

# Thermal Decomposition Characteristics of Poly[diethyl-2-(methacryloyloxy)ethyl phosphate] Using Thermogravimetric Analysis/Mass Spectrometry

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**ABSTRACT:** The thermal decomposition of poly[diethyl 2-(methacryloyloxy)ethyl phosphate] (PDMP) by free-radical polymerization was studied by the combination of pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) with thermogravimetric analysis/mass spectrometry (TG/MS), in which the former identified directly the compositions of the evolved gases and the latter could further obtain real-time evolution curves of pyrolysates. A decomposition of PDMP was a two-stage process: The dominant mechanism of the first stage was initialized by hydrolysis at the phosphate ester linkage to evolve hydroxyethyl methacrylate (HEMA), triethylphosphate, and ethanol as major products; then, subsequently, the dominant mechanism of the second stage was a main-chain random scission to form acetaldehyde and water as major products along with carbonization of about 24% char yield of a solid residue at 600°C. Therefore, the reaction of phosphate groups into the backbone of polymeric materials could provide better flame retardancy. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 821–830, 2002

**Key words:** pyrolysis; mass spectrometry; flame retardance; thermogravimetric analysis

## INTRODUCTION

Phosphorus-containing polymers are well recognized for their flame-retarding characteristics,<sup>1</sup> with increasing preference over halogen-contain-

ing polymers, which release smoke and toxic fumes during combustion. At present, the reaction of phosphorus-containing groups into the backbone of polymeric materials has become the main direction of study due to providing a better fire-retarding effect than that of the blending polymers with phosphorus-containing additives. However, their thermal decomposition behaviors have not been clear until now.

For thermal decomposition behaviors of a phosphorus-containing polymer via poly[diethyl

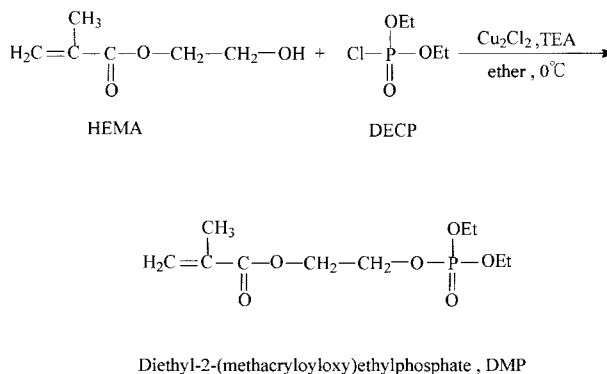
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2-(methacryloyloxy)ethyl phosphate] (PDMP), Reghunadhan Nair et al.<sup>2</sup> used thermogravimetric analysis (TG) to postulate simple thermal decomposition mechanisms with side-chain scission and anhydride formation of neighboring side chains to release phosphate ester and ether, respectively. However, there is still not enough evidence, due to the lack of direct analysis for the evolved gases during polymer pyrolysis. Thus, few studies in the literature are found on the thermal decomposition reactions of PDMP. However, there have been numerous ways to evaluate the thermal decomposition behaviors of other polymers in the literature, including pyrolysis with Fourier transform infrared reflection<sup>3</sup> (Py-FTIR), flash Py-GC/MS,<sup>4</sup> TG,<sup>5</sup> thermogravimetric analysis with Fourier transform infrared reflection<sup>6</sup> (TG/FTIR), and TG/MS,<sup>7</sup> among which Py-GC/MS has been widely applied due to its rapidity, high sensitivity, and effective separation ability of complex mixture compounds containing some pyrolysates of similar compositions. We have reported using a new stepwise Py-GC/MS method<sup>8</sup> to analyze the distribution curves of evolved gas directly during PDMP pyrolysis and to postulate its decomposition process.

TG analysis is an excellent tool to study the kinetics of thermal decomposition, which can provide information on the frequency factor, activation energy, and overall reaction order. But, it is still unable to provide enough information on the thermal degradation mechanism because of the insufficient capability of the evolved gas mixture analysis. Thus, the direct analysis of gas compositions, by continuous monitoring with a hyphenated technique of TG/MS, has received more attention in the identification of gaseous products for the mechanism study of pyrolysis. Recently, the development of the TG/MS interface design has made a significant breakthrough in stability. Such a system has been used in studying the mechanisms of polymers.<sup>9–12</sup> The interface system, as above, still cannot reach the status of an ideal<sup>13</sup> and needs more improvement. Up to now, TG/MS has been used mostly in the analysis of small-size molecules, such as CO, CO<sub>2</sub>, water, and phenol. The interface system was modified in our previous studies<sup>14–17</sup> to give high sensitivity and low interference for real-time monitoring of major gas-evolution curves during the scission of polymers. In this study, the thermal decomposition behavior of synthesized PDMP was studied by the combination of TG/MS and Py-GC/MS to determine its flame retardancy.



**Figure 1** Synthesis scheme of DMP monomer.

## EXPERIMENTAL

### Materials

The monomer, hydroxyethyl methacrylate (HEMA; Aldrich, Milwaukee, WI), was distilled under reduced pressure for purification with the addition of a molecular sieve and stored at ice temperature before use. Diethyl chlorophosphate (DECP; Aldrich) was used without further purification. The solvent tetrahydrofuran (THF; Fisher, Pittsburgh, PA) was dried and refluxed with metallic sodium under a nitrogen atmosphere, using benzophenone as an indicator, and freshly distilled before use. Triethylamine (TEA; Riedel de Haen, Berlin, Germany) was dried and refluxed with KOH under a nitrogen atmosphere and freshly distilled before use. The initiator azobisisobutyronitrile (AIBN; E. Merck, Darmstadt, Germany) was recrystallized from *n*-hexane and dissolved in benzene for storage in a refrigerator.

### Synthesis of DMP

The synthesis scheme of the diethyl 2-(methacryloyloxy)ethyl phosphate (DMP) monomer was based on the literature,<sup>2,3,8,18</sup> using HEMA and DECP in the mixture of THF, TEA, and CuCl<sub>2</sub>, as shown in Figure 1.

<sup>1</sup>H-NMR analysis of DMP for  $\delta$  (ppm) was as follows: CH<sub>3</sub> in phosphate ester: 1.4; CH<sub>3</sub> in allyl: 2.0; —OCH<sub>2</sub>: 3.8–4.3; —CH in vinyl *trans* to carbonyl: 5.5; —CH in vinyl *cis* to carbonyl: 6.1. <sup>13</sup>C-NMR analysis of DMP for  $\delta$  (ppm): —CH<sub>3</sub> in phosphate ester and —CH<sub>3</sub> in allyl: 17.2–17.4; —OCH<sub>2</sub>—: 64.9–65.8; =CH<sub>2</sub> in vinyl: 124.1; =C— in allyl: 136.5; and —C=O in carbonyl: 167.2.

These results were identical to those reported in the literature.<sup>8,18</sup>

### Polymerization of DMP

The synthesized DMP monomer was dissolved in benzene in the presence of AIBN, then deaerated under a vacuum three times and sealed in a Pyrex glass tube, which was further polymerized by a free-radical initiator, AIBN, at 70°C for 48 h to form PDMP. The molecular weight of PDMP analyzed by GPC with THF as a fluent was found to be  $\bar{M}_n = 2.62 \times 10^4$  g/mol.

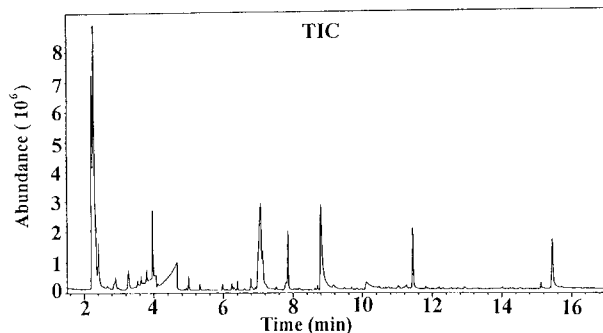
### Apparatus and Procedures

#### Py-GC/MS

The Py-GC/MS experiments were carried out using a CDS-2000 pyroprobe pyrolyzer (Chemical Data System Co.), coupled to an HP 5890 gas chromatograph that was linked to an HP 5972 quadrupole mass spectrometer. Sample aliquots of about 1.00 mg were pyrolyzed in a quartz capillary sample holder, using a platinum coil attachment with 5/16-in. inner diameter (i.d.). The pyroprobes were calibrated to ensure the accuracy of the nominal setting temperature. Flash pyrolysis, with helium carrier gas at a flow rate of 50 mL/min, and the interface of Py-GC at 250°C was increased to 750°C at a rapid heating rate of 5°C/ms for identifying pyrolysates from PDMP pyrolysis. The injector was operated at 250°C in a split mode (3.3 split ratio). The GC column was an HP-5MS (30 m  $\times$  0.25-mm i.d. with a coated film thickness of 0.25  $\mu$ m). The oven temperature of the GC was initially held at 40°C for 2 min, then programmed to 250°C at 10°C/min and held for 5 min. The GC/MS interface was set at 280°C. Mass spectra were recorded under an electron impact ionization energy at 70 eV, and the flow rate was kept constant. The MS detector scanned from 10 to 400  $m/z$  at a scan rate of 1.8 scans/s. Data analyses were performed by an HP Chem Station G1034 (version 3.00) through matching the NIST Mass Spectra Library by comparison.

#### TG/MS<sup>14-17</sup>

The TG/MS system, which combined a DuPont TA 2950 TG analyzer with a modified CDS 3500 interface and an HP 5972 quadrupole mass spectrometer, was used to perform the TG/MS experiment. The samples of about 1.00 mg were pyrolyzed in the TG, and the evolved gases were led via the CDS 3500 interface to the HP 5972 mass spectrometer to obtain the evolution curves of pyrolysates. The interface was a splitter using



**Figure 2** Chromatogram of flash pyrolysis products of PDMP by Py-GC/MS at temperature to 750°C in He.

two deactivated capillary columns of 0.53 and 0.1-mm i.d. capillary tubing, with a length of 30 cm, to split the evolved gases. The operating conditions were as follows: purge gas, helium of 99.9995% purity; temperature setting of interface, 300°C; MS range, 10–550 amu; and scan rate, 1.2 scans/s, and two computer systems were used to control the TG and MS, respectively. For analyzing the real-time evolution curves of PDMP pyrolysis, the temperatures of maximum loss rates were dependent on the thermal ramp rate (10°C/min) that was used in the experiment.

















## RESULTS AND DISCUSSION

### Thermal Decomposition Behavior of PDMP

To identify a complicated mixture of ion species by TG/MS, this study combined a hyphenated technique, Py-GC/MS, to analyze the pyrolysates of PDMP. Then, the results were used to select noninterfering specific ion species ( $m/z$ ) for TG/MS analysis to study the real-time evolution curves of pyrolysates.<sup>14-17</sup>

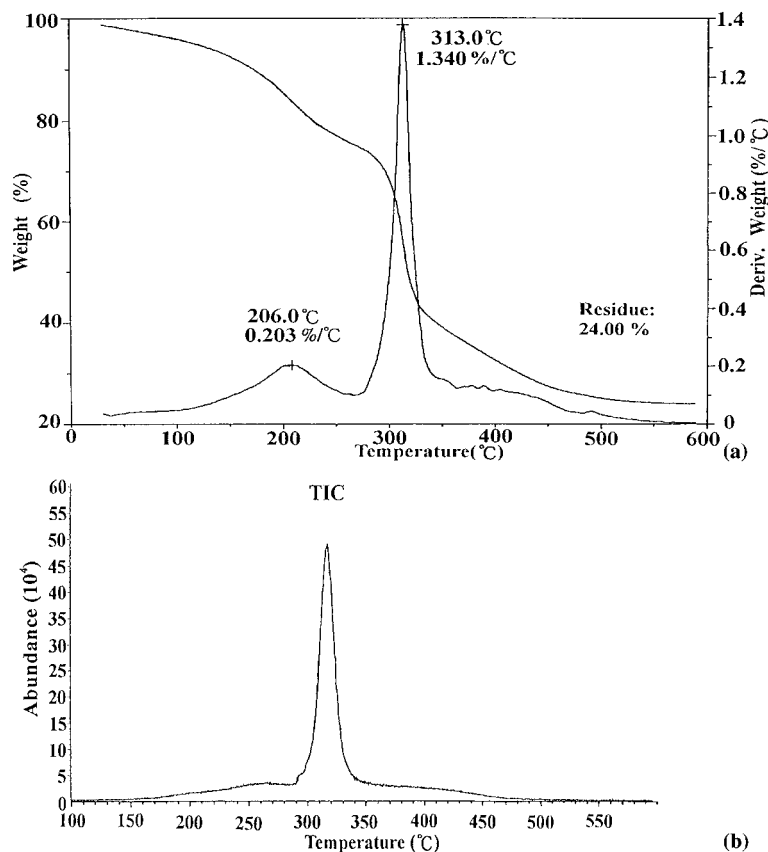
A typical pyrogram (total ion chromatography of the pyrolysates) of PDMP was obtained by flash pyrolysis<sup>8</sup> at temperature up to 750°C in He with a rapid heating rate of 5°C/ms as shown in Figure 2. The 16 major pyrolysates from PDMP, as listed in Table I, were identified by Py-GC/MS. Selective spectra were determined by comparing the mass spectra of the pyrolysates through TG/MS analysis, in which appropriate selective noninterfering ion species ( $m/z$ ) could be chosen for analyzing all the pyrolysates except the pair of 2-methyl-2-propenoic acid + 2-methyl-2-propenoic ethyl ester, which could not be separated because of the same  $m/z$  value in the specific ion

**Table I Identification of Pyrolysates in Flash Py-GC/MS of PDMP to 750°C in He<sup>12</sup>**

Compound	Retention Time (min)	Molecular Weight	Major Mass Fragments	Extract Ion for TGA/MS Analysis
 H <sub>2</sub> O	2.3	18	18	18
 Acetaldehyde	2.3	44	29,44	29
 Ethanol	2.3	46	31,45	45
 Ether	2.4	74	31,59,74	74
 1,4-Dioxane	3.3	88	88,58	88
 Methylbenzene	3.8	92	91,92,65,63,51	92
 2-Methyl-2-propenoic ethyl ester	4.0	114	69,41,99,86,114	86
 2-Methyl-2-propenoic acid	4.7	86	86,41,39,69	86
 Dimethylbenzene	5.0	106	91,106,105,77,79	106
 Trimethylbenzene	6.8	120	105,120,119,91,77	120
 HEMA	7.1	130	69,41,87	87
 2-Ethoxyethyl methacrylate	7.9	158	69,72,41,59	72
 Triethyl-phosphate	8.8	182	99,155,127	155
 Vinyl ethyl phosphoric acid ester	10.1	152	125,108,99,81	125
 [CH <sub>2</sub> =CH(CH <sub>3</sub> )COOCH <sub>2</sub> ] <sub>2</sub>	11.4	198	69,41,113	113
 DMP	15.4	266	112,69,113,41,99	112

species. The 14-set evolution curves for 15 pyrolysates were identified by TG/MS in this study. The large molecule [CH<sub>2</sub>=CH(CH<sub>3</sub>)COOCH<sub>2</sub>]<sub>2</sub>

could not be detected in this study since it might be condensed in the transfer line of TG/MS or interfered with by the mass spectra of DMP.

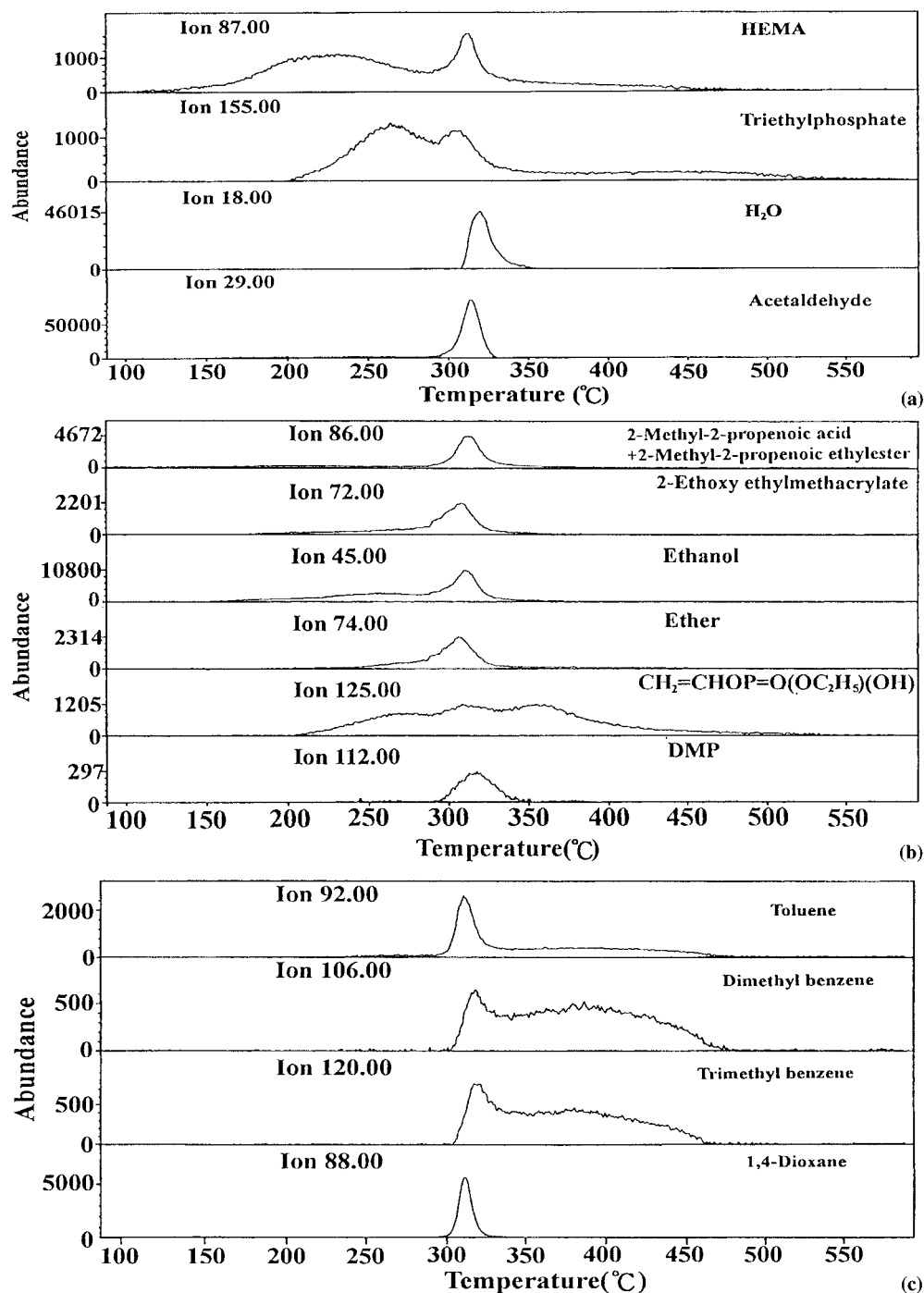


**Figure 3** (a) TG/DTG and (b) TIC curves of PDMP pyrolysis by TG/MS at a heating rate of 10°C/min in He.

The DTG (differential TG) curve of PDMP analyzed by TG/MS in He at a heating rate of 10°C/min from 30 to 600°C is shown in Figure 3(a), indicating a two-stage pyrolysis process. The maximum pyrolysis temperatures,  $T_{\max}$ , and rates,  $r_{\max}$ , in two-stage pyrolysis were found to be around 206°C ( $T_{\max1}$ ) and 0.20 wt %/°C ( $r_{\max1}$ ) for the first stage and around 313°C ( $T_{\max2}$ ) and 1.34 wt %/°C ( $r_{\max2}$ ) for the second stage. The solid residual weight remained constant with a char yield of carbonization about 24 wt % when the temperature was over 500°C, indicating that carbonization played an important role in the condensed-phase reaction. Figure 3(b) shows the total ion current (TIC) curve of PDMP analyzed by TG/MS, which is dissimilar to the DTG curve in Figure 3(a) but also reveals a two-stage pyrolysis process. At the first stage, the peak in TIC around 270°C was higher than that in DTG around 206°C, indicating that the temperature of releasing the maximum gas molecules was higher than that of the maximum weight loss. At the second stage, the peak at around 313°C was observed to

be almost the same for both DTG and TIC. In addition, the initial decomposition temperature of TIC around 110°C was similar to that of DTG. The resulting data show that our assembled TG/MS, by combining Py-GC/MS, can be used to study the decomposition process of different stages during scission of a polymer.

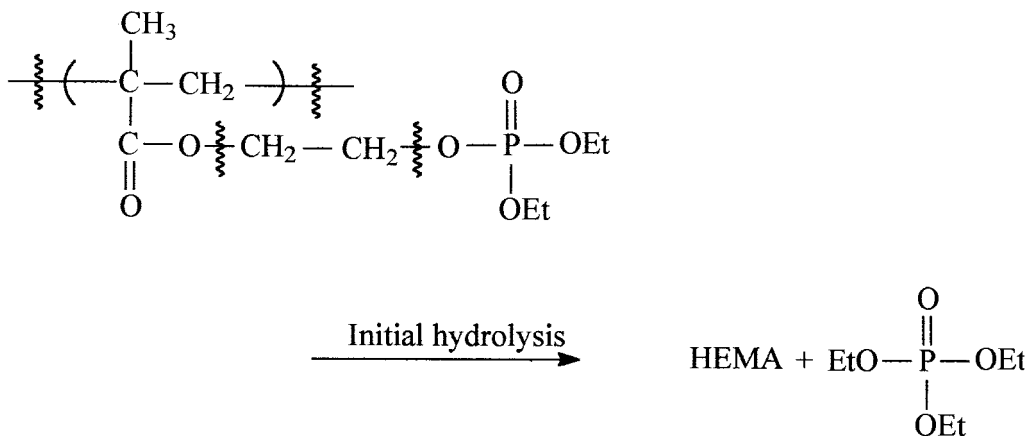
The abundance of Figure 4(a) shows the major evolution curves of HEMA, triethylphosphate, water, and acetaldehyde during the pyrolysis of PDMP by TG/MS in which two peaks were noticed in the former two but only one peak was found in the latter two. HEMA started to evolve around 110°C, being similar to that of DTG, with two peaks around 205 and 315°C. Triethylphosphate started to evolve around 200°C, with two peaks around 270 and 310°C. Two peaks of HEMA were similar to those of DTG, while for triethylphosphate, its peaks were also similar to those of TIC, as shown in Figure 3. These results indicated that the scission of PDMP should be initialized by water to produce triethylphosphate and HEMA as major products, but the former did not begin to be



**Figure 4** Evolution curves of PDMP pyrolysis by TG/MS at a heating rate of 10°C/min in He: (a) (1) HEMA; (2) triethylphosphate; (3) water (4); acetaldehyde. (b) (1) 2-Methyl-2-propenoic acid + 2-methyl-2-propenoic ethyl ester; (2) 2-ethoxyethyl methacrylate; (3) ethanol; (4) ether, (5) vinyl ethyl phosphoric acid ester; (6) DMP. (c) (1) Toluene; (2) dimethylbenzene; (3) trimethylbenzene; (4) dioxane.

detected by MS until over 200°C. Evidently, those phosphate-containing products should be reserved in the condensed phase. Besides, the evo-

lution abundance of triethylphosphate and HEMA at the first stage showed them to be major products as compared to the others. The above



Scheme 1

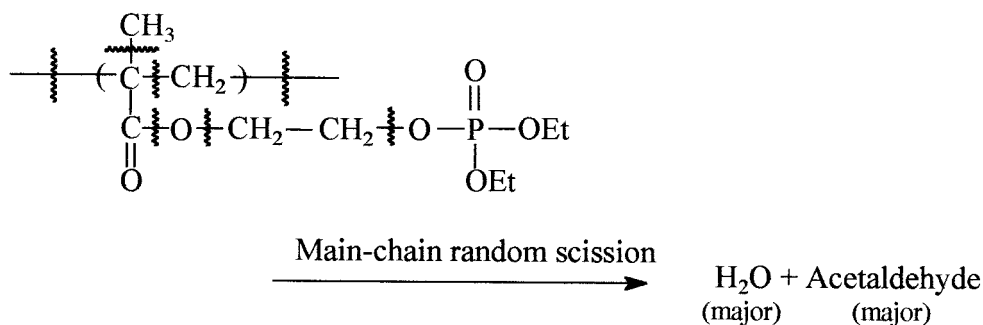
results could suggest that the thermal decomposition of PDMP should be first initialized by water, which existed in the sample,<sup>2</sup> as shown in Scheme 1.

At the second stage, the peak for HEMA and triethylphosphate at 310–320°C was similar to that for water and acetaldehyde, showing that the evolution of the former two was accompanied by that of the latter two. Acetaldehyde and water, as major products, appeared only at the second stage, which should be released from a main-chain random scission of PDMP as a dominant mechanism of this stage as shown in Scheme 2.

The requirement of hydrolysis before the peak of water during scission of PDMP exhausted the water evolved from anhydride formation, condensation of the phosphate ester, or main-chain random scission,<sup>2</sup> leading to shift the higher peak of water relative to acetaldehyde, as shown in Figure 4(a).

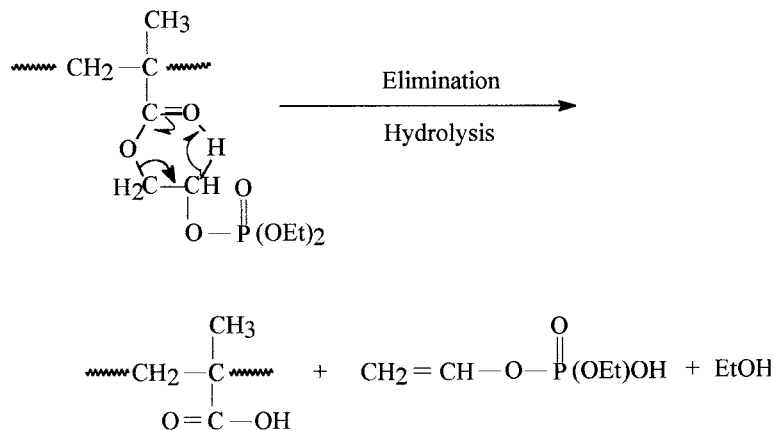
Figure 4(b) shows the evolution curves of six pyrolysates, including 2-methyl-2-propenoic acid

+ 2-methyl-2-propenoic ethyl ester, 2-ethoxyethyl methacrylate, ethanol, ether, vinyl ethyl phosphoric acid ester, and DMP. The first four pyrolysates, similar to that of HEMA, started to evolve at 110–200°C, with the maximum evolution at 310–320°C, indicating that they were first evolved along with the initial hydrolysis of PDMP and then further with random main-chain scission at the second stage. In addition, ethanol may be evolved from hydrolysis, the polycondensation of phosphate ester, an elimination reaction, or anhydride formation<sup>2</sup> during scission of PDMP as one of major products, especially at the first stage. The release of  $\text{CH}_2=\text{CHOP}=\text{O}(\text{OC}_2\text{H}_5)\text{OH}$  was similar to that of triethylphosphate and produced by an elimination reaction from PDMP pyrolysis. The evolution curve of DMP appeared only at the second stage with a peak at around 315°C, indicating that its evolution was accompanied by main-chain random scission. From the above resulting analysis, the hydrolysis of PDMP was initialized by water that existed in the sample to produce the phosphate-containing compounds,



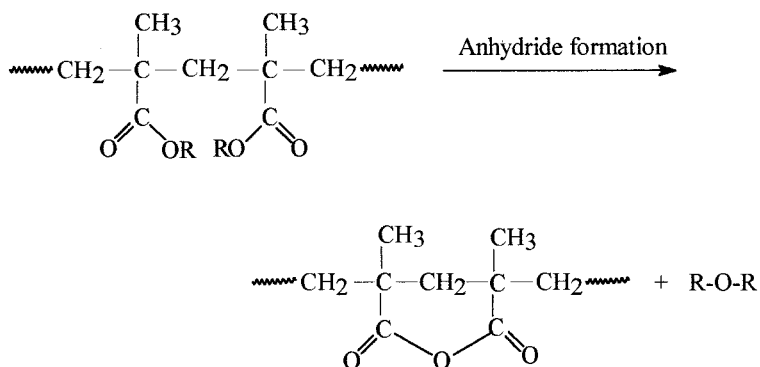
Scheme 2

(A)



(B)

Intramolecular

R = H, CH<sub>3</sub>-CH<sub>2</sub>-

Intermolecular

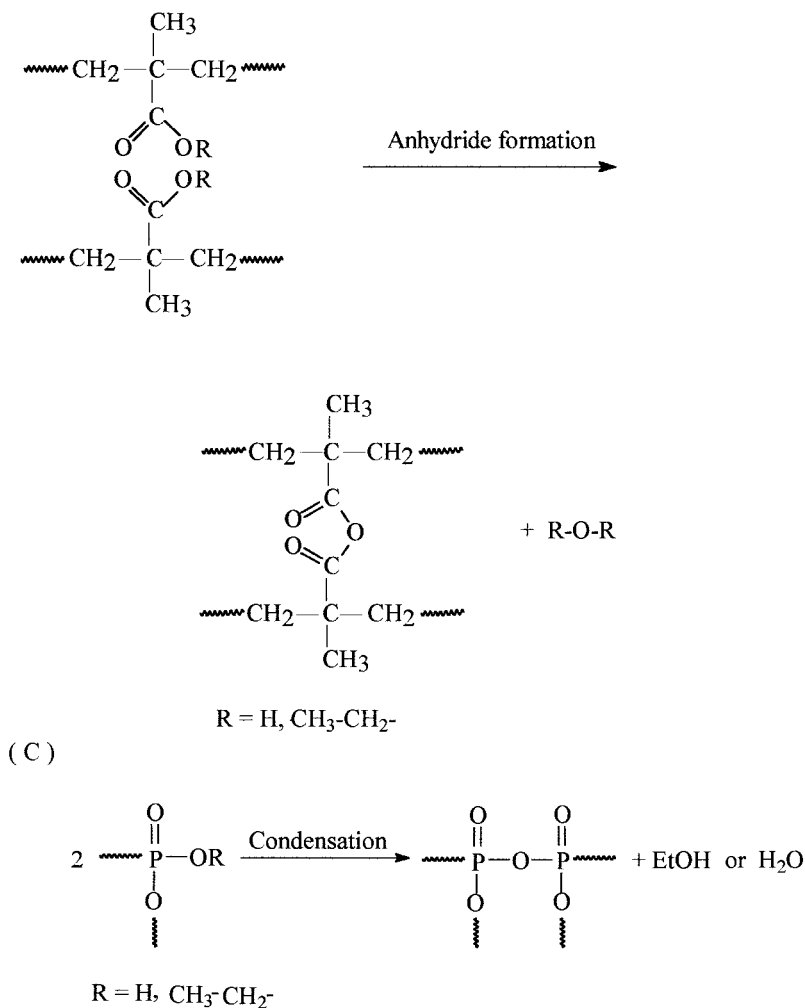
Scheme 3

and then these compounds further catalyzed this sample through the elimination reaction (A) and anhydride formation (B), intermolecular,<sup>2</sup> or produced the polycondensation (C) to evolve large amounts of small molecules such as ethanol and water as shown in Scheme 3.

Figure 4(c) shows the evolution curves of four cyclic compounds, including dimethylbenzene, tri-

methylbenzene, toluene, and 1,4-dioxane. These pyrolysates were only formed at the second stage, among which dimethylbenzene, trimethylbenzene, and toluene reached the maximum evolution at 310–320°C and were still released over 340°C, while the amount of the evolution of toluene was the largest of all the arylene-containing compounds. The maximum amount of 1,4-dioxane also appeared around 315°C and then diminished





**Scheme 3** (Continued from the previous page)

over 340°C. The arylene-containing and 1,4-dioxane compounds should be formed from scission of the unstable nonvolatile phase through chain transfer of carbonization catalyzed by the phosphate ester<sup>2</sup> in the nonvolatile phase. These phenomena, including the high char yield of solid residue and the evolution of cyclic compounds, indicated that carbonization during the scission of PDMP of the second stage should be a dominant mechanism. In addition, the above results also showed that the weight-loss curve of pyrolyzed PDMP still included the polycondensation and carbonization of phosphorus-containing compounds in the condensed phase to reduce its application reliability in the analysis of kinetic parameters, similar to the explanation of Hill et al.<sup>19</sup> for studying polymethacrylonitrile by TG.

## CONCLUSIONS

The combination of TG/MS with Py-GC/MS could obtain real-time evolution curves of pyrolysis of a polymer to analyze its thermal decomposition. By comparison of the scission of PHEMA relative to PDMP, the reaction of phosphate groups into the backbone of the former apparently changed its decomposition process from one stage to two stages via depolymerization to random main-chain scission along with carbonization, in which, despite its initial thermal stability reduced by hydrolysis, still increased the char yield of the solid residue around 600°C from nearly 0 (refs. 2 and 18) to 24%. The scission of PDMP was initialized by water, having existed in the sample, to evolve ethanol, HEMA, and triethylphosphate as major products. Then, subsequently, its dominant

decomposition of the second stage was a main-chain random scission to evolve acetaldehyde and water as major products along with the evolution of arylene-containing compounds that were induced by the chain transfer of carbonization. Carbonization gradually became the dominant mechanism of higher-temperature pyrolysis to form the higher char yield. The results analyzed by comparing TG/MS with stepwise Py-GC/MS<sup>8</sup> showed that the former could provide a more accurate mechanism of PDMP thermal decomposition than could the latter.

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