

## New phosphorus- and nitrogen-containing poly(methyl methacrylate)based copolymer

Enhanced flame retardancy and thermal stability

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#### Abstract

Pure poly(methyl methacrylate) (PMMA) always exhibits high flammability and low thermal stability. To address that, a novel reactive comonomer containing phosphorus and nitrogen elements, 4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl) phenyl diethylphosphoramidate (PDM), was successfully synthesized and then introduced into PMMA matrix through emulsion copolymerization method. The structure of PDM and as-obtained poly(MMA-*co*-PDM) copolymers was characterized using Fourier transform infrared (FT-IR), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) and <sup>31</sup>P NMR. From thermal gravimetric analysis and microscale combustion calorimeter, the poly(MMA-*co*-PDM) copolymers exhibit significantly enhanced flame retardancy and thermal stability, such as the higher degradation temperatures, and decreased peak heat release rate (maximally by 24.1%) and total heat release (maximally by 22.1%). The glass transition temperature ( $T_g$ ) values of poly(MMA-*co*-PDM) copolymers obtained by differential scanning calorimetry slightly decrease as the raising flexibility of polymer chain. The char residue analysis by scanning electron microscopy and FT-IR demonstrates that the incorporation of PDM can catalyze the charring of copolymers in condensed phase and form an excellent thermal stability char residue with aromatic structure, further preventing the inner substrate from further combustion. The detailed mechanism was proposed.

Keywords Poly(methyl methacrylate) based copolymer · Flame retardancy · Thermal property · Mechanisms

## Introduction

Poly(methyl methacrylate) (PMMA) has been widely used in building construction, plastic optical fibers and optical lenses owning to its excellent performances including good flexibility, high strength, weather resistance and dimension stability. However, the poor thermal stability and high flammability of PMMA limit its further use in many desirable

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applications [1]. Consequently, improving the thermal properties and flame retardancy of PMMA has attracted increasing attentions in recent years. Traditionally, halogenated flame retardants are widely applied in flame retardance of PMMA in virtue of their gas-phase quenching activity and high flameretardant efficiency [2–4]. Nevertheless, the utilization of some halogenated compounds has been restrained in many fields considering the environmental pollution. Therefore, there is an ever-increasing trend toward the use of environment-friendly and halogen-free alternatives.

Phosphorus-containing flame retardants, as promising "green" flame retardants for polymeric materials, have gained growing attentions thanks to their nontoxicity [5, 6]. In general, the physical incorporation of phosphorus based flame retardants into polymers often leads to deteriorated mechanical property and leaching-out phenomenon owning to the poor compatibility [7, 8]. An alternative technique is to use some reactive flame retardants, and several works have been investigated to enhance the flame retardancy of PMMA with

chemical modification of the preformed homopolymers or simple copolymerization of monomers [9]. Tian et al. [10] synthesized a novel phosphorus-containing monomer with  $\alpha$ hydroxy phosphonate PHMA and MMA via fragmentation chain transfer polymerization, and the resultant copolymer exhibited remarkably enhanced thermal stability and flame retardancy. Du et al. [11] introduced a phosphorus-containing flame-retardant DEAMP into PMMA shell to fabricate a nanoencapsulated phase change materials (NanoPCMs), and the incorporation of 20% DEAMP rendered the NanoPCMs with a 39.7% decrease in peak heat release rate (PHRR) and a 18.4% decrease in total heat release (THR). Jiang et al. [12] investigated the flame-retardant effect of a novel PMMAbased copolymer (PMMA/DOPO-AA), and the as-fabricated copolymer demonstrated an increased limited oxygen index value by 4.1 and a decreased PHRR by 34.7%. In general, the relatively low content is required for the material to achieve sufficient flame retardancy and a good distribution is formed due to the chemical bond between the matrix and flame retardants, resulting in an increased durability of flame retardance in polymer [13, 14]. However, the flame-retardant efficiency of most single phosphorus-containing reactive flame retardants is relatively low. According to the previous literature, the synergic nitrogen-phosphorous flame retardant can effectively prevent materials from thermal damage by degrading into nonvolatile gas and forming carbonization layers [15–17]. Nitrogen- and phosphorous-containing compounds have been received more than ever attention in both academic and industry fields.

Inspired by the aforementioned concepts, a novel comonomer containing phosphorus and nitrogen elements was synthesized and copolymerized with methyl methacrylate (MMA) to prepare poly(MMA-*co*-PDM) copolymers. The structure of the comonomer and copolymers was confirmed by <sup>1</sup>H NMR, <sup>31</sup>P NMR and FT-IR spectra. The thermal properties and thermal degradation behaviors of the copolymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The flammability of poly(MMA-*co*-PDM) copolymers was evaluated by microscale combustion calorimetry (MCC). With the help of SEM and FT-IR, the detailed mechanisms for flame retardancy enhancement were proposed.

## Experimental

## Materials

Methyl methacrylate (MMA), sodium dodecyl benzene sulfonate (SDBS) and potassium persulfate were provided by Tianjin Damao Chemical Reagent Factory (Tianjin, China). Phenyl dichlorophosphate (PDCP) was supplied by Changzhou Xuanming Chemical Industry Co., Ltd. (Changzhou, China). Maleic anhydride (MAH), p-aminophenol and N, N-dimethylformamide (DMF) were provided by Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Phosphorus pentoxide, diethylamine (DEA), triethylamine (TEA), tetrahydrofuran (THF), isopropyl alcohol and deionized water were all reagent grades and purchased from Guangzhou Qianhui Chemical Glass Instrument Co., Ltd. (Guangzhou, China).

# Synthesis of *N*-(4-hydroxyphenyl) maleimide (HPM)

MAH (11 g) and DMF (50 mL) were firstly added into a 250 mL three-necked glass flask equipped with a mechanical stirrer and a nitrogen inlet. The mixture was stirred under nitrogen atmosphere until MAH was dissolved completely in DMF. Next, p-aminophenol (10 g) was added dropwise to the above solution and maintained stirring at room temperature for 2 h. And the mixture of phosphorus pentoxide (5.5 g) and sulfuric acid (2.5 g)dissolved in DMF (50 mL) were then fed dropwise into the solution, and the reaction mixture was heated to 80 °C and kept at refluxing temperature for another 6 h. Then, the product was cooled and poured into 500 mL ice water and a yellow precipitate was obtained. The precipitate was filtered and washed several times with deionized water. Finally, the precipitate was recrystallized in isopropanol alcohol and dried at 50 °C by vacuum rotary evaporation. The synthesis route of HPM is illustrated in Scheme 1a.

## Synthesis of 4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)phenyl phenyl diethylphosphoramidate (PDM)

PDM was designed based on Scheme 1b. PDCP (21.1 g, 0.1 mol) and THF (80 mL) were firstly fed into a 250-mL three-neck flask loaded with a reflux condenser and a mechanical stirrer in the ice bath. Then, TEA (21.6 g, 0.21 mol) was added to the system after 30 min and HPM (19 g, 0.1 mol) dissolved in THF (20 mL) was added dropwise into the mixture and kept stirring for another 4 h at 0 °C. Next, the mixture was heated to room temperature and continually stirred for another 10 h. Finally, the precipitated triethylamine salt was removed by filtration, and the solution was then rotary evaporated to remove the solvent and unreacted reactants under reduced pressure to obtain a yellow viscous liquid.

## Preparation of poly(MMA-co-PDM) copolymers

The poly(MMA-*co*-PDM) copolymers were prepared by emulsion polymerization, and the schematic process of the



Scheme 1 Synthesis route and structure of a HPM and b PDM



Scheme 2 The schematic synthesis route of poly(MMA-co-PDM) copolymers

reaction is presented in Scheme 2. Firstly, 30 mL MMA (27.4 g) and 240 mL distilled water were poured into a 500-mL three-necked flask under nitrogen atmosphere at room temperature and kept stirring for 30 min. Then, 1.37 g PDM (5 mass% compare to MMA) was added into the mixture and stirred for 1 h until it was completely dissolved. Afterward, 10 mL SDBS solution (0.015 mol  $L^{-1}$ ) was added into the mixture and stirred for 1 h to obtain a homogeneous emulsion. Then, 60 mL potassium persulfate (0.078 g) solution was fed dropwise to the above-mentioned homogeneous emulsion; the reaction temperature was heated to 70 °C and reflux for 10 h. The emulsion was cooled to room temperature until the polymerization was completed. At last, the emulsion was placed in a beaker and frozen for 12 h at -10 °C, the product was obtained by centrifugation with distilled water several times to remove the unreacted emulsifier and catalysts and dried at 40 °C. Other copolymers with various amounts of PDM were obtained by the same procedure. The poly(MMA-co-PDM) copolymer with 0 mass%, 5 mass%, 10 mass%, 15 mass% PDM (the mass ratio of PDM to MMA) is abbreviated to MP, MP5, MP10, MP15, respectively.

#### Measurements and characterization

FT-IR spectrum was recorded in transmittance mode using VERTEX 33 (Bruker, Germany) in a spectrometer in a range of 4000–400 cm<sup>-1</sup> with a range resolution of  $4 \text{ cm}^{-1}$ .

<sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were registered with a Bruker AV400 NMR spectrometer (400 MHz) operating in the Fourier transform mode using deuterated chloroform (CDCl<sub>3</sub>) as solvent for PDM.

TG was conducted on a TGA STA449 F3 IR thermal gravimetric analyzer (Netzsch, Germany) from room

temperature to 700 °C at a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

DSC was carried out on a DSC 204F1 Phoenix (Netzsch, Germany) under nitrogen flow from 30 to 200 °C at a heating and cooling rate of 10 °C min<sup>-1</sup> to investigate the thermal properties of all the samples.

MCC tests were carried out on a Govmak MCC-1 microscale combustion calorimeter. About 6–8 mg of powdery sample was heated from 25 to 650 °C at a heating rate of 1 °C s<sup>-1</sup> under nitrogen. Then, the pyrolysis products were mixed with oxygen (20 mL min<sup>-1</sup>) prior to entering a 900 °C combustion furnace, and the combustion heat of the pyrolysis products was measured by oxygen consumption principle.

SEM images were obtained with a scanning electron microscope FEI Quanta FEG 250 at an accelerating voltage of 10.0 kV.

## **Results and discussion**

#### Synthesis and structure characterization

The chemical structure of HPM and PDM was characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR and FT-IR. Figure 1a shows the FT-IR spectrum of HPM and PDM. The most significant absorptions of HPM can be observed at 3484 cm<sup>-1</sup> and 1701 cm<sup>-1</sup> corresponding to –OH and C=O vibration, respectively [18–20]. The absorption peaks at 1597 cm<sup>-1</sup> and 1520 cm<sup>-1</sup> are attributed to the aromatic vibration of benzene, and the peak at 831 cm<sup>-1</sup> corresponds to disubstitution vibration of benzene [21, 22]. And, the absorption at 1415 cm<sup>-1</sup> and 690 cm<sup>-1</sup> is assigned to C– N–C stretching vibration and C=C vibration of maleimide ring, respectively [23, 24]. These above results reveal that



Fig. 1 a FT-IR spectra of HPM and PDM, b <sup>1</sup>H NMR spectra of PDM, c <sup>31</sup>P NMR spectra of PDM and d FT-IR spectra of MP and MP15

the precursor HPM is fabricated successfully as Scheme 1a. As shown in Fig. 1a, the emerged absorption of PDM monomer at 2975 cm<sup>-1</sup> is assigned to C–H antisymmetric stretching of  $-CH_3$ , and the new bands at 1269 cm<sup>-1</sup> and 1039 cm<sup>-1</sup> correspond to P=O vibration and P-O stretching vibration, respectively [15]. Besides, the absorption of -OH is significantly reduced for the reason of the chemical reaction between HPM and PDCP.

Figure 1b, c presents the <sup>1</sup>H and <sup>31</sup>P NMR spectra of PDM, respectively. The <sup>1</sup>H NMR spectrum of PDM displays some characteristic peaks: the peak at 1.07 ppm corresponds to the protons of  $-CH_3$ ; the peak at 3.24 ppm corresponds to the protons of  $-CH_2-$ ; the peaks at 7.15–7.40 ppm are attributed to the protons of aromatic ring; and the strong peak at 6.83 ppm is attributed to the -CH=CH- protons of maleimide ring. The peak at 7.26 ppm is attributed to CDCl<sub>3</sub>. The <sup>31</sup>P NMR spectra of PDM show a strong single peak at 0.58 ppm, and the weak peak at

- 18.17 ppm is caused by some impurity. These results further confirm that PDM has been successfully synthesized.

The poly(MMA-*co*-PDM) copolymers were prepared by emulsion polymerization, and the FT-IR spectra of MP and MP15 copolymers are illustrated in Fig. 1d. The absorption bands of pure MP around 2997 cm<sup>-1</sup>, 2952 cm<sup>-1</sup> (asymmetric) and 2841 cm<sup>-1</sup> (symmetric) are assigned to C–H stretching vibrations. The peaks appeared at 1485 cm<sup>-1</sup> and 1438 cm<sup>-1</sup> correspond to the bending vibration bands of the methyl (–CH<sub>3</sub>) group, while the peaks around 1387 cm<sup>-1</sup> are attributed to the deformation mode of the methylene (–CH<sub>2</sub>–) group. In addition, the stretching vibrations and bending vibrations of the carbonyl (C=O) group appear at 1728 cm<sup>-1</sup> and 753 cm<sup>-1</sup>, respectively [25, 26]. It can be seen that some new characteristic peaks arise after the reaction between MMA and PDM. For PM15 copolymers, the aromatic vibrations of benzene appear at  $1592 \text{ cm}^{-1}$  and  $1512 \text{ cm}^{-1}$ . Besides, the new bands at 1039 cm<sup>-1</sup> correspond to P–O stretching vibration and the emerged sharp peaks at 690 cm<sup>-1</sup> is assigned to the C=C vibration of maleimide ring. These results indicate the successful copolymerization between MMA and PDM.

#### Thermal properties analysis

The thermal properties of the poly(MMA-co-PDM) copolymers were analyzed by DSC, and the second heating segments curves are presented in Fig. 2. The glass transition temperature  $(T_g)$ , one of important thermal parameters, can be used to characterize polymers and other amorphous or semicrystalline materials, and the  $T_{g}$  data of the samples are represented in Table 1. In general, the  $T_{\rm g}$  values of the poly(MMA-co-PDM) copolymers are shifted to a lower temperature with the loading of PDM, indicating that the incorporation of PDM can plasticize the neat MP. In detail, the  $T_{g}$  values of MP5, MP10 and MP15 copolymers decrease by 1.4 °C, 9.6 °C and 5.9 °C compared with MP. The main reason is that the increased free volume in the molecules caused by the relatively higher molecular mass of PMD leads to the raising flexibility of polymer chain, resulting in the decreased  $T_{g}$  values of poly(MMA-co-PDM) copolymers.

In order to study the thermal stability of poly(MMA-*co*-PDM) copolymers, TG test of all samples was employed. The TG curves of all samples under N<sub>2</sub> atmosphere are illustrated in Fig. 3, and the corresponding data are summarized in Table 1.  $T_{0.1}$  corresponding to the temperature at 10% mass loss is defined as the onset degradation temperatures, while  $T_{0.5}$  corresponding to the temperature at 50% mass loss is used as the measure of half degradation temperatures. And the solid char yields at 500 °C and 600 °C are obtained from TG curves. The mass loss process of pure MP mainly occurs in the range of 160–430 °C,



Fig. 2 DSC curves of poly(MMA-co-PDM) copolymers

while the poly(MMA-co-PDM) copolymers begin to degrade at a higher temperature compared to pure MP, which is mainly caused by the presence of maleimide ring structure in PDM molecular. In detail, the  $T_{0,1}$  and  $T_{0,5}$ values of MP15 sample increase gradually from 316.6 to 370.6 °C and from 371.5 to 401.8 °C, respectively, as PDM content rises to 15 mass%. It can be clearly found that the introduction of PDM can enhance the decomposition temperature of pure MP. Furthermore, pure MP has no carbon residue at 500 °C, while the corresponding char residue of copolymers at 500 °C rises from 0.7 mass% for MP5 to 2.6 mass% for MP15. Even if it goes up to 600 °C, there is still 2.4 mass% char left in the MP15 sample. The char yields of poly(MMA-co-PDM) samples are increased slightly with the increasing PDM content. The char formed in the condensed phase can inhibit the transfer of oxygen, heat and flammable gaseous products [27, 28]. As a result, the copolymers containing PDM can notably enhance the thermal stability and char residue.

#### Flame retardancy

To evaluate flammability properties of the copolymers, all samples were characterized by microscale combustion calorimeter (MCC). Figure 4 elaborates the HRR curves of poly(MMA-co-PDM) copolymers versus temperatures, and the relevant PHRR and THR values are listed in Table 1. As illustrated in Fig. 4, both PHRR and THR values of the copolymers are shifted to lower values with the addition of PDM. For example, the THR and PHRR of pure MP are 28.0 kJ  $g^{-1}$  and 379.0 W  $g^{-1}$ , respectively, while the incorporation of 15.0 mass% PDM leads to a 22.1% maximum decrease in THR (21.8 kJ  $g^{-1}$ ) and a 24.1% maximum decrease in PHRR (287.5 W  $g^{-1}$ ). In addition, the poly(MMA-co-PDM) copolymers reach the peak of the heat release rate at a higher temperature compared with neat MP. These results confirm that the flame retardancy of MP is enhanced remarkably with the raised PDM feed. The improvement of flame retardancy in MCC test is closely related to the enhanced thermal decomposition temperature and the increased char yield in TG test.

#### Flame-retardant mechanism analysis

To explore the specific mechanism of char formation on the enhanced flame retardancy of poly(MMA-*co*-PDM) copolymers, the char residue of all samples was obtained by heating all samples with the same mass in a muffle furnace at 500 °C for 15 min. Figure 5a elaborates the optical photographs of the char residue for poly(MMA-*co*-PDM) copolymers, and the char structure was studied by SEM at different magnification. As shown in Fig. 5a, pure MP has been completely decomposed at 500 °C and almost

Samples	PDM content/ mass%	$T_{\rm g}$ /°C	<i>T</i> <sub>0.1</sub> /°C	<i>T</i> <sub>0.5</sub> /°C	Char at 500 °C/mass%	Char at 600°C/mass%	PHRR/W $g^{-1}$	THR/KJ g <sup>-1</sup>
MP	0	124.7	316.6	371.5	0	0	379.0	28.0
MP5	5.0	123.3	366.6	393.1	0.7	0.7	349.1	23.8
MP10	10.0	115.1	370.5	401.2	2.0	1.7	316.7	21.0
MP15	15.0	118.8	370.6	401.8	2.6	2.4	287.4	21.8

Table 1 Composition, flame retardancy and thermal properties of MMA/PDM copolymers



Fig. 3 TG curves of poly(MMA-co-PDM) copolymers under  $\mathrm{N}_{\mathrm{2}}$  atmosphere

no residue is left, while the char yields of poly(MMA-*co*-PDM) copolymers are obviously increased as the PDM content rises, consistent with the previous TG data. And it can be clearly observed that a compact and integrate char is formed for MP5, MP10 and MP15 samples. With the increased PDM loading, the char structure becomes much rough and dense and a relatively uniform char is observed for MP15 copolymers by SEM at high magnification

 $(\times 5000)$ . The dense char layer can hinder the release of flammable gases and inhibit the heat and mass transfer in the burning area, preventing the internal substrate from further combustion. Furthermore, the presence of a bubble-like structure especially in Fig. 5b, d can intuitively demonstrate that the gas product volatilized during the pyrolysis process is inhibited by the formed char residue. These results illustrate that the catalytic charring effect of PDM is favorable for the improvement of flame retardancy in MP matrix.

In order to further evaluate the thermal degradation process of the samples, FT-IR spectra of the char residue obtained at different temperatures for MP and MP15 copolymers are explained in Fig. 6. FT-IR spectra of pure MP reveals absorption bands  $\upsilon$  (cm<sup>-1</sup>): 2997 cm<sup>-1</sup> and 2952 cm<sup>-1</sup> (C–H asymmetric stretching); 2841 cm<sup>-1</sup> (C– H symmetric stretching); 1485 cm<sup>-1</sup> and 1438 cm<sup>-1</sup> (–CH<sub>3</sub> bending vibration); 1728 cm<sup>-1</sup> and 753 cm<sup>-1</sup> (C=O); and 1387 cm<sup>-1</sup> (–CH<sub>2</sub>–) [29, 30]. The relative intensity of these characteristic peaks of MP decreases sharply as the increased temperature, suggesting that the main decomposition of MP occurs at this stage. However, the main peaks can still be detected at 380 °C for neat MP.

The FT-IR spectrum of MP15 (Fig. 6b) is similar to that of MP. Some new characteristic peaks of PDM emerge:



Fig. 4 Heat release rate of poly(MMA-co-PDM) copolymers



**Fig. 5 a** Optical photographs of the char residue for poly(MMA-*co*-PDM) copolymers. **b–d** SEM images of char residues for MP5, MP10 and MP15 at low magnification (× 100), respectively; **e–g** SEM images of char residues for MP5, MP10 and MP15 at high magnification (× 5000), respectively

 $1592 \text{ cm}^{-1}$  and  $1512 \text{ cm}^{-1}$  (aromatic vibrations); 1039  $\text{cm}^{-1}$  (P–O stretching) and 690  $\text{cm}^{-1}$  (C=C vibration of maleimide ring). However, the degradation patterns of MP15 are a little different from that of MP. The relative intensity of MP15 is decreased sharply as the temperature rises to 190 °C, and the basic peaks are all maintained. However, the peak values of MP15 at above 310 °C are much weaker compared with MP because of the initial thermal degradation of PDM units. That is consistent with the TG results: the mass loss of the copolymer is shifted to a higher temperature. In addition, the intensity of the peak has a little increase at 380 °C, especially the maximum intensity of P-O stretching vibration at 1039 cm<sup>-1</sup>, owing to the formation of polyphosphate during the degradation of PDM. When the temperature reaches 430 °C, almost all characteristic peaks disappear, indicating that MP15 copolymers have been completely decomposed. And there is almost one strong peak around  $1630 \text{ cm}^{-1}$  left above 430 °C, indicating that the aromatic structure is stably existed in the char residue. The excellent thermal stability of the formed char contributes to the flame-retardant enhancement for MP15 copolymers.

## Conclusions

In this work, a novel reactive flame retardant containing phosphorus and nitrogen elements was successfully synthesized and incorporated into PMMA matrix through emulsion polymerization. The as-fabricated poly(MMA-



Fig. 6 FT-IR spectra of a MP and b MP15 copolymers obtained at different temperatures

co-PDM) copolymers exhibit significantly enhanced flame retardancy and thermal stability, such as the higher degradation temperature, decreased PHRR by 24.1% and THR by 22.1%. The compact and dense char layer formed by the catalytic charring effect of PDM in condensed phase can inhibit the diffusion of flammable gas products into the flame zone and prevent the inner of copolymers from further combustion. In addition, the aromatic structure is stably existed in the char residue and the excellent thermal stability of the formed char contributes to the flame-retardant enhancement for MP15 copolymers. This work not only endows a promising reactive monomer for PMMA with excellent combined properties of thermal stability and flame retardancy, but also stimulates more efforts for creating effective flame retardants for polymers.

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