Synthesis and Properties of Polyphosphoester and Diphenyl Phosphoroxy Derivative for Flame Retardant Poly(ethylene terephthalate)

Xiujuan Tian*, Shan Huang, Jinjin Wang, Pengcheng Yang, and Kai Yang

College of Materials Science and Engineering, Shandong University of Science and Technology, 579 Qianwangang Road, Economic & Technical Development Zone, Qingdao, China
*308052024@qq.com

A polyphosphoester flame retardant, polyphenylphosphonic acid (2-(diphenyloxyphosphoryl)-1,4-phenol) (PPSFR) was synthesized and applied to flame retarded poly(ethylene terephthalate) (PET). The flame retardancy and thermal stability of the PET/PPSFR were investigated by limiting oxygen index (LOI), vertical burning test (UL-94) test and thermogravimetric analysis (TGA) in nitrogen and air. LOI values increased from 21 for pure PET to 40 for flame retardant PET, and UL-94 V-0 materials were obtained with the 5 wt% PPSFR. The TGA results indicated that incorporation of PPSFR significantly enhanced the char yield and the thermal stability of char layer at higher temperature. The thermal degradation behaviors of PET/PPSFR were analyzed by thermogravimetric analysis/infrared spectrometry (TGA-FTIR), pyrolysis gas chromatography-mass spectrometry (PY-GC/MS), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). Although the addition of PPSFR does not change the degradation mechanism of PET, the contents of the deep pyrolysis products of PET are inhibited. Phosphorus in the form of phosphate compounds concentrates on the surface of aromatic carbon layer and promotes PET dehydration into protective charcoal. PPSFR plays a role of flame retardant in condensed phase and gas phase.

Keywords: Polyphosphoester flame retardant, PET, Thermal stability, Flame retardant performance, Thermal degradation

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the major classes of thermoplastic polyester. With many outstanding performances, PET is widely applied in various industries with strict requirements on material combustion and safety performance. PET is an inflammable material, and the flame retardant treatment of PET has attracted wide research attention worldwide [1-3].

Phosphorus-based flame retardant is an important category in flame-retardant systems and is widely used as additive in engineering plastics because of its smoke-free, non-toxic, and non-corrosive products [4,5]. Traditional organic phosphorus flame retardants (OPFR) are mainly low molecular compounds with poor thermostability, strong volatility, easy migration, unsatisfying compatibility with polymers and outstanding influence on mechanical-physical properties of polymers. Therefore, developing polyphenyl phosphate and high-molecular-weight polyphosphoester with excellent heat resistance, compatibility, and easy-to-use is necessary for development of phosphorus based flame retardant. Ma synthesized polyphosphoester by phenyl-phosphoryl dichloride and bisphenol S solution polycondensation, which can make the oxygen index of PET higher than 28% [6]. Li synthesized bisphenol A bis(diphenyl phosphate) oligomer successfully with phosphorus oxychloride, biphenol A, and phenol under the catalysis of Friedel-Crafts, and its 5% decomposition temperature ($T_{5\%}$) could
reach as high as 375 °C [7]. Wang synthesized high-molecular-weight phosphonate by using phenylphosphonic dichloride and biphenol A through melt phase polycondensation [8]. LOI value of PET could reach 30.0% at 15% dose. In addition, 9,10-dihydro-9-oxa-10-phosphaphen-anthrene-10-oxide (DOPO) is a kind of high efficiency fire retardant, and its derivatives has become one of key research topics [9,10]. Chang synthesized PDPPP which contains phosphorus in both main chain and side chain by using the derivative of DOPO (DOPO-HQ) and BPOD. PDPPP can endow PET excellent flame retardant performance and promote the char yield to 11.8% (600 °C) at 8% dose, whereas the char yield of pure PET under the same temperature was only 1.9% [11].

In this paper, a new polyphosphoester flame retardant (PPSFR) was designed and synthesized with DPO-HQ and phenylphosphonothionic dichloride (DCPPS) through melt phase polycondensation method. And the PPSFR was used to modify PET. The chemical structure of PPSFR was characterized by Fourier transform infrared spectroscopy (FTIR), ¹H NMR, and ³¹P NMR. The thermostability and combustion performance of PET/PPSFR were investigated through TGA, LOI, and UL-94 tests. The PET/PPSFR flame-retardant mechanism was analyzed by TGA-FTIR, PY-GC/MS, XPS and SEM/EDS.

2. Experimental

2.1. Materials
Phenyl thiophosphonyl dichloride (DCPPS) was commercially obtained from Qingdao Fusilin Chemical Science and Technology Co., Ltd. (China). 2-(Diphenylphosphinyl)-1,4-benzenediol (DPO-HQ) was synthesized according to our previous study [12,13]. Commercial PET with an intrinsic viscosity of 0.64 dL/g was provided by FSPG Hi-Tech Co., Ltd. 1,2-Dichloromethane and petroleum ether (LC grade) were purchased from Qingdao Zhengye Reagent Instrument Co., Ltd.

2.2. Synthesis of PPSFR
Mixtures of 0.1 mol (20.99 g) DCPPS, 0.1 mol (31.01 g) DPO-HQ and 0.02 mol (0.22 g) anhydrous calcium chloride (catalyst) were added into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, condenser and gas vent. All the reactants were heated and stirred until completely melted into liquid. The reactants were stirred at 160 °C for 30 min and 230 °C for another 2 h. The produced hydrogen chloride gas was removed by nitrogen gas. Then cooled down to the room temperature and got the crude product. The crude product was dissolved in 100 mL 1,2-dichloromethane and slowly poured into 100 mL petroleum ether. The precipitate was filtered and washed with petroleum ether and then dried at 120 °C for 6 h. About 45.62 g PPSFR (white powder, 87.7% yield) was obtained. The synthetic route is presented in Scheme 1.

![Scheme 1. Synthesis of PPSFR.](image)

2.3. Preparation of flame-retarded PET
The flame retardant and PET were dried in a vacuum oven under 120 °C for 12 h before use, and then premixed using high-speed mixer, blended extrusion, cooled, cut and dried with twin-screw extruder. The composition of PET and flame retardant were shown in Table 1.

| Sample P /% | PPSFR /g | PET /g |
|-------------|----------|--------|
| PET         | 0        | 100    |
| PET/PPSFR1  | 0.138    | 99     |
| PET/PPSFR3  | 0.414    | 97     |
| PET/PPSFR5  | 0.691    | 95     |
| PET/PPSFR8  | 1.105    | 92     |

2.4. Measurements
Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 380 FTIR spectrophotometer with KBr pellets. Spectra in an optical range of 400-4000 cm⁻¹ were obtained by averaging 32 scan at a resolution 4 cm⁻¹.

Nuclear magnetic resonance (¹H NMR and ³¹P NMR) spectra of the synthesized PPSFR were obtained on an Aglient 400-MR. Samples were analyzed in deuterated DMSO with tetramethylsilane (TMS) as an internal standard.

The thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/DSC1 apparatus under nitrogen or air atmosphere (50 mL/min) at a heating rate of 10 °C/min from 100 °C to 700 °C.

The LOI values were measured on an HC22 apparatus equipped with an Oxygen Analyzer, according to ASTM-D2863 standard and dimensions of bars of 130 mm × 6.5 mm × 4.0 mm. The vertical burning tests (UL-94) were carried
out on a CZF-1 apparatus according to ASTMD635 testing procedure, with sheet dimensions of 130 mm × 13 mm × 4 mm.

Thermogravimetric analysis/infrared spectroscopy (TGA-FTIR) of the samples was performed using the NETZSCH TG 209 F1 thermogravimetric analyzer that was interfaced to the BRUKER VERTEX FTIR. About 10 mg samples were put in an alumina crucible and heated from 100 to 700 °C at a heating rate of 10 °C/min.

Py-GC/MS analyses were made on a system combined with an SHIMADZU QP 2010 plus GC/MS, and CDS 5150 Pyrolyzer.

Morphological studies on char residues were performed using FEI Nova Nano SEM450 scanning electron microscopy at an acceleration voltage of 10 kV.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab Mark II spectroscopy (VG Scientific Ltd., UK) by using Al Kα excitation radiation (hν=1361.6 eV).

3. Results and discussion

3.1. Chemical structure of PPSFR

The FTIR spectrum of PPSFR is shown in Fig. 1. Main absorption bands and corresponding structure are 3053 cm⁻¹(Ar-H), 1614 cm⁻¹, 1590 cm⁻¹, 750~690 cm⁻¹ (benzene skeleton absorption), 1176 cm⁻¹ (P=O), 642 cm⁻¹ (P=S), 921 cm⁻¹ (P-O-C(Ar)), and 1468 cm⁻¹ (P-Ar) [11,14]. Furthermore, the -OH stretching vibration absorption peak of DPO-HQ at 3140 cm⁻¹ disappears almost completely [13], indicating the thorough polycondensation and large degree of polymerization of PPSFR.

The ¹H NMR and ³¹P NMR of PPSFR are shown in Fig. 2. ¹H NMR mainly has an absorption peak of proton on the benzene ring. The absorption peaks of -OH proton on DPO-HQ at δ=9.73 ppm and δ=9.06 ppm disappear. Two absorption peaks were observed on ³¹P NMR at δ=25.08 ppm and δ=-19.20 ppm, which are the absorption peaks of P atoms on P=S and P=O. Meanwhile, the absorption peak of P atom on DPO-HQ at δ=27.72 ppm disappears. This finding reflects that the raw material DPO-HQ completely participated into the reaction and produced the target product PPSFR.

3.2. Flame retardancy

The influence of flame retardant on PET flame retardation was analyzed by UL-94 and LOI tests. Detailed data are listed in Table 2. As can be seen from Table 2, modified PET passed V-0 level at 5% dose of PPSFR, and the corresponding LOI reached 34%. By observing the test process, the use of PPSFR can effectively inhibit smoke during the combustion. And the combustion of flame-retardant PET was accompanied with certain molten drops which could take away the heat of combustion.
3.3. Thermal Properties of flame retardant PET

The TGA of PPSFR, PET and PET/PPSFR was performed in nitrogen and air to investigate the thermostability of PPSFR and PET/PPSFR (Fig. 3). Detailed data are listed in Table 3. The initial decomposition temperature $T_{5\%}$ (temperature at 5% weight loss) of PPSFR was 298 °C, which was higher than the processing temperature of most polymers. The char yield of PPSFR at 700 °C was 11.64%. PET did not degrade until 370 °C, indicated the high thermostability of the synthesized flame retardant. This condition is applicable to the flame retardation of PET. We suppose no chemical effect occurred between flame retardant and PET. Then based on the linear calculation [15] to TGA data of all the components of PET, the theoretical TGA value ($M$) could be gained by:

$$M = A \times \text{wt\% of FR} + B \times (100-\text{wt\% of FR})$$  \hspace{1cm} (1)

Where A and B are the TGA data of flame retardant and PET respectively. The calculated results are shown in Table 3. Pure PET, PPSFR, and PET/PPSFR are further degraded in nitrogen. $T_{5\%}$ and the maximum decomposition temperature ($T_{\text{max}}$) of PET are 401 °C and 434 °C, respectively. The char residues at 600 °C is 11.64%. With the increase of PPSFR dose, $T_{5\%}$ and $T_{\text{max}}$ remain basically same, while as the char residues increased greatly and exceeded theoretical value. It fully implied the synergistic charring effect between PPSFR and PET during the degradation process. Moreover, the growth rate of char residues in PET increased sharply with the increase of PPSFR dose.

It is worth mentioning that the char residues of modified PET with 8% PPSFR content was 49.85% higher than the theoretical amount.

Different from the degradation behaviors in nitrogen, pure PET and PET/PPSFR were degraded in two steps in air. The first step was the oxidative degradation of polymers, and the second step was the oxidative degradation of char layer formed in the first step. The $T_{5\%}$ of pure PET was 374 °C, and no
char residues was found at 600 °C. With the increasing of PPSFR content, the $T_{5\%}$ increased significantly, but the $T_{\text{max}1}$, $T_{\text{max}2}$ and char residues at 600 °C had little fluctuation. This finding showed that air could delay the early PET degradation caused by PPSFR and improve the initial thermostability of flame-retardant PET system, but it failed in improving the thermostability of PET dramatically in high temperature. This condition would be due to the oxygen in air which could facilitate the degradation of PET. Thereby, the weight loss caused by thermal decomposition of PET in air was higher than that in nitrogen under the same temperature. Moreover, air flow in the test was set to 50 mL/min, which is different from that in actual combustion. In fact, the char yield would be higher in actual combustion than that in the test. Because the continuous air flow provided in the test was conducive to the volatilization of emergent gas and accelerates the oxidization of samples [16].

3.4. TGA-FTIR analysis

To analyze the effects of flame retardant on the thermal degradation of PET, the changes of emergent gas were detected by TGA-FTIR. The composition of the emergent gas could be determined from infrared spectra at different periods. The results of TGA-FTIR are shown in Fig. 4.

According to the tests results, pure PET and flame-retardant PET had basically same degradation products, mainly including CO$_2$ (2373-2354 cm$^{-1}$, 780-600 cm$^{-1}$), CO (2215-2149 cm$^{-1}$), water (4000-3400 cm$^{-1}$, 1300-1800 cm$^{-1}$), and benzene-ring compounds (1514 cm$^{-1}$, benzene ring skeleton absorption) [17,18]. Based on the comparison between PET and PET/PPSFR8, PET began to produce the absorption peaks of H$_2$O and CO$_2$ at 400 °C (30 min). The absorption peak intensity reached maximum at 440 °C. The emergent gas released by PET/PPSFR8 were mainly produced within 28-40 min. The absorption peaks of H$_2$O and CO$_2$ were not observed until 380 °C, and the peak intensity reached maximum at 440 °C. The content of emergent gas reduced sharply at high-temperature region and no new gas was produced above 520 °C. These results were in accordance with the TGA analysis.

The Gram-Schmidt (GS) curves of pure PET, PET/PPSFR8, and functional group profiles (FGP) are shown in Fig. 5. The GS curve is a quantitative measurement of total infrared absorption and is expressed by the variation curve of emergent gas concentration with time or temperature. FGP is the variation curve of infrared absorption intensity of several regions on every spectrum with time or temperature [19].

![FTIR spectra of products for PET (A) and PET/PPSFR8 (B) at different temperatures.](image)

Fig. 4. FTIR spectra of products for PET (A) and PET/PPSFR8 (B) at different temperatures.

Although pure PET and PET/PPSFR8 had the similar degradation process, the PET/PPSFR8 had a lower degradation temperature. And the emergent gas concentration from pure PET was higher than that from flame-retardant PET, especially aromatic compounds. Consequently, the addition of PPSFR can reduce the release of combustible gas. In condition, the infrared absorption intensity of H$_2$O and CO$_2$ for flame-retardant PET was almost the same as that for pure PET. The emergent inert gas and vapor will not only dilute oxygen in air and decompose high polymer into flammable gaseous products but also carry away abundant heat to lower the temperature on material surface and terminate the combustion. These results realize the gas-phase flame retardation of PPSFR.
3.5. PY/GC-MS analysis

The combustion of polymers is closely related with their thermal decomposition. Flammable volatile matters caused by pyrolysis are requirements for maintaining combustion. Therefore, the pyrolysis chromatography of polymers has important significance to research on flame retardation. Figure 6 is the chromatogram of pyrolysis products of pure PET and PET/PPSFR8 in air at 15 s under 800 °C, and the major pyrolysis products and relative contents are shown in Table 4. The high-temperature pyrolysis products of PET/PPSFR8 were similar with those of pure PET in term of composition, indicating that PPSFR would not change the high-temperature pyrolysis mechanism of PET. However, the pyrolysis product concentration changes dramatically after PPSFR was added.

![Fig. 5. Curves of Gram-Schmidt (GS) and functional group profile (FGP) for PET and PET/PPSFR8.](image)

![Fig. 6. Pyrograms of PET and PET/PPSFR8 at 800 °C.](image)

| No. | Pyrolysis Products | PET Total area /% | PET/PPSFR8 Total area /% |
|-----|--------------------|-------------------|--------------------------|
| 1   | CO₂                | 1.52              | 1.41                     |
| 2   | CH₃CHO             | 6.25              | 1.26                     |
| 3   | CH₂(CH₂)₄CH₂       | 1.78              | 0                        |
| 4   | C₆H₆               | 5.55              | 7.85                     |
| 5   | C₆H₅CH₃            | 7.00              | 2.03                     |
| 6   | C₆H₅C₂H₅           | 3.87              | 0.92                     |
| 7   | C₆H₅C₂H₅           | 6.82              | 2.14                     |
| 8   | C₆H₅CHO            | 1.95              | 5.12                     |
| 9   | CH₂CH₅C₆H₄CHO      | 3.73              | 1.25                     |
| 10  | C₆H₄COCH₃          | 16.56             | 6.13                     |
| 11  | C₆H₅CO₂H           | 10.64             | 7.19                     |
| 12  | C₆H₅C₄H₄           | 3.16              | 1.71                     |
| 13  | C₆H₅COOH           | 4.30              | 39.57                    |
| 14  | C₆H₅C₆H₅           | 7.79              | 2.49                     |
| 15  | C₆H₅CH₂C₂H₅        | 1.36              | 0.49                     |
| 16  | CH₃C₂H₅C₂H₅        | 1.44              | 3.70                     |
| 17  | CH₃COC₄H₄COOC₃H₃   | 2.69              | 8.43                     |

The contents of low molecular pyrolysis products (e.g. acetaldehyde, methylbenzene, and ethylbenzene) decrease to different extents. The contents of many macromolecular products increase to different extents. For example, the content of benzoic acid increases significantly from 4.30% in pure PET to 39.57% in PET/PPSFR8, which reflected that PPSFR could inhibit the decarboxylation of benzoic acid effectively. The contents of 4-methyl diphenyl and vinyl...
terephthalate increased from 1.44% and 2.69% in pure PET to 3.70% and 8.43% in PET/PPSFR8. Therefore, the involvement of PPSFR could decrease the contents of the deep pyrolysis products of PET to different extents. But it could increase the contents of early pyrolysis products. In other words, PPSFR inhibits the deep pyrolysis of PET [20].

In addition to these mentioned on Table 4, thiophenol and diphenyl sulfide also produced during the pyrolysis of PET. The generation of sulfated productions due to the low bond energy of P=S bond. So both P and S element can produce a small molecule component or free radical capable which can trap free radicals. It is important to restrain the reaction in gaseous phase.

3.6. XPS analysis

XPS can reflect the microscopic variation of binding energy among different elements in flame-retardant PET samples, which is greatly helpful to the analysis of flame-retardant mechanism. The XPS of flame-retardant PET under different temperatures is shown in Fig. 7 and the corresponding atom concentrations are listed in Table 5.

It can be seen from Fig. 7 that due to the low content of PPSFR, C 1s was mainly the spectral peak of PET. The -COO- peak decreased with the increase of temperature and disappeared at 500 °C. The peak at 285 eV was contributed to -C-C-, and the peak intensity increased gradually with temperature rising. It indicated that the original structure was destroyed during the PET degradation process and the aroma char layer structure was generated. This finding was confirmed by the relative content changes of carbon and oxygen in Table 5. There are two kinds of P atoms with different chemical environments in PPSFR. According to previous TGA analysis, PET decomposed in large scale from 350-500 °C, accompanied with oxidation of P=S. From Fig. 7, we can see that S content is very small at 450 °C and cannot be detected at 500 °C. This result also confirmed that S could be decomposed and volatilized under low temperature. After 500 °C, phosphorus content of samples increased significantly, indicating the P gathering on char layer surface after the thermal decomposition of PET. Furthermore, the binding energy of P 2p at 500 °C moved upward to 134.6 eV, which implied the formation of phosphoric acid or metaphosphoric acid in the char layer [21].
Table 5. Atomic concentrations of PET/PPSFR8 at different temperatures.

| $T/\degree C$ | C 1s% | O 1s% | P 2p% | S 2s% | P/S | P/C | O/C |
|--------------|-------|-------|-------|-------|-----|-----|-----|
| RT           | 68.90 | 29.92 | 0.83  | 0.35  | 2.37| 0.012| 0.43|
| 400          | 68.66 | 31.34 | 1.06  | 0.39  | 2.72| 0.015| 0.46|
| 450          | 79.73 | 18.51 | 1.72  | 0.04  | 43  | 0.022| 0.23|
| 500          | 86.35 | 11.59 | 2.06  | 0    | -   | 0.024| 0.13|

To sum up, flame retardant was easy to be decomposed in early heating period of PET, thus causing P gathering on char layer surface, accelerating decomposition of PET into carbon and forming condensed phase flame retardation.

3.7. SEM/EDS analysis

The surface morphology and energy spectral analysis of burnt pure PET and flame-retardant PET are shown in Fig. 8. PET had thin and fragile char layers which were full of holes. After PPSFR was added, the area proportion and diameter of holes on the material surface decline significantly. Meanwhile, the char layer structure was thickened. According to energy spectral analysis, the char layer was rich in oxygen, phosphorus, and carbon. Acids (e.g. phosphoric acid and polyphosphoric acid), which are produced by thermal decomposition of flame retardant, covered on material surface and form a layer of non-volatile protective film [21,22]. This result agreed with that of the XPS analysis.

4. Conclusions

The sulfur-containing polyphosphonate, PPSFR was synthesized. PET/PPSFR samples with different P contents are prepared. According to LOI and vertical combustion test results, PPSFR has outstanding flame retardation. PET with 5% dose of PPSFR can pass UL-94 V-0 rate, and the corresponding LOT can reach as high as 34%. PSSFR can delay PET degradation, improve the thermostability, and has the synergetic carbon formation with PET. The involvement of PPSFR does not change the degradation mechanism of PET but inhibits the deep pyrolysis of PET significantly. Inert gas and vapor produced by the thermal decomposition of PPSFR can dilute oxygen in air and flammable gaseous produced from polymer decomposition. The mass phosphoric acid compounds produced by the thermal decomposition of PPSFR can facilitate the formation of aromatic carbon layer structure and gather on the carbon layer, making PPSFR realize the synergistic flame retardation between gas phase and condensed phase.

References

1. L. Chen, X.-C. Bian, R. Yang, and Y.-Z. Wang, Compos. Sci. Technol., 72 (2012) 649.
2. G. Beyer, Wire Cable Technol. Int., 32 (2004) 60.
3. M.-J. Niu, X.-F. Li, J.-Z. Chen, and S.-B. Xu, Polym. Mater. Sci. Eng., 18 (2002) 202.
4. K. S. Annakutty and K. Kishore, Polymer, 29 (1988) 756.
5. P. Kannan, Gangadhara, and K. Kishore, Polymer, 38 (1997) 4349.
6. S.-J. Ma, J. Liao Yang Petrochemical College, 16 (2000) 26.
7. B.-H. Li, Y.-X. Qu, and F. Xin, J. Beijing Inst. Technol., 16 (2007) 340.
8. X.-D. Tang, X.-T. Chen, Y.-Z. Wang, K.-K. Yang, B. Wang, and D.-C. Wu, Acta. Polym. Sin., 3 (1998) 372.
9. A. Schafer, S. Seibold, W. Lohstroh, O. Walter, and M. Doring, J. Appl. Polym. Sci., 105 (2007) 685.
10. M. Ciesielski, A. Schafer, and M. Doring, Polym. Adv. Technol., 19 (2008) 507.
11. Y. Chang, Y. Wang, D. Ban, B. Yang, and G. Zhao,
12. X. J. Tian, Z. W. Wang, Q. Yu, and J. Gao, *Polym. Mater. Sci. Eng.*, **30** (2014) 31.
13. X. J. Tian, Z. W. Wang, Q. Yu, Q. Y. Wu, and J. Gao, *Chem. Res. Chin. Univ.*, **30** (2014) 868.
14. W. Liu, L. Chen, and Y. Z. Wang, *Polym. Degrad. Stabil.*, **97** (2012) 2487.
15. D. Hoang and J. Kim, *Macromol. Res.*, **21** (2013) 184.
16. Y. Z. Wang, C. Y. Zheng, and D. C. Wu, *Chem. Res. Chin. Univ.*, **4** (1996) 339.
17. H.-M. Zhu, J.-H. Yan, X.-G. Jiang, Y.-E. Lai, and K.-F. Cen, *Hazard Mater.*, **153** (2008) 670.
18. K. Wu, L. Song, Y. Hu, H.-D. Lu, B.-K. Kandola, and E. Kandare, *Prog. Org. Coat.*, **65** (2009) 490.
19. Y. W. Tang, *Donghua University Press*, (2009) pp 12-22.
20. Y. Deng, Y.-Z. Wang, D.-M. Ban, X.-H. Liu, and Q. Zhou, *J. Anal. Appl. Pyrolysis*, **76** (2006) 198.
21. Y.-Y. Chai and J.-X. Liu, *Chemical Industry Press*, (1993) pp 46-48.
22. S.-M. Nomakin and G.-E. Zaikov, *Polym. Degrad. Stabil.*, **51** (1996) 343.