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Cyclic polyphosphoesters synthesized by acyclic diene metathesis polymerization and ring closing metathesis

Liang Ding *, Rong Lu, Jing An, Xueqin Zheng, Jun Qiu

School of Materials Engineering, Yancheng Institute of Technology, Yancheng 224051, China

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ABSTRACT

This article describes the synthesis of cyclic polyphosphoester (PPE) by the ring-closing metathesis (RCM) of different difunctional linear PPEs. Linear PPE precursors were prepared through a selective head-to-tail acyclic diene metathesis polymerization of phenyl dienephosphate monomer using 2-hydroxyethyl acrylate as a selective chain terminator, followed by the transformation of the terminal acrylate functional group into a hydroxyl group utilizing a thiol-Michael addition click reaction. These products were then reacted with the corresponding acyl chloride containing a vinyl end group. The subsequent end-to-end intramolecular coupling reaction was performed under highly dilute conditions. The successful transformation of the linear PPE precursors to cyclic PPE was confirmed by NMR spectroscopy and gel permeation chromatography. The thermal and flame retardant properties of linear and cyclic PPEs were investigated, and their thermal degradation and flame retardance were evaluated, as these are important features for future applications.

1. Introduction

Phosphorus-containing polymers are frequently used as flame-retardant materials because a protective char is formed during combustion [1]. Flame retardance has become a highly desirable polymer property [2]. Poly(phosphoester)s (PPEs), potentially degradable and biocompatible polymers with repeating phosphoester bonds along the backbone, are prominent flame retardant materials [3,4]. The chemical versatility of the monomeric phosphate allows for the design of functional materials with tunable and complex architectures and a wide range of properties. Over the past several decades, research efforts to explore new phosphorus-containing polymers have predominantly focused on linear phosphorus polymers with side-chain or main-chain architectures [5–9].

In contrast to linear polymers, cyclic polymers with various chemical structures, compositions, molecular characteristics, and architectures have attracted extensive attention in macromolecular science due to the absence of chain ends [10]. Cyclic polymers usually have a smaller hydrodynamic volume, higher refractive index, reduced viscosity, and higher glass transition temperature. These unique properties have thus led to novel properties or improved performance in many fields such as drug delivery, liquid crystal behavior, and self-assembly [11–13]. Recently, the synthesis of cyclic polymers has experienced rapid development because of advances in synthetic technology [14]. However, few reports are available on cyclic PPEs due to the challenges associated with these more demanding synthetic procedures.

Cyclic polymers can generally be prepared by a variety of strategies. Intramolecular ring closure from linear precursors to cyclic polymers is a popular method for widely available monomers [15–17]. Among the diverse approaches to intramolecular ring closure, ring-closing metathesis (RCM) has been developed as a powerful tool for the synthesis of various carbocyclic and heterocyclic ring systems of different sizes over the last few years, but RCM is infrequently used to synthesize cyclic polymers and has not often been combined with the other synthetic strategies [17–20]. Xie prepared cyclic poly(ε-caprolactone) (PCL) via RCM, ring closing enyne metathesis, and click reactions of different difunctional linear PCLs prepared by ring-opening polymerization of ε-caprolactone and subsequent reaction with acyl chloride containing a vinyl or azido end group [21].

Acyclic diene metathesis (ADMET) polymerization is a quantitative reaction that can tolerate many functional groups, yields only the desired linear polymer, and releases ethylene as a byproduct [22]. Usually, symmetric α,ω-dienes are used to obtain polymers with a defined repeat unit structure. Meier recently introduced the concept of a selective head-to-tail ADMET polymerization using a monomer containing both a terminal double bond and an acrylate. Such monomers polymerize with high cross metathesis selectivity, enabling access to different polymer architectures if a selective and irreversible chain transfer agent (mono- or multi-functional acrylate) is added [23,24]. The chain transfer agent

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* Corresponding author. Tel.: +86 515 88298872.
E-mail address: dl1984911@ycit.edu.cn (L. Ding).

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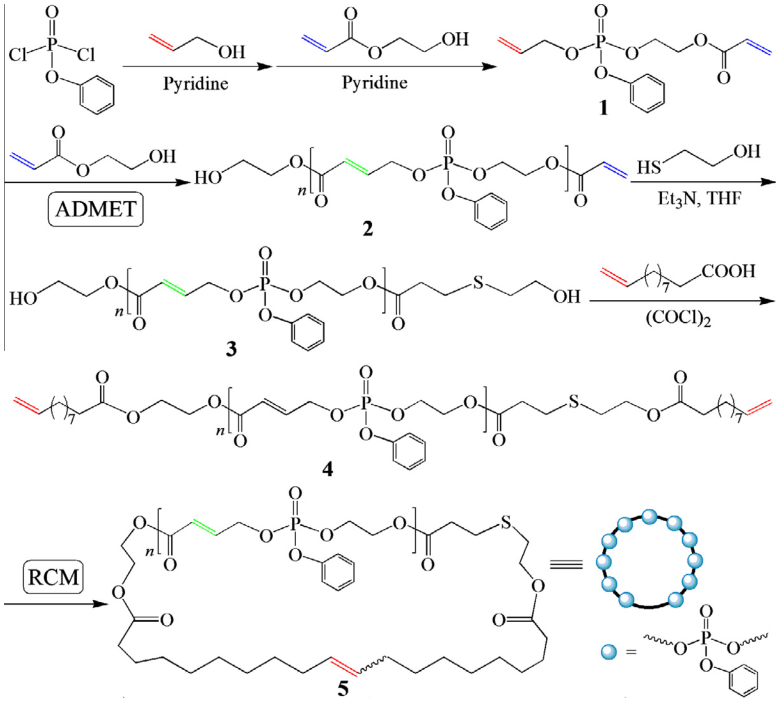

Scheme 1. Schematic representation of the synthesis of cyclic PPEs.

allows control over the molecular weight and direct functionalization of the ADMET polymer by selective reaction with one of the end groups (terminal double bond). Based on this principle, diverse homopolymers and (amphiphilic) diblock copolymers were synthesized, and they can be regarded as the linear precursors for the preparation of cyclic polymers.

Consequently, building on our experience with ADMET polymerization and RCM, we wanted to exploit the cross metathesis selectivity between terminal olefins and acrylates to synthesize defined PPEs architectures. This synthesis was accomplished via ADMET polymerization to obtain the linear precursor in the presence of Grubbs catalyst, followed by RCM to obtain the cyclic PPEs (Scheme 1).

2. Experimental

2.1. Materials

Phenyl dichlorophosphate (99%), 2-hydroxyethyl acrylate (>96%), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda–Grubbs second generation catalyst) (98%), acrylic acid (99%), benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (first generation Grubbs catalyst) (98%), 2-mercaptoethanol (98%), undecylenic acid (99%), allyl alcohol (98%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI·HCl, 99%), and 4-dimethylaminopyridine (DMAP) (98%) were purchased from Energy Chemical and used as received without purification. Solvents were distilled over drying agents under nitrogen prior to use. Triethylamine (Et_3N) and pyridine were freshly distilled and dried.

2.2. Characterization

^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in $CDCl_3$ on a Bruker DPX spectrometer. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) in an instrument equipped with an Isocratic HPLC pump, a refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 μm bead size; 10^3, 10^4, and 10^5 Å pore size). GPC measurements were carried out at 35 °C using THF as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. Matrix-assisted laser desorption ionization time-of-flight mass measurement (MALDI-TOF MS) was performed using a Bruker Biflex III MALDI-TOF mass spectrometer equipped with a 337 nm nitrogen laser producing 3 ns pulses. Mass spectra were recorded in the linear or reflector delayed extraction mode with an accelerating voltage of 19 kV and a delay time of 200 ns. All data were reprocessed using the Bruker XTOF software. The 1,8,9-trihydroxyanthracene (dithranol) matrix was dissolved in $CHCl_3$ (10 mg/mL), and the solution was mixed with the polymer solution (8.0 mg/mL in $CHCl_3$). Then, 1.0 μL of the analyte solution was spotted directly onto the thin layer formed by depositing 1.0 μL of saturated NaI cationizing agent in methanol. Thermogravimetric analysis (TGA) was performed using an SDTA851e/SF/1100 TGA Instrument under N_2 flow at a heating rate of 10 °C/min from room temperature to 800 °C. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer Pyris 1 instrument in a nitrogen atmosphere. All the samples were first heated from room temperature to 200 °C and then held at this temperature for 3 min to eliminate the thermal history, and then the samples were quenched to −80 °C and heated again from −80 to 200 °C at 10 °C/min. GC/MS measurements were performed with a Varian Saturn 2100 GC/MS system with GC-3900 using a VF-5 MS, 30 m × 0.25 mm × 0.25 μm diffused silica capillary column. Elemental analysis (EA) was conducted with an Elementar Vario EL. Thin layer chromatography (TLC) was performed on silica gel TLC cards (0.20 mm layer thickness). Limiting oxygen index (LOI) values were measured on a Stanton Redcroft instrument provided with an oxygen analyzer in vertical tests. The samples were impregnated on glass fiber plaques using concentrated solutions of the polymers in THF, and LOI values were taken as the average of three measurements.