Synthesis and Degradation Properties of Heat-resistant Polymer based on Cyclotriphosphazene

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Synthesis and Degradation Properties of Heat-resistant Polymer based on Cyclotriphosphazene

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Abstracts. The thermal performance and the decomposition mechanism of the cyclotriphosphazene based homopolymer were investigated by means of TGA, DTG and integrated TG/FTIR analysis. The thermal decomposition of the homopolymer between 100 and 800 °C includes two stages; the initial degradation temperature of the first stage is about 377 °C with the 292 kJ/mol of average decomposition activation energy. Accordingly, the possible thermal decomposition mechanism of the homopolymer was proposed. In addition, the LOI (34.3 %) calculated from the amount of char remaining indicates the homopolymer is self-extinguishing in air.

1. Introduction
The phosphazene based polymers have received a great interest thanks to their superior properties, such as superior thermal resistances, excellent biodegradability, chemical stability and high refractive index. Polyphosphazene materials have broad application fields and development space due to their chemical structure designability and material function diversity [1-3].

Several optical resins were prepared by copolymerizing cyclotriphosphazenes and olefine monomers in our previous research [4-6]. In this paper, the thermal and degradation performance of the homopolymer based on cyclotriphosphazene were investigated and its thermal decomposition mechanism was discussed. The experiment data show clear evidence for the heat-resistant and halogen-free flame retardant of cyclotriphosphazene units.

2. Experimental

2.1. Polymer Synthesis
The homopolymer based on cyclotriphosphazenes was synthesized in this laboratory according to the literature [4], as illustrated in Scheme 1.
2.2. Analytical Methods
The thermogravimetry analysis was performed on a Netzsch thermal analyzer at the heating rates of 5, 8, 10, 15, 20, 30 and 40 °C/min from ambient temperature to 900 °C under the nitrogen flow. A combination of Simultaneous DSC-TGA Instrument and Nicolet IR-380 infrared spectrometer was used for decomposition mechanism analysis. The homopolymer sample was heated from 40 °C to 900 °C at 10 °C/min heating rate under nitrogen flow, while the decomposed gas product was characterized online by infrared spectrometer.

3. Results
3.1 Thermal Decomposition Behavior of the Homopolymer
Fig. 1a and 1b show the TGA and DTG curves of the thermal decomposition of the homopolymer composed of cyclotriphosphazenes at different heating rate in N2, and the corresponding experimental data are listed in Table 1. The initial degradation temperature of the homopolymer \( t_0 \) is all above 326 °C in different heating rate, which is much higher than that of ordinary thermoplastic optical resins such as polystyrene and polymethylmethacrylate [5-6].

Two inflection points can be found from the TGA curves, and the corresponding DTG curves have two minima, which indicates that the thermal decomposition of the homopolymer between 100 °C and 800 °C includes a two-stage reaction. For example, when the heating rate is 10 °C/min, the homopolymer undergoes the first stage thermal degradation between 300 °C and 400 °C, reaching the maximum degradation rate at 341.6 °C, the weight loss at this stage is 40.9 %. The second stage of thermal degradation is between 400 °C and 800 °C, reaching the maximum degradation rate at 451 °C, the weight loss at this stage is 9.83 %. The average activation energy of decomposition for the first stage is 292 kJ/mol calculated by the Flynn-Wall-Ozawa method.

According to the semi-empirical formula [4], the limiting oxygen index (LOI) of the homopolymer could be calculated from the char yield at 850 °C. The char yield of the homopolymer at 850 °C is 40.1 % (Table 1), accordingly the calculated LOI value is 34.3%, which means the homopolymer may be self-extinguishing in air atmosphere.
Figure 1. a) Dynamic TGA and b) DTG curves for the homopolymer at different heating rates in N₂

Table 1. Parameters of TG and DTG curves of cyclotriphosphazene homopolymer in N₂

| β/°C·min⁻¹ | t₀/°C | tₘₐₓ/°C | w/% |
|------------|-------|---------|-----|
| 5          | 326.1 | 333.0   | 40.4|
| 8          | 333.0 | 339.5   | 36.1|
| 10         | 336.6 | 341.6   | 40.1|
| 15         | 340.2 | 345.3   | 40.2|
| 20         | 344.4 | 348.8   | 39.4|
| 30         | 348.7 | 352.1   | 36.5|
| 40         | 349.9 | 356.3   | 36.4|

β: Heating rate; t₀: Initial degradation temperature; w: Char yield at 850 °C

3.2. Thermal Decomposition Products of the Homopolymer

Two infrared spectra shown in Fig. 2 indicate the volatile products of the two-step thermal decomposition of the homopolymer in N₂, respectively. In the infrared spectrum of the volatile products of step I (29.59-30.40 min), strong absorption peaks at 669 and 2358 cm⁻¹ come from carbon dioxide (CO₂), medium strong absorption peaks at 3646, 1608, 1508, 1267 cm⁻¹ come from phenol, weak absorption peaks at 3580 and 1758 cm⁻¹ come from benzoic acid, which indicates the main volatile products are CO₂, phenol and a little of benzoic acid. In the infrared spectrum of the step II (41.53 min), there are only a few weak absorption peaks, indicating little phenol and little water are released.
3.3. Thermal Decomposition Mechanism of the Homopolymer

Based on the results from TGA, DTG and infrared spectra analysis of the volatile gas, the decomposition model of the homopolymer in N₂ is proposed, as shown in scheme 2. In the first stage of thermal degradation of the homopolymer, the C-O and P-O bonds of the cyclic triphosphazene unit’s break, releasing a large amount of CO₂, phenol and little benzoic acid, and simultaneously forming phosphate. In the second stage, the C-C bonds are broken, a small amount of phenol and water are released, carbonaceous char and some phosphorus compounds are left.

Scheme 2. Possible mechanism of the two-stage thermal decomposition of the homopolymer in N₂

4. Conclusions

A heat-resistant homopolymer based on cyclotriphosphazene was prepared by free radical polymerization. As compared with ordinary thermoplastic optical resins, the homopolymer exhibits much higher thermal stability due to the crosslinked structures. The LOI value (34.3 %) calculated by char yield according to the semi-empirical method indicates the homopolymer is self-extinguishing in air.

The decomposition behavior of the homopolymer includes two stages between 100 °C and 800 °C in N₂. In the first stage, the breaking of the C-O and P-O bonds of the cyclic triphosphazene units
releases CO₂ and phenol, in the second stage the breaking of C-C bonds results in the mass loss.

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