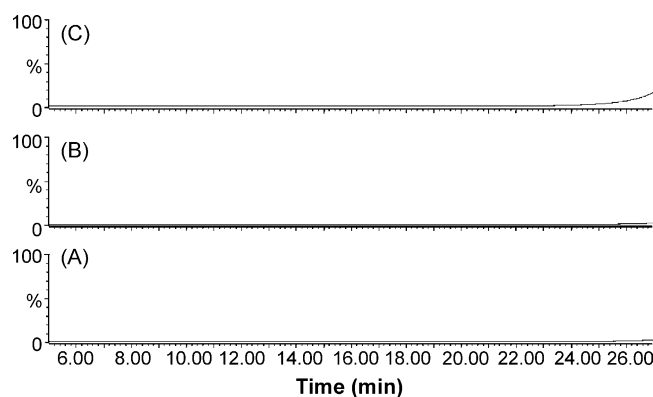


Fig. 1. Chromatograms of the digestion species of PHS upon liquid extraction and GC–MS detection. Digestion temperatures: (A) 25 °C, (B) 80 °C, (C) 140 °C; total ion counts: 5.64E+5.

3.3. Headspace solid-phase microextraction

Solid-phase microextraction (SPME), which was developed by Pawliszyn et al. in 1990, is an attractive and widely used method for sample concentration and matrix separation [25,26]. This technique has the advantages of a high recovery, a more-efficient matrix separation, a low detection limit, and the ability to use rapid and solvent-free extraction methods. Thus, we adapted SPME and GC–MS methods to probe the digestion species.

Prior to SPME, the digestion solution had to be neutralized; we used NaOH solution. The experimental conditions we used for the SPME and GC–MS analysis basically followed those described in the literature [25,28–32]. Fig. 2 displays HS–SPME–GC–MS chromatograms of the products of the microwave digestion of PHS conducted under different reaction temperatures. Fig. 2A illustrates that 20 molecules are extracted from the solution at room temperature. From database searches, we identified these molecules as (1) 2,2,6-trimethyloctane, (2) 2,5,6-trimethyloctane, (3) 2,2,6-trimethyldecane, (4) 3-methyl-5-propylnonane, (5) 2,6,6-trimethyldecane, (6) 2,6,9-trimethyldecane, (7) 2,6,10-trimethyldodecane, (8) 2-ethyl-1-hexanol, (9) 4-ethyl-2,2,6,6-tetramethylheptane, (10) 2,7,10-trimethyldodecane, (11) 1-octadecane, (12) 2,2,3,4,6,6-hexamethylheptane, (13) 3-methylheptane, (14) nonadecane, (15) 2,6,10,14-tetramethylpentadecane, (16) 2,2,11,11-tetramethyldodecane, (17) 2,6,10,15-tetramethylheptadecane, (18) 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)tridecane, (19) 2,6-di-*tert*-butyl-4-methylphenol, and (20) 2,4-di-*tert*-butylphenol, respectively. When the digestion temperature was elevated to 80 °C, the intensity of various molecules was reduced significantly in the resulting chromatogram. This observation suggests that PHS and its digestion products were decomposed by the action of nitric acid. Interestingly, only three of these molecules (2-ethyl-1-hexanol, 2,6-di-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butylphenol) were present in the chromatogram after digestion at 140 °C. The digestion efficiency of PHS is

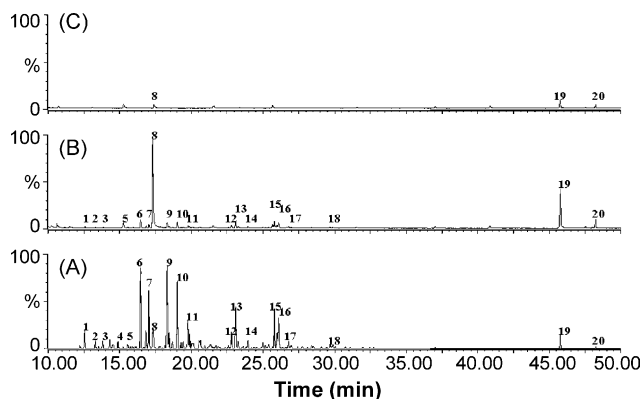


Fig. 2. HS-SPME-GC-MS chromatograms of the products of microwave digestion of poly(4-hydroxystyrene) at different reaction temperatures: (A) 25 °C, (B) 80 °C, (C) 140 °C. Peak identification: (1) 2,2,6-trimethyloctane, (2) 2,5,6-trimethyloctane, (3) 2,2,6-trimethyldecane, (4) 3-methyl-5-propylnonane, (5) 2,6,6-trimethyldecane, (6) 2,6,9-trimethyldecane, (7) 2,6,10-trimethyldodecane, (8) 2-ethyl-1-hexanol, (9) 4-ethyl-2,2,6,6-tetramethylheptane, (10) 2,7,10-trimethyldodecane, (11) 1-octadecane, (12) 2,2,3,4,6,6-hexamethylheptane, (13) 3-methylheptane, (14) nonadecane, (15) 2,6,10,14-tetramethylpentadecane, (16) 2,2,11,11-tetramethyldodecane, (17) 2,6,10,15-tetramethylheptadecane, (18) 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)tridecane, (19) 2,6-di-*tert*-butyl-4-methylphenol, (20) 2,4-di-*tert*-butylphenol; total ion counts: 1.02E+6.

>80% (see below). Table 3 summarizes the retention time, name, formula, and relative area for each peak at the various temperatures. The peak area is obtained from three replicates. Despite the fact that PHS contains a benzene moiety in each unit, it is interesting that only two compounds (2,6-di-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butylphenol) contain benzene rings after microwave digestion; the other detectable species are aliphatic compounds. Most of these aliphatic compounds are alkanes (C11–C28), and only one species (2-ethyl-1-hexanol; C8) is an alcohol. We note that other non-volatile species exist in the digestion solution, but these species are not easily detected.

3.4. Classifying the degradation species

To better understand the digestion reactions that lead to the detectable species, we classified the compounds in Table 3 into three categories: alkanes (Type A), alcohols (Type B), and aromatics (Type C). Fig. 3 illustrates the effect that the digestion temperature has on the response of peak area for the detectable species. The abundances of the alkane species decrease as the digestion temperature increases. This observation implies that PHS is degraded into alkanes, and that these alkanes are then oxidized by nitric acid. The alkane species are totally decomposed at reaction temperatures >100 °C. The alcohol and aromatic species in Fig. 3 initially increase in abundance as the reaction temperature increases, but then they decrease upon further increase in temperature. The temperature at which the alcohols' abundance begins to decrease is higher than that for the aromatic species. The question

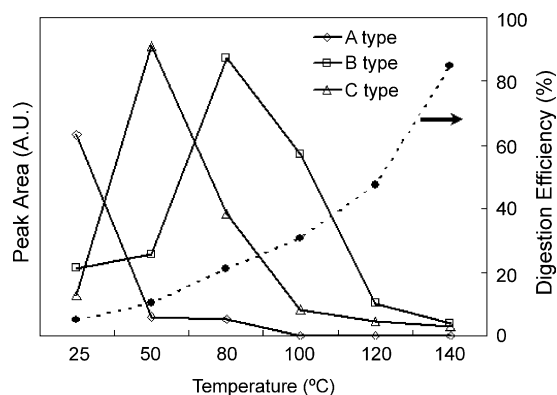


Fig. 3. Peak areas, obtained by solid-phase microextraction and GC-MS, of the three classes of products from the digestion of poly(4-hydroxystyrene) at different temperatures. The dashed line is the digestion efficiency for poly(4-hydroxystyrene).

arises: Why do these latter two species behave differently with respect to the Type A species? In essence, we observe in Fig. 3 that the digestion efficiency of PHS increases gradually as the reaction temperature increases. The observation, that a relationship exists between the digestion efficiency of PHS and the abundances of the detectable volatile species, seems to suggest that the digestion process is very complicated and involves degradation, digestion, oxidation, and recombination mechanisms.

PHS contains benzene groups, but after microwave digestion, only two of the detectable compounds contain benzene units. We have used chemical bond simulation [33] to determine the most likely bonds will cleave and to understand the formation of alkanes (Type A) during microwave digestion. Table 4 lists the bond lengths within the repeating units of PHS. Bond “c” is longer than the others in the phenyl group, irrespective of the number of repeating units. This observation suggests the bond “c” is more scissile than bond “d–j”. When comparing bonds “a–c”, we find that bond “c” is the shortest, especially at higher repeating unit. This is because bond “c” links sp^2 - and sp^3 -hybridized C atoms, whereas bond “a” and “b” both link two sp^3 -hybridized C atoms. This phenomenon suggests that the bonds tethering adjacent monomer units are the easiest to cleave. Hence, the Type A compounds originate from the scission of bonds “c” and “a” (or “b”), which explains why 17 alkanes are observed by HS-SPME and GC-MS analysis. In addition, it still has the other possibility that the benzene ring might be fragmented and undergone complicated rearrangements to form the alkanes.

The origin of the Type B compound, 2-ethyl-1-hexanol, is difficult to identify at first glance of the structure of PHS. Hence, we subjected two simple model compounds, phenol and 4-ethylphenol, to the same nitric acid digestion conditions. It is interesting to note from their GC-MS chromatograms that 2-ethyl-1-hexanol is a product of the digestion of both of these molecules. Table 5 reveals that the amounts of 2-ethyl-1-hexanol products obtained from the

Table 3
 Digestion products of poly(4-hydroxystyrene) and their peak areas ($n = 3$) at different temperatures as measured by solid-phase microextraction

Peak	Retention time (min)	Compound name	Formula	25 °C	50 °C	80 °C	100 °C	120 °C	140 °C
1	12.55	2,2,6-Trimethyloctane	C ₁₁ H ₂₄	142762 ± 6424	13645 ± 5943	9377 ± 973	–	–	–
2	13.29	2,5,6-Trimethyloctane	C ₁₁ H ₂₄	72182 ± 4645	7566 ± 721	4683 ± 698	–	–	–
3	13.82	2,2,6-Trimethyldecane	C ₁₃ H ₂₈	67739 ± 4598	9021 ± 1045	6520 ± 978	–	–	–
4	14.88	3-Methyl-5-propylnonane	C ₁₃ H ₂₈	52951 ± 6765	8068 ± 1765	3975 ± 632	–	–	–
5	15.53	2,6,6-Trimethyldecane	C ₁₃ H ₂₈	36556 ± 5764	8575 ± 1397	6999 ± 935	–	–	–
6	16.47	2,6,9-Trimethyldecane	C ₁₃ H ₂₈	676115 ± 39764	74395 ± 7173	67656 ± 7308	–	–	–
7	17.03	2,6,10-Trimethyldodecane	C ₁₅ H ₃₂	490169 ± 87134	48533 ± 5673	34773 ± 6512	–	–	–
8	17.35	2-Ethyl-1-hexanol	C ₈ H ₁₈ O	191565 ± 29831	231250 ± 24981	785202 ± 43761	515646 ± 93429	92675 ± 6276	34449 ± 2945
9	18.30	4-Ethyl-2,2,6,6-tetramethylheptane	C ₁₃ H ₂₈	723143 ± 12974	58317 ± 9141	44263 ± 9962	–	–	–
10	19.02	2,7,10-Trimethyldodecane	C ₁₅ H ₃₂	568792 ± 24781	55621 ± 6217	47591 ± 8925	–	–	–
11	19.75	1-Octadecane	C ₁₈ H ₃₈	244377 ± 35872	23827 ± 1365	19608 ± 1743	–	–	–
12	22.79	2,2,3,4,6,6-Hexamethylheptane	C ₁₃ H ₂₈	145260 ± 9897	24170 ± 4745	22187 ± 1254	–	–	–
13	23.11	3-Methylheptane	C ₁₈ H ₃₈	359762 ± 34212	54615 ± 4196	49600 ± 3923	–	–	–
14	23.96	1-Nonadecane	C ₁₉ H ₄₀	67275 ± 8731	12986 ± 2769	12964 ± 3461	–	–	–
15	25.82	2,6,10,14-Tetramethylpentadecane	C ₁₉ H ₄₀	341631 ± 24921	67138 ± 21981	58536 ± 8182	–	–	–
16	26.11	2,2,11,11-Tetramethyldodecane	C ₁₆ H ₃₄	253908 ± 34976	48872 ± 6548	39150 ± 2176	–	–	–
17	26.80	2,6,10,15-Tetramethylheptadecane	C ₂₁ H ₄₄	64827 ± 9824	16548 ± 2874	11679 ± 1973	–	–	–
18	29.69	2,2,4,10,12,12-Hexamethyl-7-(3,5,5-trimethylhexyl)tridecane	C ₂₈ H ₅₈	35359 ± 4931	11296 ± 3721	7400 ± 1032	–	–	–
19	45.77	2,6-Di- <i>tert</i> -butyl-4-methylphenol	C ₁₅ H ₂₄ O	114680 ± 7631	820175 ± 32974	344671 ± 29761	75067 ± 9987	43215 ± 3218	26441 ± 8132
20	48.22	2,4-Di- <i>tert</i> -butylphenol	C ₁₄ H ₂₂ O	11965 ± 1934	76419 ± 5987	77738 ± 9273	35137 ± 2873	28763 ± 3454	23471 ± 4263

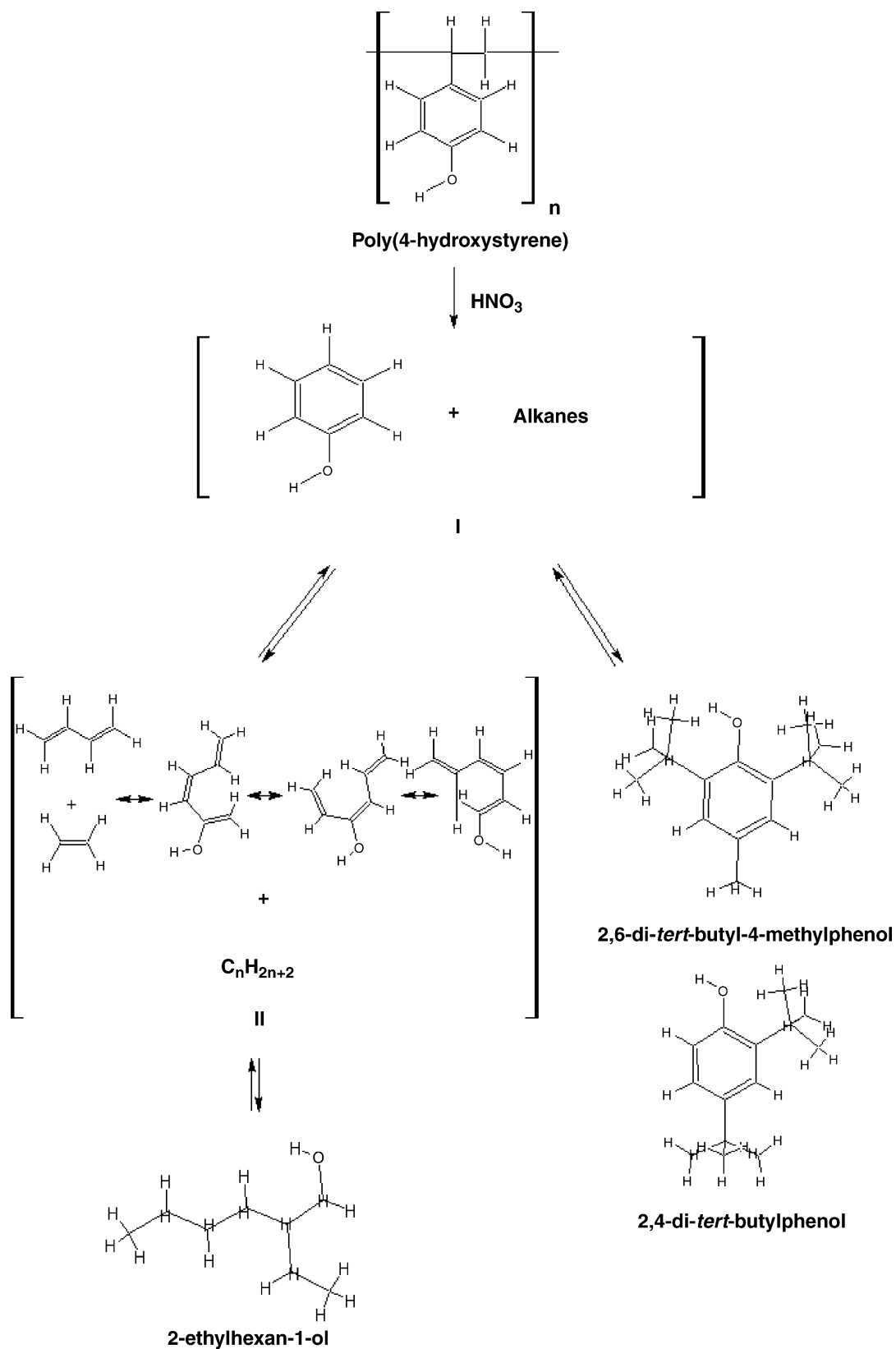
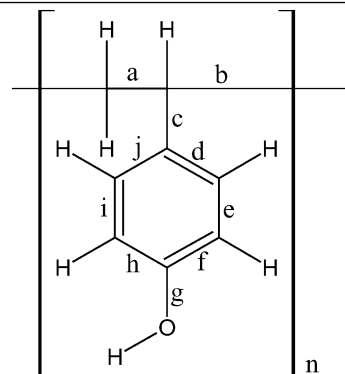


Fig. 4. The mechanism of microwave-assisted digestive degradation of poly(4-hydroxystyrene) in the presence of nitric acid.

Table 4
Poly(4-hydroxystyrene) bond lengths (Å), as a function of the number of monomer units, calculated using ACD Labs Freeware 5.0 software

Position	<i>n</i>			
	3	6	9	12
a	1.50	1.52	1.53	1.56
b	1.50	1.52	1.53	1.56
c	1.49	1.48	1.47	1.47
d	1.36	1.35	1.35	1.34
e	1.36	1.35	1.35	1.34
f	1.36	1.35	1.35	1.34
g	1.33	1.33	1.33	1.32
h	1.36	1.35	1.35	1.34
i	1.36	1.35	1.35	1.34
j	1.36	1.35	1.35	1.34



digestions of both phenol and 4-ethylphenol increase as the reaction temperature increases up to 80 °C, but then they decrease as the temperature rises further. The peak area is obtained from three replicates. These observations indicate that 2-ethyl-1-hexanol is the product of digestion of the phenol units of PHS. The digestion of PHS must break bonds “a” to “c” to release an aryl group that then decomposes by the action of the acid to give fragments that recombine to become, ultimately, 2-ethyl-1-hexanol. Although studying digestion products under high temperature and oxidizing conditions is very difficult, the use of simple model compounds can be an effective means of clarifying the complex processes that occur.

Finally, let us consider the Type C digest products, 2,6-di-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butylphenol. The digestion of PHS fragments bonds “a”, “b”, and “c” to release an aryl unit, which may react with other digestion products to form the Type C compounds. We observe in Table 3 that the peak area of 2,6-di-*tert*-butyl-4-methylphenol is at least 10-fold higher than that of 2,4-di-*tert*-butylphenol when digestion occurs at either 25 or 50 °C, but this peak ratio decreases gradually as the temperature is raised from 50 to 140 °C. These results imply that 2,6-di-*tert*-butyl-4-methylphenol is more stable than 2,4-di-*tert*-butylphenol during microwave digestion.

Table 5

Peak areas (*n* = 3) of 2-ethyl-1-hexanol, recorded using headspace solid-phase microextraction, after the digestion of phenol and 4-ethylphenol at different temperatures

Temperature (°C)	Phenol	4-Ethylphenol
25	174267 ± 9265	165841 ± 9787
50	421929 ± 12974	525085 ± 18854
80	1292764 ± 21926	1107981 ± 16984
100	631040 ± 10487	467407 ± 12984
120	265437 ± 7653	137547 ± 9219
140	87867 ± 3479	21881 ± 4569

3.5. The mechanism of the microwave degradation of PHS

Taking the findings above into account, in Fig. 4 we propose degradation mechanisms for PHS subjected to nitric acid digestion. The reaction of PHS with nitric acid in a closed vessel leads to the detachment of phenol and alkanes. The detached alkanes further digest with nitric acid to create a number of C11–C28 compounds, i.e., Type A compounds. Some phenols and alkanes (I) will react together with the nitric acid to form other intermediates (II), which, after bond scission and recombination, yield 2-ethyl-1-hexanol that can be detected by HS-SPME and GC-MS. Reactions of the bond scission products of the alkanes with phenols lead to adducts 2,6-di-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butylphenol.

The species formed from the microwave-mediated degradation of PHS in the presence of nitric acid detected by HS-SPME and GC-MS analysis, and we have proposed degradation mechanisms on the basis of the bond lengths in the polymer. Microwave digestion in this high-temperature and -pressure system is a very complicated process. The chemical species are not easy to detect and analyze in the nitric acid environment, especially the non-volatile species. This study proposes a method to analyze the volatile species present in the digestion solution at various reaction temperatures. The possible reaction pathways can be understood by measuring the abundances of the digestion species as functions of temperature.

Acknowledgment

We thank the National Science Council, Taiwan, for supporting this research financially through contracts NSC 92-2113-M-492-002.

References

- [1] S.M. Sze, *Semiconductor Devices: Physics and Technology*, 2nd ed., Wiley, New York, 2002 (Chapter 1).
- [2] G.S. May, S.M. Sze, *Fundamentals of Semiconductor Fabrication*, Wiley, New York, 2004 (Chapters 4–8).
- [3] International Technology Roadmap for Semiconductors, Semiconductor Industry Association, 2003. <http://public.itrs.net/>.
- [4] F.-H. Ko, J.-K. Lu, T.-C. Chu, C.-T. Chou, L.-T. Hsiao, H.-C. Lin, *J. Anal. At. Spectrom.* 15 (2000) 715.
- [5] M. Quirk, J. Serda, *Semiconductor Manufacturing Technology*, Prentice-Hall, New Jersey, 2001, p. 621.
- [6] C.-C. Yang, F.-H. Ko, M.-Y. Wang, T.-K. Wang, S.-C. Wu, *J. Electrochem. Soc.* 147 (2001) 3853.
- [7] F.-H. Ko, M.-Y. Wang, T.-K. Wang, *Anal. Chem.* 71 (1999) 5413.
- [8] J.-K. Lu, F.-H. Ko, T.-C. Chu, Y.-C. Sun, M.-Y. Wang, T.-K. Wang, *Anal. Chim. Acta* 407 (2000) 291.
- [9] P.-H. Chi, F.-H. Ko, C.-T. Hsu, H.-L. Chen, C.-K. Yang, Y.-C. Sun, M.-H. Yang, *J. Anal. At. Spectrom.* 17 (2002) 358.
- [10] H.M. Kingston, L.B. Jassie, *Anal. Chem.* 58 (1986) 2534.
- [11] M. Wurfels, E. Jackwerth, M. Stoepler, *Anal. Chim. Acta* 226 (1989) 1.
- [12] S. Nakashima, R.E. Sturgeon, S.N. Willie, S.S. Berman, *Analyst* 113 (1988) 159.
- [13] M. Wurfels, E. Jackwerth, M. Stoepler, *Anal. Chim. Acta* 226 (1989) 31.
- [14] J.Y. Yang, M.H. Yang, S.M. Lin, *Anal. Chem.* 62 (1990) 146.
- [15] F.-H. Ko, H.-L. Chen, *J. Anal. At. Spectrom.* 16 (2001) 1337.
- [16] H.S. Joglekar, S.D. Samant, J.B. Joshi, *Water Res.* 25 (1991) 135.
- [17] C. Bencher, C. Ngai, B. Roman, S. Lian, T. Vuong, *J. Photochem. Photobiol. A* 148 (2002) 183.
- [18] C.J. Martino, P.E. Savage, *Ind. Eng. Chem. Res.* 38 (1999) 1775.
- [19] C.J. Martino, P.E. Savage, *Ind. Eng. Chem. Res.* 38 (1999) 1784.
- [20] C.J. Martino, P.E. Savage, *Ind. Eng. Chem. Res.* 36 (1997) 1385.
- [21] C.J. Martino, P.E. Savage, *Ind. Eng. Chem. Res.* 36 (1997) 1391.
- [22] S. Gopalan, P.E. Savage, *J. Phys. Chem.* 98 (1994) 12646.
- [23] T.D. Thornton, P.E. Savage, *Ind. Eng. Chem. Res.* 31 (1992) 2451.
- [24] T.D. Thornton, D.E. Ladue, P.E. Savage, *Environ. Sci. Technol.* 25 (1991) 1507.
- [25] J. Pawliszyn, *Application of Solid Phase Microextraction*, Royal Society of Chemistry, Cambridge, 1999 (Chapters 43–44).
- [26] Z. Mester, R. Sturgeon, J. Pawliszyn, *Spectrochim. Acta B* 53 (1998) 239.
- [27] M.-C. Monje, C. Privat, V. Gastine, F. Nepveu, *Anal. Chim. Acta* 458 (2002) 111.
- [28] H. Kataoka, H.L. Lord, J. Pawliszyn, *J. Chromatogr. A* 880 (2000) 35.
- [29] R.A. Doong, S.M. Chang, *Anal. Chem.* 72 (2000) 3647.
- [30] M. Liompart, M. Pazos, P. Landin, R. Cela, *Anal. Chem.* 72 (2001) 5858.
- [31] M.E. Miller, J.D. Stuart, *Anal. Chem.* 71 (1999) 23.
- [32] H.L. Lord, J. Pawliszyn, *J. Chromatogr. A* 885 (2000) 153.
- [33] ACD Labs Freeware 5.0, Advanced Chemistry Development Inc., <http://www.acdlabs.com/>.