Reactive & Functional Polymers 73 (2013) 1242–1248

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

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

ARTICLE INFO

Article history:
Received 4 May 2013
Received in revised form 22 June 2013
Accepted 24 June 2013
Available online 1 July 2013

Keywords:
Macrocycles
Polyphosphoester
Selective head-to-tail acyclic diene metathesis polymerization
Ring-closing metathesis

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].

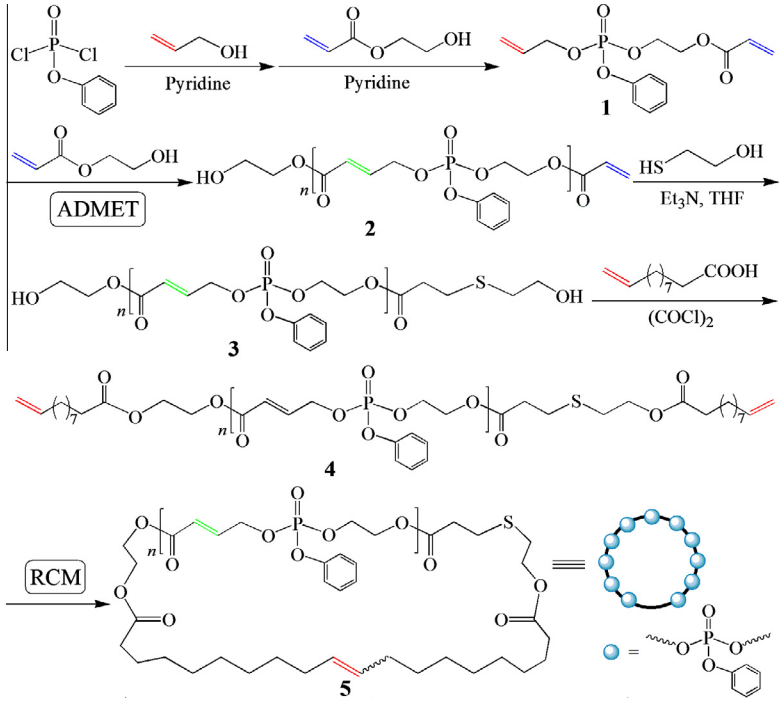
In contrast to linear polymers, cyclic polymers with various chemical structures, compositions, molecular characteristics, and architectures have attracted extensive attention in macromolecular science due to the absence of chain ends [10]. Cyclic polymers usually have a smaller hydrodynamic volume, 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 multifunctional acrylate) is added [23,24]. The chain transfer agent

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

1381-5148/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2013.06.011



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.

Polymerizations were carried out in Schlenk tubes using of a nitrogen flow to drive off the ethylene condensate for ADMET.

2.3. Synthesis of phenyl diene phosphate (**1**)

In a round bottom flask, phenyl dichlorophosphate (6.33 g, 30 mmol) was dissolved in 100 mL of dry CH_2Cl_2 and cooled to 0 °C. Allyl alcohol (1.57 g, 27 mmol) and pyridine (2.61 g, 33 mmol) were added to this solution by a syringe, and then stirred for 8 h under nitrogen flow. The solution was cooled to 0 °C; 2-hydroxyethyl acrylate (3.14 g, 27 mmol) and pyridine (2.61 g, 33 mmol) were added by a syringe; and the reaction was stirred overnight at room temperature. The progress of the reaction was monitored by TLC using methylene chloride/petroleum ether (5:1) as the eluent (an R_f value of 0.5 was obtained from TLC). After repeatedly washing with 1 M HCl and deionized water, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Then, the crude product was purified by silica gel chromatography and eluted with methylene chloride/petroleum ether (1:1) to give the clear colorless liquid **1** (6.12 g, 72.6% yield). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.36–7.31 (m, 2H, *m*-ArH), 7.23–7.19 (d, 2H, *o*-ArH), 7.13–7.09 (m, 1H, *p*-ArH), 6.38–6.33 (d, 1H, OCOCH=CH), 6.21–6.19 (m, 1H, OCOCH=CH), 6.00–5.97 (m, 1H, CH_2=$CHCH_2O$), 5.83–5.74 (d, 1H, OCOCH=CH), 5.29–5.18 (d, 2H, CH_2=$CHCH_2O$), 4.32–4.28 (m, 2H, CH_2CH_2OCOCH=CH_2), 4.21–4.17 (d, 2H, CH_2=$CHCH_2O$), 3.88–3.84 (m, 2H, CH_2CH_2-$OCOCH$=CH_2). ^{13}C NMR ($CDCl_3$), δ (ppm): 165.45, 152.26, 136.90, 130.65, 129.13, 128.08, 120.29, 117.11, 116.17, 68.86, 68.12, 67.05. ^{31}P NMR, δ (ppm): −6.11. GC: single peak was observed. EI/MS: Calcd. for $C_{14}H_{17}O_6P$: 312.3; found: 312.2. Anal. calcd for C: 53.85, H: 5.49, O: 30.74; Found C: 53.84, H: 5.45, O: 30.77.

2.4. General procedure for ADMET polymerizations in the presence of a selective chain terminator

In a nitrogen-filled Schlenk tube, monomer **1**, the desired amount of the selective chain terminator (2-hydroxyethyl acrylate), and CH_2Cl_2 were degassed by three freeze–vacuum–thaw cycles. The mixture was heated to 40 °C while stirring and then a solution of Hoveyda–Grubbs second generation catalyst (0.5 mol% with respect to monomer **1**) in 0.5 mL of CH_2Cl_2 was degassed following the same procedure. After the reaction mixture was stirred for 24 h, the polymerization was quenched by adding THF (2 mL) and ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of methanol, and the precipitate was isolated by filtration and dried under vacuum for 24 h to give the ADMET polymers **2**. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.49–7.35 (m, *m*-ArH), 7.21–7.01 (m, *o*-ArH + *p*-ArH), 6.99–6.86 (m, OCOCH=CH), 6.47–6.35 (d, OCOCH=CH), 6.18–6.07 (m, OCOCH=CH), 5.95–5.78 (m, OCOCH=CH + OCOCH=CH), 4.49–4.31 (m, $OCOCH$=$CHCH_2$ + CH_2CH_2OCO + $HOCH_2CH_2OCO$), 3.92–3.83 (m, CH_2CH_2OCO + $HOCH_2$-CH_2OCO). GPC: M_n = 4600, M_w/M_n = 1.34 for **2a**; M_n = 6800, M_w/M_n = 1.42 for **2b**; M_n = 9200, M_w/M_n = 1.51 for **2c**; NMR: M_n = 3200 for **2a**; M_n = 6500 for **2c**.

2.5. End group functionalization of **2** via a thiol-Michael addition click reaction

The ADMET polymers **2** (1.0 mmol), 2-mercaptoethanol (0.32 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) were dissolved in 10 mL of THF in a Schlenk tube and stirred overnight at room temperature. The product was then precipitated quantitatively from methanol and dried under vacuum for 24 h to give the linear PPE (*l*-PPE) **3** with two hydroxyl end groups. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.53–7.39 (m, *m*-ArH), 7.29–7.06 (m, *o*-ArH + *p*-ArH), 6.98–6.81 (m, OCOCH=CH), 5.92–5.70 (m, OCOCH=CH), 4.61–4.26 (m, $OCOCH$=$CHCH_2$ + CH_2CH_2OCO + $HOCH_2CH_2OCO$), 3.88–3.73 (m, CH_2CH_2OCO + $HOCH_2CH_2OCO$ + $HOCH_2CH_2SCH_2$), 2.73 (m, $HOCH_2CH_2SCH_2$), 2.67–2.52 (m, $HOCH_2CH_2SCH_2$ + $HOCH_2CH_2SCH_2CH_2$). GPC: M_n = 4500, M_w/M_n = 1.35 for **3a**; M_n = 9600, M_w/M_n = 1.56 for **3c**; NMR: M_n = 3200 for **3a**; M_n = 6500 for **3c**.

2.6. Synthesis of linear PPE bearing two vinyl end groups (**4**)

Under a nitrogen atmosphere, $(COCl)_2$ (2.6 mL, 30 mmol) was added by syringe to undecylenic acid (1.1 g, 6.0 mmol) at room temperature with rapid stirring. After 6 h, the excess $(COCl)_2$ was removed in vacuo to yield 10-undecenoyl chloride, which was then added by syringe to the solution of **3** (0.6 mmol) in 10 mL of CH_2Cl_2 and 1.0 mL (7.5 mmol) dry triethylamine at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The precipitate was filtered off and the filtrate was washed with water; then the organic layers were dried over anhydrous Na_2SO_4, and the concentrated residue was precipitated twice from methanol and dried for 24 h in a vacuum oven to afford the diene end-functionalized polymer **4** at high yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.47–7.32 (m, *m*-ArH), 7.25–7.05 (m, *o*-ArH + *p*-ArH), 7.00–6.86 (m, OCOCH=CH), 5.93–5.71 (m, $OCOCH$=CH_2 + CH_2-CH=$CHCH_2$), 4.99–4.85 (m, CH_2=$CHCH_2CH_2$), 4.43–3.96 (m, $OCOCH$=$CHCH_2$ + CH_2CH_2OCO + $OCOCH_2CH_2OCO$ + $OCOCH_2CH_2OCO$ + CH_2-$CH_2SCH_2CH_2OCO$), 3.91–3.68 (m, CH_2CH_2OCO), 2.77–2.56 (m, $CH_2CH_2SCH_2CH_2OCO$ + $CH_2CH_2SCH_2CH_2OCO$ + $CH_2CH_2SCH_2CH_2OCO$), 2.36–2.25 (m, $OCOCH_2CH_2CH_2$), 2.09–2.01 (m, CH_2=$CHCH_2$), 1.75–1.68 (m, $OCOCH_2CH_2CH_2$), 1.46–1.25 ($CH_2CH_2CH_2CH_2CH_2$). ^{31}P NMR, δ (ppm): −6.39. GPC: M_n = 4800, M_w/M_n = 1.30 for **4a**; M_n = 9500, M_w/M_n = 1.52 for **4c**; NMR: M_n = 3400 for **4a**; M_n = 6600 for **4c**.

2.7. Synthesis of cyclic PPEs (**5**) by RCM

A solution of **4** (0.025 mmol) in CH_2Cl_2 was degassed with three freeze–vacuum–thaw cycles to obtain an initial *l*-PPEs precursor **4** concentration of 5×10^{-5} mol/L, and in the presence of N_2 sparging, first generation Grubbs catalyst was added (8.3 mg, 0.01 mmol). The reaction mixture was stirred for 48 h at 40 °C. After cooling, the solvent was removed under reduced pressure and the residue was precipitated in methanol, filtered and dried under vacuum to obtain cyclic PPE (*c*-PPE) at a high yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.52–7.29 (m, *m*-Ar*H*), 7.25–7.07 (m, *o*-ArH + *p*-ArH), 7.03–6.88 (m, OCOCH=CH), 5.92–5.76 (m, OCOCH=CH), 5.47–5.36 (m, CH_2CH=$CHCH_2$), 4.52–4.16 (m, $OCOCH$=$CHCH_2$ + CH_2CH_2OCO + $OCOCH_2CH_2OCO$ + $OCOCH_2CH_2OCO$ + $CH_2CH_2SCH_2CH_2$ OCO), 3.87–3.65 (m, CH_2CH_2OCO), 2.78–2.53 (m, $CH_2CH_2SCH_2CH_2$ OCO + $CH_2CH_2SCH_2CH_2OCO$ + $CH_2CH_2SCH_2CH_2OCO$), 2.27–1.71 (m, $OCOCH_2CH_2CH_2$ + CH_2CH=$CHCH_2$ + $OCOCH_2CH_2CH_2$), 1.49–1.12 (CH_2CH_2 $CH_2CH_2CH_2$). ^{31}P NMR, δ (ppm): −6.31. GPC: M_n = 3900, M_w/M_n = 1.38 for **5a**; M_n = 7300, M_w/M_n = 1.45 for **5c**; NMR: M_n = 3300 for **5a**; M_n = 6300 for **5c**.

3. Results and discussion

3.1. Head-to-tail ADMET polymerization of diene monomer

ADMET polymerization monomer **1** was synthesized by an esterification reaction of phenyl dichlorophosphate with allyl alcohol and 2-hydroxyethyl acrylate in the presence of a pyridine base. The crude product was purified by column chromatography to provide pure colorless liquid **1** with a good yield of 72.6%. The ^{1}H NMR spectrum (Fig. 1a) showed the resonance signals of CH_2=CHOCO— protons (*g*, *h*) at 6.34 ppm, 5.78 ppm, CH_2=CHOCO— protons (*f*) at 6.19 ppm, CH_2=$CHCH_2O$— protons (*a*) at 5.28–5.26 ppm, and

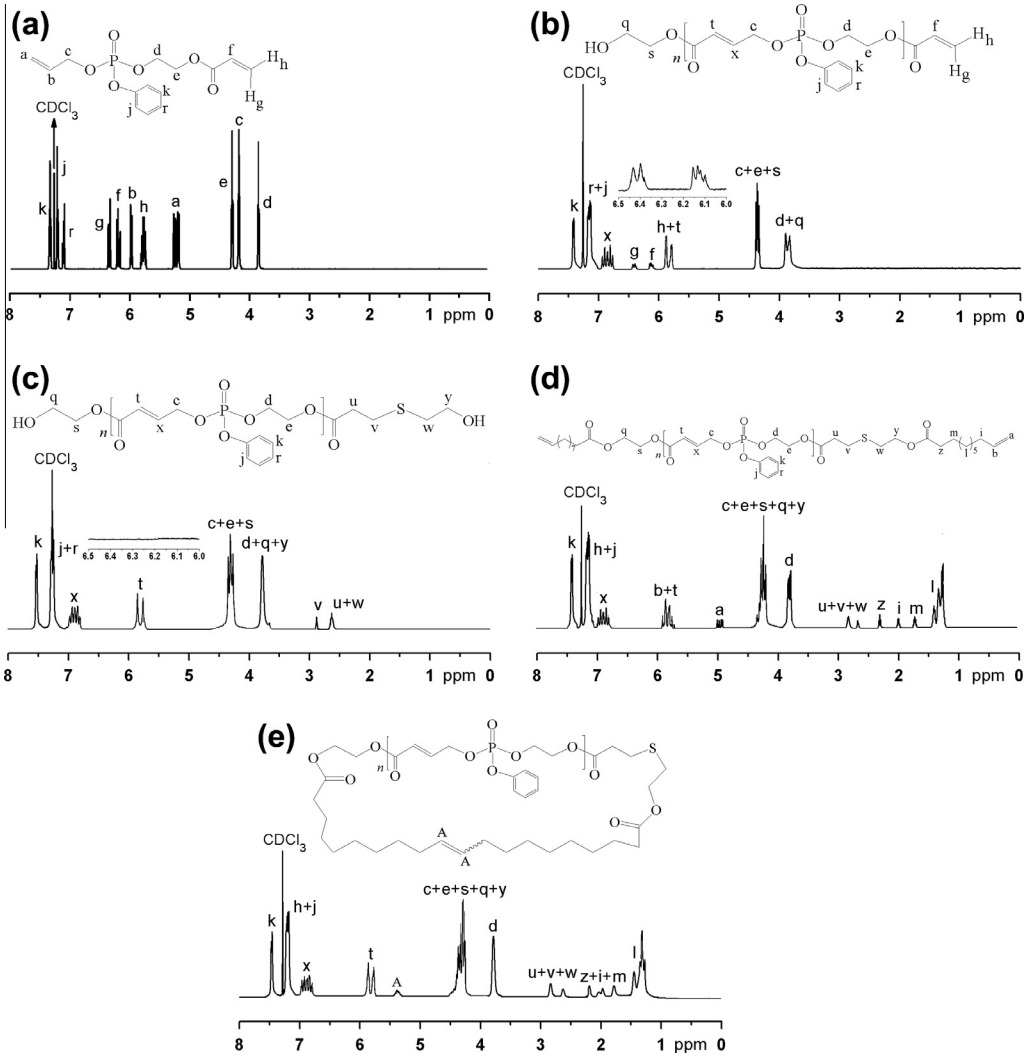


Fig. 1. ^{1}H NMR spectra for (a) phenyl diene phosphate compound **1**, (b) the ADMET polymer **2a**, (c) the linear PPE **3a** bearing two hydroxyl end groups **3**, (d) diene end-functionalized PPE **4a**, and (e) cyclic PPE **5a**.

CH_2 = $CHCH_2O$— protons (*b*) at 5.98 ppm. Furthermore, the molecular weight (M_n = 312.2) of **1** was identified by MS to be in good accordance with the calculated value, and the product is also highly pure as estimated from the single peak of the GC chromatogram. All of these points confirmed the successful preparation of monomer **1** with the expected structure.

Diene monomers containing both a terminal olefin and an acrylate functional group will only polymerize by head-to-tail addition, and a high terminal olefin-to-acrylate metathesis selectivity of 97% can be achieved when using the Hoveyda–Grubbs second generation catalyst [23]. The allyloxy functionality has been proven not to be self-reactive in ADMET polymerization, perhaps due to the lack of sufficiently strong metathesis reactivity, but it can participate in cross metathesis with acrylate in an equilibrium step propagation condensation fashion, based on the electron-rich feature of the allyloxy functionality itself [25–27]. Therefore, a monomer bearing both an allyloxy functionality and an acrylate functional group will have higher metathesis selectivity. If mono-functional acrylate is added, diverse homopolymers and diblock copolymers are synthesized. As the mono-functional acrylate can only react with one end of the polymer chain (acrylates have a very low tendency to dimerize during olefin metathesis due to the negative neighboring group), it can be considered a selective chain terminator [23,24].

Based on this principle, we chose the commercially available 2-hydroxyethyl acrylate to act as a selective chain terminator in the ADMET polymerization of monomer **1**. Varying the [Monomer]/[chain terminator] ratio should allow for the synthesis of PPEs with different molecular weights (Fig. 2 and Table 1). The reaction of **1** and the chain terminator 2-hydroxyethyl acrylate at a 10:1 ~ 20:1 M ratio yielded the PPEs **2**. Increasing the molar ratio led to a moderate increase in the polymer molecular weight (M_n) from 4600 to 9200, with a reasonably low polydispersity index (PDI) ranging from 1.34 to 1.51.

Moreover, the head-to-tail metathesis selectivity of PPEs **2** could be validated by the ^{1}H NMR analysis. Fig. 1b showed the ^{1}H NMR spectrum of **2a**, in which a new peak (*x*) appeared at 6.99–6.86 ppm due to the formation of internal α, β-unsaturated ester functions. Importantly, the terminal allyloxy (*a*, *b*) disappeared after ADMET polymerization indicating a head-to-tail metathesis selectivity of >99%. By comparing the peak integration areas of internal α, β-unsaturated ester protons on the PPE backbone at 6.99–6.86 ppm (H_x) with that of olefinic protons at the end of the PPE backbone at 6.21–6.19 ppm (H_f), the average degree of polymerization (*n*) was calculated using the following formula: $n = S_x/S_f = 10$. The integrated ratio was used to determine the number-average molecular weight of PPE **2**, $M_{n,NMR} = (S_x/S_f) \times M_{(1)}$

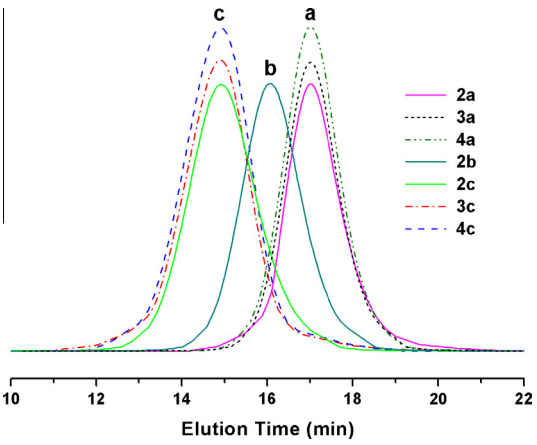


Fig. 2. GPC traces of the linear PPEs **2**, **3**, and **4**.

Table 1
Analytical data of PPEs prepared via head-to-tail ADMET polymerization with selective chain stopper.

Polymer	[M]/[CS]	t (h)	Yield[a] (%)	$M_{n,GPC}$[b]	PDI[b]	$M_{n,NMR}$[c]
2a	10:1	24	92	4600	1.34	3200
2b	15:1	24	88	6800	1.42	nd[d]
2c	20:1	24	91	9200	1.51	6500

[a] Obtained gravimetrically from the dried polymer.
[b] Number average molecular weight (M_n) and polydispersed index (PDI) were determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.
[c] $M_{n,NMR} = (S_x/S_f) \times M_{(1)} + M_{(CS)} - M_{(ethylene)}$ was calculated by ^{1}H NMR spectroscopy, where $M_{(1)} = 312$, $M_{(CS)} = 116$, and $M_{(ethylene)} = 28$ are the molar masses of monomer **1**, chain stopper, and ethylene, respectively.
[d] Not determined.

$(312) + M_{(CS)}\,(116) - M_{(ethylene)}\,(28) = 3200$. However, the value of $M_{n,GPC}$ was higher than that of $M_{n,NMR}$, which could be due to differences in the hydrodynamic volume of PPE or differences in the polystyrene standards used for calibration. In the IR spectrum of the ADMET polymer **2a** in Fig. 3a, the absorption bands' characteristic peaks at 3420, 2921, 1725, 1597, 1512, 1295, 1126, and 1065 cm^{-1} were attributed to the stretching vibrations of hydroxyl groups, unsaturated C═C—H and saturated C—H, ester (C═O), P═O, P—O, and —O—C (P—O—C), respectively. All of these results demonstrated the success of ADMET polymerization.

3.2. End group functionalization of linear PPEs

The generated ADMET PPEs **2** contain acrylate end groups, allowing for the direct functionalization of these macromolecules. The thiol-Michael addition click reaction is an advantageous tool because it is a rapid and quantitative reaction that achieves high conversion with little to no photoinitiator under atmospheric conditions, and it is insensitive to water and oxygen [23,28–30]. Acrylate-functionalized polymers are known to react rapidly with thiols by the thiol-Michael addition click reaction [23,30]. Therefore, we reacted PPEs **2** with mercaptoethanol in the presence of triethylamine catalyst. The reaction proceeded at room temperature until complete and selective functionalization of the acrylate end groups **3** was achieved, and the products were then subjected to ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum and the corresponding peak assignments of **3a** are shown in Fig. 1C. After **2** reacted with mercaptoethanol, two groups of new resonance peaks appeared at v (2.73 ppm) and u, w (2.67–2.52 ppm), which can be ascribed to the protons of methylene. Importantly, the resonance signals of terminal acrylate protons (g,h,f) at 6.47–6.35 ppm and 6.18–6.07 ppm completely disappeared, indicating the complete transformation of the terminal acrylates into hydroxyls. The IR spectrum for **3a** is shown in Fig. 3b, and the absorption bands were almost identical to those in **2a**. Furthermore, the GPC elution curves of **3** displayed nearly the same M_ns and PDIs as those of **2** (Table 2 and Fig. 2), suggesting that ADMET polymer **2** has a similar backbone structure to that of *l*-PPEs **3**.

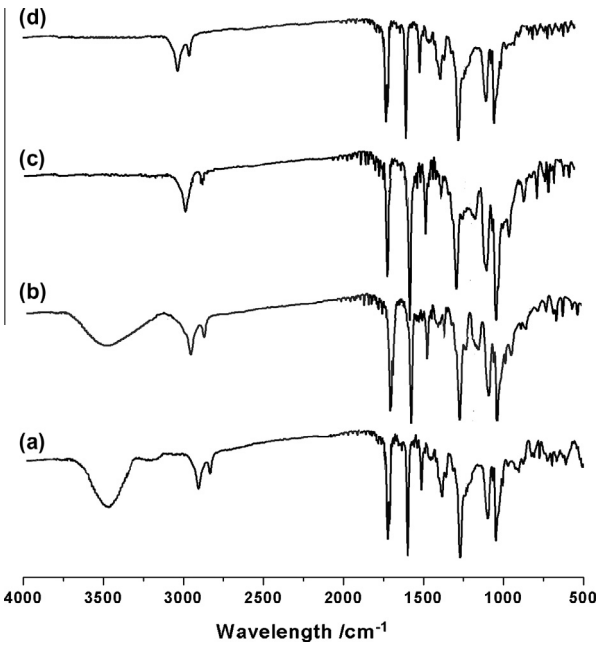


Fig. 3. FTIR spectra for (a) the ADMET polymer **2a**, (b) the linear PPE **3a** bearing two hydroxyl end groups, (c) diene end-functionalized PPE **4a**, and (c) cyclic PPE **5a**.

Table 2
Characteristics of linear and cyclic PPEs via RCM[a].

Polymer	Yield[b] (%)	$M_{n,GPC}$[c]	PDI[c]	$M_{n,NMR}$	LOI[g]
3a	98	4500	1.35	3200[d]	23.2
4a	96	4800	1.30	3400[e]	23.6
5a	81	3900	1.38	3300[f]	24.5
3c	83	9600	1.56	6500[d]	24.2
4c	90	9500	1.52	6600[e]	24.6
5c	92	7300	1.45	6300[f]	25.3

[a] Reaction conditions for preparation of **5**: reaction temperature = 40 °C, reaction time = 48 h, $[M]_0 = 5 \times 10^{-5}$ mol/L.
[b] Obtained gravimetrically from the dried polymer.
[c] Number average molecular weight (M_n) and polydispersed index (PDI) were determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.
[d] $M_{n,NMR} = (2S_t/S_v) \times M_{(1)} + M_{(CS)} + M_{(mercaptoethanol)} - M_{(ethylene)}$ was calculated by ^{1}H NMR spectroscopy.
[e] $M_{n,NMR} = (4S_x/S_a) \times M_{(1)} + M_{(CS)} + M_{(mercaptoethanol)} + 2 \times M_{(undecylenic\ acid)} - M_{(ethylene)}$ was calculated by ^{1}H NMR spectroscopy.
[f] $M_{n,NMR} = (2S_t/S_A) \times M_{(1)} + M_{(CS)} + M_{(mercaptoethanol)} + 2 \times M_{(undecylenic\ acid)} - 2 \times M_{(ethylene)}$ was calculated by ^{1}H NMR spectroscopy.
[g] LOI values were taken as the average of three measurements.

The esterification of **3** with an excess of 10-undecenoyl chloride, which was synthesized by reacting undecylenic acid with oxalyl chloride, was carried out at room temperature in the presence of triethylamine to produce the *l*-PPE precursors **4**. The ^{1}H NMR spectrum of **4a** (Fig. 1d) showed the resonance signals of terminal olefinic protons at 5.78 ppm (b) and 4.99 ppm (a). Moreover, the resonance signals of methylene protons z (2.36–2.25 ppm), i (2.09–2.01 ppm), m (1.75–1.68), and l (1.46–1.25 ppm) can also be clearly observed, corresponding to the chemical structure of undecylenic acid. Comparing the IR spectrum of the *l*-PPEs precur-

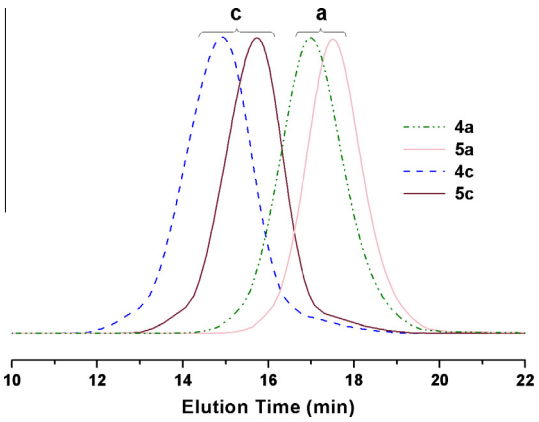


Fig. 4. GPC traces of the linear PPEs **4** and the cyclic PPEs **5**.

sor **4a** with **3a**, we can also clearly observe in Fig. 3c that a strong absorption peak at 3400 cm^{-1} disappeared, while the other absorption bands exhibited no significant change. All of these points confirmed that the esterification reaction was successful and that the terminal hydroxyls were completely transformed into terminal double bonds. The M_ns and PDIs of **4** were similar to those of polymers **2** and **3** because their structures were similar (Table 2 and Fig. 2).

3.3. Preparation of cyclic PPEs via RCM of linear PPEs

The ADMET polymer **4** was telechelic, with two vinyl end groups, and thus could be considered a functional linear precursor for the preparation of cyclic polymers. Therefore, *c*-PPEs **5** were finally obtained when the intramolecular cyclization reaction was achieved under highly dilute conditions by the end-to-end RCM reaction between terminal alkene groups on the *l*-PPE precursor **4**. The RCM reaction was performed at a low concentration of [**4**] $=5 \times 10^{-5}$ mol/L to ensure that most of the *l*-PPE precursor reacted in the intramolecular cyclization reaction because the concentration of the linear polymer is usually the primary factor determining whether an a,ω-functionalized precursor will prefer cyclization or condensation [31].

Fig. 1e shows the ^{1}H NMR spectrum of the RCM product *c*-PPE **5a**. New resonance peaks *A* at 5.36 ppm appeared after RCM cyclization and can be ascribed to the protons of internal carbon–carbon double bonds. When compared with the spectrum of *l*-PPE **4a**, peaks *a* and *b* at 4.99 and 5.78 ppm in Fig. 1d almost disappeared in Fig. 1e after RCM, indicating successful ring closure of the linear PPEs via RCM. Monomodal peaks can be observed in the GPC chromatogram (Fig. 4) for the as-obtained *c*-PPEs **5** with relatively low PDIs (Table 2). Most importantly, we can also clearly observe the clean shift of the elution peak of *c*-PPEs **5** to the lower molecular weight position from Fig. 4, compared to those of *l*-PPE precursors **4**, which can be ascribed to the lower hydrodynamic volume of *c*-PPEs. These findings confirmed that the intramolecular ring closure was complete. The cyclic PPE **5a** and its linear precursor **4a** were also examined by MALDI–TOF MS spectra (Fig. 5). The peaks were separated by 284 mass units, corresponding to the molecular weight of the monomer unit (284.20). We were able to calculate the average degree of polymerization (DP_n) by analyzing these peaks [16a]. For example, the highest peak at 3364.8 in Fig. 5b corresponded to **5a** with a DP_n of 10, which was derived from the following formula: $M_{(\text{each monomer unit})}$ (284) $\times$ DP_n + $M_{(\text{end groups of } \mathbf{4a})}$ (512) − $M_{(\text{ethylene})}$ (28) = 3364.8. Similarly, the DP_n of **4a** was calculated by the formula: $M_{(\text{each monomer unit})}$ (284) $\times$ DP_n + $M_{(\text{end groups of } \mathbf{4a})}$ (512) = 3392.6, and DP_n was again 10. Moreover, the M_ns of **4a** and **5a** calculated from the MALDI–TOF spectra are 3406 and 3378, which are in good agreement with the values determined by GPC and calculated via ^{1}H NMR. As the cyclic PPE product is produced from a linear precursor, elimination of an ethylene molecule should result in a molecular weight difference of 28 mass units, as confirmed from the M_ns of the two polymers. Moreover, the absorption bands of *c*-PPE **5a** in the IR spectrum (Fig. 3d) were almost identical to those of the *l*-PPE precursor **4a**. Therefore, we concluded that the backbone composition of the *l*-PPE precursor is similar to that of the resulting *c*-PPE.

3.4. Thermal properties of linear and cyclic PPEs

The DSC traces of typical PPEs are shown in Fig. 6a, and the thermal stability was examined by TGA under a nitrogen atmosphere (Fig. 6b). The flexible P—O—C groups in the backbone commonly result in PPEs with low glass transitions (T_g = −40 °C) [32]. The Fox equation for these polymeric systems estimated the T_g at −30 °C for a PPE homopolymer, which is consistent with the role of the internal plasticizer of the phosphoester monomer itself [26]. The *l*-PPE **4a** and *c*-PPE **5a** exhibited different T_gs at −35.6 and −24.9 °C, without a melting peak (Fig. 6a). The olefinic double bonds in the polymer microstructure resulted in the typical low T_g of PPEs in this case.

The TGA curves in Fig. 6b exhibit a one-step degradation process, and the temperature range of 10% weight loss was determined at 396 and 405 °C, demonstrating the good thermal stability of these polymers. Moreover, the thermal degradation of PPEs leads to the formation of the phosphorus containing char, which acts as a protective layer for the polymer surface. The char yield is an important contributor to the flame retardance of polymers, as high char yields always lead to high flame retardant activity of phosphorus flame retardants [1c]. The char yield of *l*-PPE **4a** and *c*-PPE **5a** obtained at 800 °C reached a maximum of approximately 10% in both PPE series.

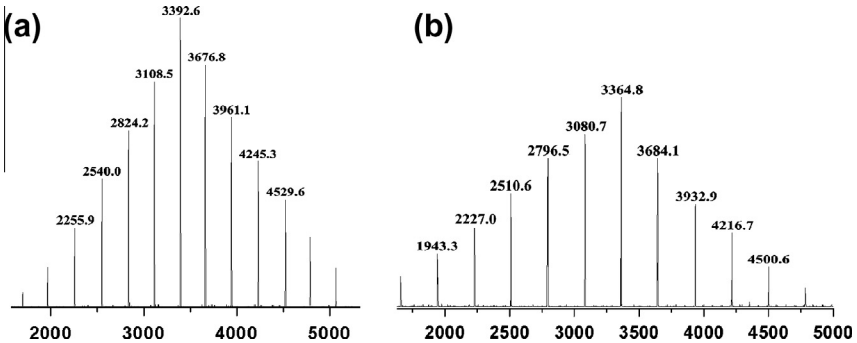


Fig. 5. MALDI–TOF MS spectra of (a) the linear PPE **4a** and (b) the cyclic PPE **5a**.

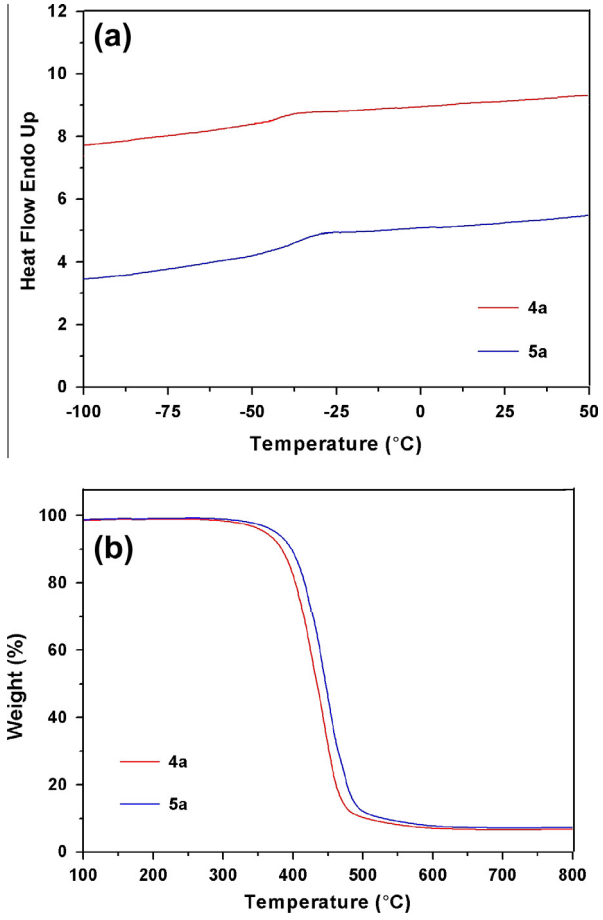


Fig. 6. Thermal properties of the linear and cyclic PPEs: (a) DSC traces and (b) TGA curves.

Furthermore, the flame retardant properties of linear and cyclic PPEs were evaluated using the limiting oxygen index (LOI) test. The LOI is the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will only support the flaming combustion of a certain material. Usually, a material is considered to have no flame retardant properties when the LOI value is less than 21 [1,2]. The samples in this work were prepared by a similar method to that reported by Meier et al. [1a]. Concentrated solutions of each polymer in THF were used to impregnate glass fiber probes. We used these probes instead of standard probes due to the lack of consistence among the obtained polymers. Table 2 reports the LOI values. A distinct and steady increase in the LOI with an increasing *l*-PPE molecular weight was observed, corresponding to increasing phosphorus content. The LOI values of the *c*-PPEs were higher than those of the corresponding *l*-PPEs, reaching a maximum value of 25.3 for *c*-PPE **5c**. These values revealed that the *c*-PPEs exhibited better flame retardant properties than the *l*-PPEs.

4. Conclusion

A novel cyclic PPE was successfully prepared via RCM of difunctional linear PPE precursors under highly dilute conditions. The linear PPE bearing an end acrylate functional group was first synthesized through a selective head-to-tail ADMET polymerization of phenyl dienephosphate monomer using 2-hydroxyethyl acrylate as a selective chain terminator. The end functional group was then transformed into a hydroxyl group by a thiol-Michael addition click reaction and finally was reacted with corresponding acyl chloride containing a vinyl end group to obtain linear PPE precursors. The linear and cyclic PPEs were characterized in detail by NMR, FTIR, GPC, MALDI–TOF MS, DSC, and TGA measurements. LOI values up to 25.3 were obtained for PPEs, indicating the favorable flame retardant properties of cyclic PPEs. These results may provide valuable guidance for the synthesis of linear and cyclic polymers, especially functional polyolefins.

Acknowledgments

We thank the Initial Scientific Research Foundation of Yancheng Institute of Technology for financial support of this research. We also thank Dr. Zhenshu Zhu at China Pharmaceutical University for his kind help with the MALDI–TOF MS experiments.

References

[1] (a) L.M.D. Espinosa, J.C. Ronda, M. Galia, V. Cadiz, M.A.R. Meier, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 5760–5771;
(b) E. Cakmakc, Y. Mulazim, M.V. Kahraman, N.K. Apohan, React. Funct. Polym. 71 (2011) 36–41;
(c) T. Kawahara, A. Yuuki, K. Hashimoto, K. Fujiki, T. Yamauchi, React. Funct. Polym. 73 (2013) 613–618.
[2] D.J. Irvine, J.A. McCluskey, I.M. Robinson, Polym. Degrad. Stab. 67 (2000) 383–396.
[3] P. Klosinski, S. Penczek, Macromolecules 16 (1983) 316–320.
[4] Y.C. Wang, Y.Y. Yuan, J.Z. Du, X.Z. Yang, J. Wang, Macromol. Biosci. 9 (2009) 1154–1164.
[5] G. David, E. Ortega, K. Chougrani, A. Manseri, B. Boutevin, React. Funct. Polym. 71 (2011) 599–606.
[6] H.R. Allcock, E.C. Kellam, Macromolecules 35 (2002) 40–47.
[7] S. Lu, I. Hamerton, Prog. Polym. Sci. 2 (2002) 1661–1712.
[8] K.L. Opper, B. Fassbender, G. Brunklaus, H.W. Spiess, K.B. Wagener, Macromolecules 42 (2009) 4407–4409.
[9] K.L. Opper, D. Markova, M. Klapper, K. Mullen, K.B. Wagener, Macromolecules 43 (2010) 3690–3698.
[10] (a) N. Hadjichristidis, H. Iatroua, M. Pitsikalisa, J. Mays, Prog. Polym. Sci. 31 (2006) 1068–1132;
(b) H. Oike, React. Funct. Polym. 67 (2007) 1157–1167.
[11] (a) G.Y. Shi, X.Z. Tang, C.Y. Pan, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 2390–2401;
(b) G.Y. Shi, C.Y. Pan, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 2620–2630.
[12] Y.Q. Dong, Y.Y. Tong, B.T. Dong, F.S. Du, Z.C. Li, Macromolecules 42 (2009) 2940–2948.
[13] X.J. Wan, T. Liu, S.Y. Liu, Biomacromolecules 12 (2011) 1146–1154.
[14] (a) X. Xu, N.C. Zhou, J. Zhu, Y.F. Tu, Z.B. Zhang, Z.P. Cheng, X.L. Zhu, Macromol. Rapid Commun. 31 (2010) 1791–1797;
(b) Y. Zhang, X. Zhu, N.C. Zhou, X.R. Chen, W. Zhang, Y.G. Yang, X.L. Zhu, Chem. Asian J. 7 (2012) 2217–2221.
[15] D. Pantazis, D.N. Schulz, N. Hadjichristidis, J. Polym, Part A: Polym. Chem. 40 (2002) 471–485.
[16] (a) Y. Tezuka, R. Komiya, Macromolecules 35 (2002) 8667–8669;
(b) Z. Jia, Q. Fu, J. Huang, Macromolecules 39 (2006) 5190–5193.
[17] M. Schappacher, A. Deffieux, Science 319 (2008) 1512–1515.
[18] W.Y. Yang, E. Lee, M. Lee, J. Am. Chem. Soc. 128 (2006) 3484–3485.
[19] P.H. Deshmukh, C. Schulz-Fademrecht, P.A. Procopiou, D.A. Vigushin, R.C. Coombes, A.G.M. Barrett, Adv. Synth. Catal. 349 (2007) 17–83.
[20] K. Adachi, S. Honda, S. Hayashi, Y. Tezuka, Macromolecules 41 (2008) 7898–7903.
[21] M.R. Xie, J.X. Shi, L. Ding, J.X. Li, H.J. Han, Y.Q. Zhang, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 3022–3033.
[22] J.E. Schwendeman, A.C. Church, K.B. Wagener, Adv. Synth. Catal. 344 (2002) 597–613.
[23] L.M.D. Espinosa, M.A.R. Meier, Chem. Commun. 47 (2011) 1908–1910.
[24] M. Winkler, J.O. Mueller, K.K. Oehlenschlaeger, L.M.D. Espinosa, M.A.R. Meier, C.B. Kowollik, Macromolecules 45 (2012) 5012–5019.
[25] L. Ding, M.R. Xie, D. Yang, C.M. Song, Macromolecules 43 (2010) 10336–10342.
[26] F. Marsico, M. Wagner, K. Landfester, F.R. Wurm, Macromolecules 45 (2012) 8511–8518.
[27] L. Ding, G.D. Yang, M.R. Xie, D.Y. Gao, J.H. Yu, Y.Q. Zhang, Polymer 53 (2012) 333–341.
[28] M.J. Kade, D.J. Burke, C.J. Hawker, J. Polym. Sci., Part A: Polym. Chem. 48 (2010) 743–750.
[29] M.L. Koh, D. Konkolewicz, S. Perrier, Macromolecules 44 (2011) 2715–2724.
[30] M.R. Xie, L. Ding, Z.W. You, D.Y. Gao, G.D. Yang, H.J. Han, J. Mater. Chem. 22 (2012) 14108–14118.
[31] P. Hodge, S.D. Kamau, Angew. Chem. Int. Ed. 42 (2003) 2412–2414.
[32] S. Zhang, A. Li, J. Zou, L.Y. Lin, K.L. Wooley, ACS Macro Lett. 1 (2012) 328–333.