



Synthesis and Thermal Performance of Poly(cyclotriphosphazene-acetylferrocene) Derivative

ZHENGPING ZHAO* and FENGYING YU

Zhijiang College of Zhejiang University of Technology, Hangzhou 310024, P.R. China

Corresponding author: E-mail: sjzhao1990@163.com

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Amino nucleophilic reagents were prepared by using acetylferrocene and diamines and then the iron-phosphazene derivative was first synthesized by the nucleophilic substitution reaction of hexachlorocyclotriphosphazene and the amino nucleophilic reagent. FT-IR curve proved that the aim product was synthesized and the chlorine atom of iron-phosphazene derivative did not completely replaced. The thermal performance of the iron-phosphazene derivative was examined by TGA. This suggests that the iron-phosphazene derivative began to degrade at 200 °C and still has 25 % residue at 700 °C. The residues morphology of the iron-phosphazene derivative was also examined. The surface of residues was smooth, fibrous arrangement and has a certain orientation structure. EDS confirmed that the main components of the high-temperature calcined residues were C, P and Fe.

Keywords: Hexachlorocyclotriphosphazene, Ferrocene, Iron-phosphazene derivative, Thermal performance.

INTRODUCTION

As energy saving and efficiency requirements, the working temperature of power machinery become more and more high. Hence high temperature lubricating problem of the supporting components and transmission components also become more and more outstanding. Solid lubrication plays an important role in solving high temperature lubricating problem and the high temperature solid lubricant is the bottleneck of the high-temperature solid lubrication technology¹⁻³. Scientists proposed a high temperature solid lubricant coating which was formed at friction surface by the deposition or reaction of organo-metallic compounds^{4,5}.

Polyphosphazenes as an organic-inorganic hybrid polymer is a class of novel macromolecules containing alternate phosphorus-nitrogen single and double bonds with two changing organic side groups to be prepared new specific functions materials. Because the phosphorus-nitrogen bonds are extremely flexible due to the low torsional energy and a large variety of side groups, polyphosphazenes can be made with a wide range of chemical and physical properties, like excellent heat resistance, cold-resistant, water-tolerant, solvent resistance, radicalization resistance and flame retardant performances in many areas⁶⁻¹¹.

In this work, on the basis of the synthesis of hexachlorocyclotriphosphazene and acetylferrocene, a new iron-phosphazene derivative was first synthesized by introducing ferrocene groups to cyclotriphosphazene. It will be used as the addition-type monomers selected on the basis of the tribopoly-

merization concept in the further vapor phase lubrication study. Its physical chemistry properties including structures, thermal properties and degradation behavior are studied.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (HCCP) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (m.p. = 112.5-113 °C). Phenol, THF, ferrocene, acetic anhydride, H₃PO₄ and ethylene diamine were obtained from Sinopharm Chemical reagent Co., Ltd (Shanghai China). All chemicals and solvents were provided commercially by Sinopharm Chemical Regents Co. Ltd (China) and used without further purification unless other-wise noted. All glassware was dried in an oven under vacuum before use.

Synthesis of acetylferrocene: Ferrocene (37.2 g, 0.2 mol), acetic anhydride (125 mL) and phosphoric acid (20 mL) were added into a 500 mL round bottom flask with a drying tube filled calcium chloride in the ultrasonic oscillator. Start ultrasonic oscillators with a given time and temperature, using thin layer chromatography (TLC) to track reaction process. Completed the reaction, the mixture was poured into a beaker containing 250 g crushed ice, stirred and cooled slowly adding solid sodium bicarbonate solution to control solution pH value at 6-7. After 0.5 h ice-cooling, negative-pressure filtration and washed with deionized water twice. The solid was dried under vacuum at 50 °C for 24 h to get brown crude product and recrystallized with petroleum ether to yield acetyl ferrocene directly as an orange powder.

Synthesis of poly(cyclotriphosphazene-ferrocene) derivative: Acetyl ferrocene (22.8 g, 0.02 mol), ethylenediamine (10 mL) and 6-8 drops of glacial acetic acid were dissolved in 100 mL ethanol in a three-neck flask equipped with a refluxing condenser under stirring and nitrogen atmosphere, heating reflux 24 h. After reaction, most of the solvent was removed by vacuum distillation, cooled in a refrigerator, washed with ethanol and ether several times repeatedly, over silica gel column chromatography and vacuum dried to obtain the products ferrocene schiff bases.

Ferrocene Schiff bases (16.2 g, 0.06) and triethylamine (10 mL) were dissolved in 80 mL tetrahydrofuran in a three-neck flask equipped with a refluxing condenser under stirring and nitrogen atmosphere. To this, a solution of tetrahydrofuran (50 mL) dissolving hexachlorocyclotriphosphazene (3.48 g, 0.01 mol, synthesized as described in the literature⁹) was added dropwise, heating reflux 24 h. After reaction, cooling filtered, washed with acetone and water several times repeatedly and dried under vacuum to obtain the objective products.

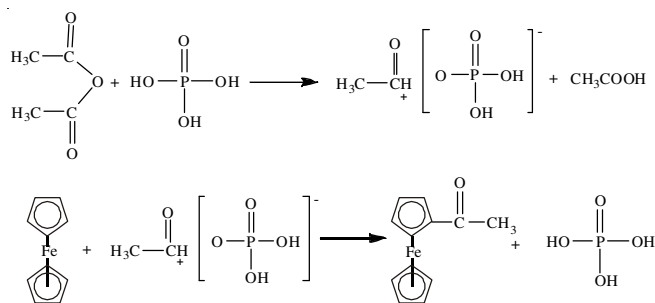
Measurements: FT-IR spectra of all samples were recorded using polymer granule on a Perkin-Elmer Wellesley MA spectrophotometer. The ¹H NMR spectra were recorded on a Varian DRX 400 NMR spectrometer with the operating frequency at 400 MHz using CDCl₃ or DMSO as a solvent, using TMS as inner reference and H₃PO₄ (85 %) as external reference. Elemental analysis was carried out using a Heraeus CHN-O rapid elemental analyzer with acetanilide as a standard. Thermogravimetric analysis (TGA) was performed on a TGA 7 instrument (PerkinElmer) thermal analysis system. Sample weight taken was 2-4 mg. The solid residue of the samples degraded to various extents was also prepared using the TGA instrument under nitrogen atmosphere. The microstructures of solid residues were recorded using a Cambridge S250MK3 scanning electron microscope (U.K.). X-ray photoelectron spectroscopy measurements were performed on a Bruker AXS-D8 Avance X-ray diffractometer with a copper target (40 kV, 15 mA).

RESULTS AND DISCUSSION

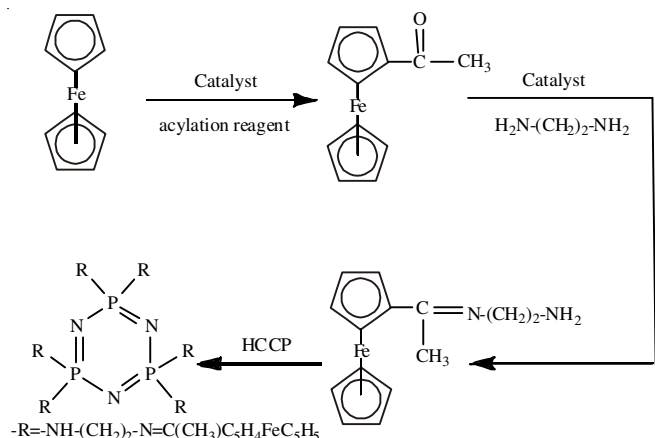
Synthesis mechanism and characterization of acetylferrocene and poly(cyclotriphosphazene-ferrocene) derivative: Acetyl ferrocene synthesis accords with Friedel-Crafts reaction. Under the catalysis of phosphoric acid or anhydrous aluminum chloride, acetic anhydride generated acetyl positive ions first and then electrophilic substitute with the ferrocene on cyclopentadienyl anion. The reaction mechanisms are depicted in **Scheme-I**.

Using acyl ferrocene and diamines to synthesize a nucleophile containing terminal amino groups and then nucleophilic substitution reacted with hexachlorocyclotriphosphazene to obtain poly(cyclotriphosphazene-ferrocene) derivative. The reaction mechanisms are depicted in **Scheme-II**.

The chemical structure of the acetylferrocene was confirmed by FT-IR as shown in Fig. 1. The absorption peak at 1656 cm⁻¹ corresponds to carbonyl group which improved that acylation reaction occurred on cyclopentadienyl rings. There are two symmetrical peaks at 1004 and 1108 cm⁻¹ indicated that only one hydrogen atom on the cyclopentadienyl ring is substi-



Scheme-I: Reaction mechanism of acetylferrocene



Scheme-II: Reaction mechanism of poly(cyclotriphosphazene-ferrocene) derivative

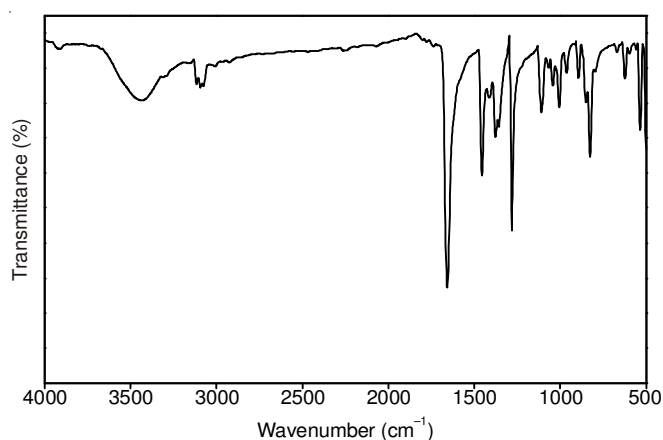
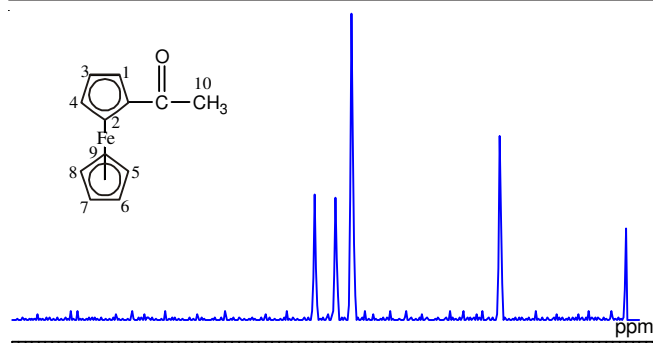


Fig. 1. FT-IR spectrum of acetylferrocene

tuted. A broad band at 3434 cm⁻¹ is due to C-H vibrational absorption in cyclopentadiene ring. 825.53 and 1109.04 cm⁻¹ are corresponds to the C-C groups.

The chemical structure of the acetylferrocene was also confirmed by ¹H NMR as shown in Fig. 2. The chemical shift corresponding to the shigeru is noticeable found at 4.19 ppm on C5-C9. Due to the electronic absorption effect of carbonyl, chemical potential along in the low field. The peak at 4.36 ppm corresponds to the H proton of C3 and C4, 4.67 ppm corresponds to C1 and C2, 1.91 ppm corresponds to C10.

The reaction of acetyl ferrocene with diamines can produce Schiff base ferrocene, which is a reversible reaction. Removal of the water formed in the reaction could facilitate the reaction. The FTIR spectrum of the product of acetyl ferrocene reaction with ethylene diamine is shown in Fig. 3. The figure shows a

Fig. 2. ^1H NMR spectrum of acetylferrocene

characteristic absorption peak due to the carbonyl group at 1656 cm^{-1} disappears, C=N stretching vibration appeared at 1640 cm^{-1} , which indicated that amino and carbonyl condensation generated the imine. Above 3000 cm^{-1} presents broad absorption peak is due to the N-H absorption peak indicating that there is a terminal amino group in the product. 1100 and 1000 cm^{-1} is due to the ferrocene cyclopentadienyl ring and C-H bending vibration indicating that the product is mono-substituted ferrocene iron derivative. 815 cm^{-1} is due to the vertical Mau ring disk ring C-H bending vibration absorption peak. 480 cm^{-1} is due to the asymmetric stretching vibration absorption peak of ferrocene.

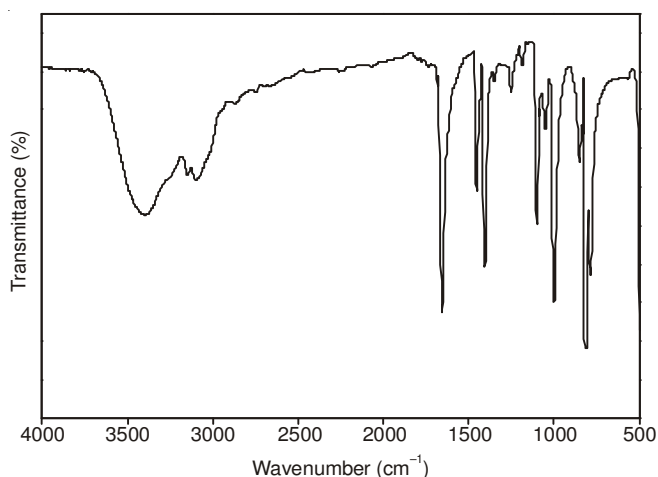


Fig. 3. FT-IR spectrum of Schiff base ferrocene

The chemical structure of the poly(cyclotriphosphazene-ferrocene) derivative was confirmed by FT-IR as shown in Fig. 4. The band at 1478 and 1586 cm^{-1} corresponds to the benzene ring, 1260 and 1200 cm^{-1} are assigned to P=N groups, 940 cm^{-1} is due to P-O-Ar groups, indicating that the presence of the cyclotriphosphazene structure. 3425 cm^{-1} is due to the N-H stretching vibration absorption peak. 466 , 806 and 1033 cm^{-1} are due to the characteristic absorption peak of cyclopentadienyl ring. The results demonstrate that the poly(cyclotriphosphazene-ferrocene) derivative has the expected chemical structure.

Thermal characterization of poly(cyclotriphosphazene-ferrocene) derivative: Thermal properties of the poly(cyclotriphosphazene-ferrocene) derivative was examined by TGA at $20\text{ }^\circ\text{C}/\text{min}$ up to $700\text{ }^\circ\text{C}$ under nitrogen shown in Fig. 5. The curve showed that the poly(cyclotri-phosphazene-ferrocene)

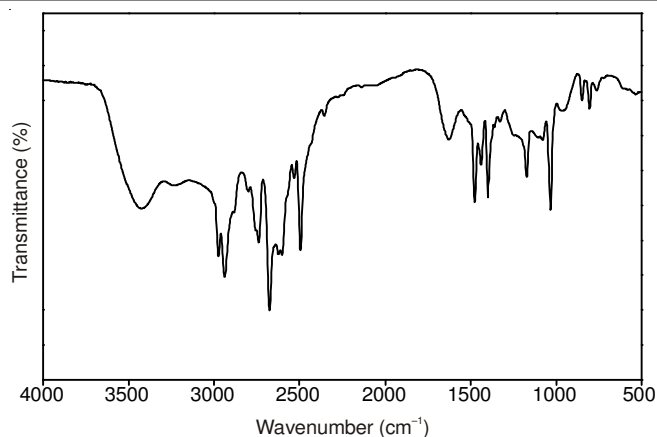


Fig. 4. FT-IR spectrum of poly(cyclotriphosphazene-ferrocene) derivative

derivative has one mainly thermolysis step. The derivative presents an initial degradation temperature at $170\text{ }^\circ\text{C}$ which due to the C=N bond ruptured, a maximum thermal decomposition rate temperature at $250\text{ }^\circ\text{C}$ conformed to the pyrolysis of phosphazene ring and yielding a char residue of 25.35% at $700\text{ }^\circ\text{C}$. The TGA results indicated that the poly(cyclotriphosphazene-ferrocene) derivative has the higher thermal decomposition rate of late and solid residues.

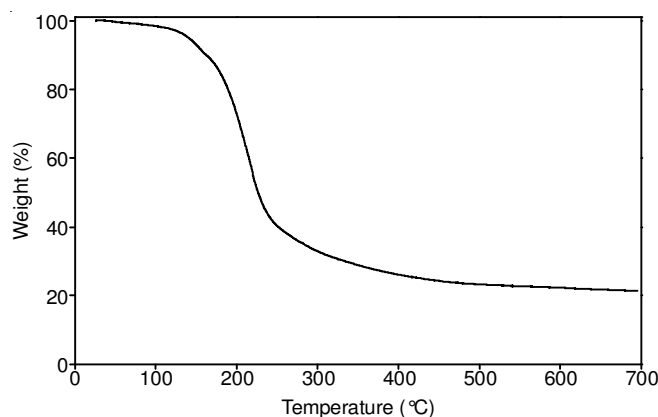


Fig. 5. TGA curves of poly(cyclotriphosphazene-ferrocene) derivative

To further investigate their influence, the residues of the poly(cyclotriphosphazene-ferrocene) derivative obtained from the TGA measurements, from room temperature to $700\text{ }^\circ\text{C}$ with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ in air, were analyzed by SEM. Fig. 6 illustrates the morphology of the pyrolysis residues. It is clear that the surface layer of solid residues has been grumous, for the pyrolysis of phosphazene rings and syneresis of P-O-P took place. It proves that the cyclotriphosphazene rings produce phosphoric acid or metaphosphoric acid during pyrolysis which acts in the condensed phase promoting char formation on the surface. The calcination residue has smooth surface, shows fibrous arrangement and the structure has a certain orientation, which are conducive to disperse and form a dense film deposited on the surface of high temperature friction.

In order to study the component of the solid residues, EDS measurements were performed and the spectrum is illustrated in Fig. 7. From the curve, we can see that N elements characteristic absorption peaks were approached with C element and susceptible to interference with it to affect the

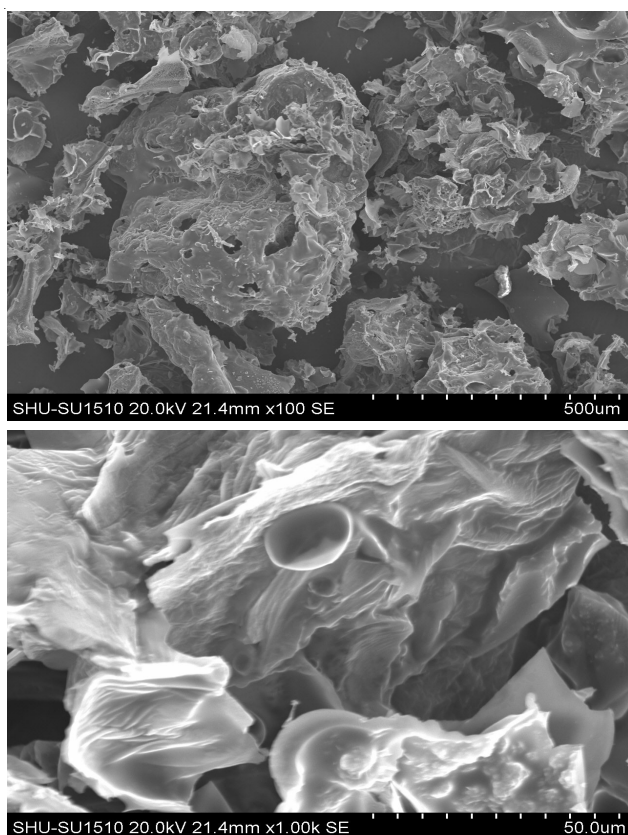


Fig. 6. Morphology of the solid residues of the derivative

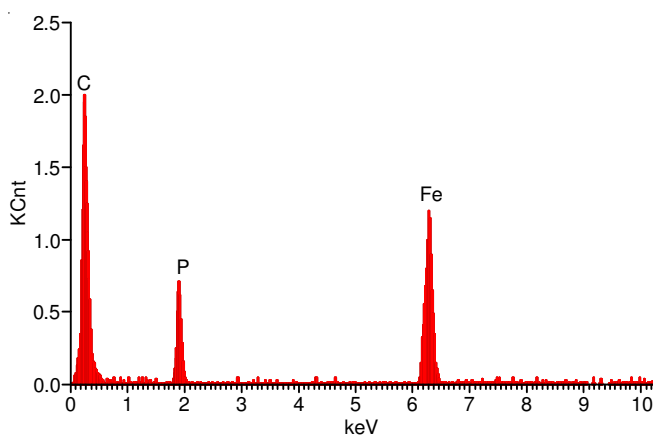


Fig. 7. EDS spectrum of the solid residues of the derivative

measurement results, so the measurement results only show the content of C, P, Fe without N or other weaker peak elements. EDS measurements indicate that the main components of

calcined product residues are C, P and Fe. C mass fraction is 55.5, P is 20.64 and Fe is 23.86 %. C and Fe could be used as high temperature solid lubricant at a certain high temperature friction and lubrication, so that the poly(cyclotriphosphazene-ferrocene) derivative has potential applications in the field of high-temperature lubrication.

Conclusion

Using acetyl ferrocene and diamines to synthesize terminal amino nucleophile and then nucleophilic substitution with hexachlorocyclotriphosphazene to obtain a novel poly(cyclotriphosphazene-ferrocene) derivative. FT-IR spectrum confirmed the existence of phosphazene ring and ferrocene structures, which proved the correct and feasibility of synthetic route. Poly(cyclotriphosphazene-ferrocene) derivative has the initial decomposition temperature of 200 °C and the solid residue rate is 25 % at 700 °C. The cyclotriphosphazene rings produce phosphoric acid or metaphosphoric acid during pyrolysis which acts in the condensed phase promoting char formation on the surface. EDS measurements indicate that the main components of the thermo-decomposition residues are C, P and Fe, which deduce that the poly(cyclotriphosphazene-ferrocene) derivative has potential applications in the field of high-temperature lubrication.

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