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Ladder- and bridge-like polynorbornene with phosphate linker: facile one-pot synthesis and excellent property

Liang Ding,^{*,†} Junmei Zhang,[‡] Lingfang Wang,[†] Chengshuang Wang[†]

[†] *School of Materials Engineering, Yancheng Institute of Technology, Yancheng, 224051, China*

[‡] *No. 52 Institute of China Ordnance Industries Yantai Branch, Yantai, 264000, China*

Fax: (+)86-515-88298872; E-mail: dl1984911@ycit.edu.cn

ABSTRACT: A facile one-pot synthesis of novel bridge-like polymer was accomplished by a sequential ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization. A telechelic double-stranded poly(norbornene dicarboximide) (PNBI) with two terminal alkenyl groups was first prepared through the third generation Grubbs catalyst-mediated ROMP of bis(NBI) derivative, bearing a phosphate linker, in the presence of a symmetrical multifunctional terminating agent, and was then utilized as a macromonomer in subsequent ADMET polymerization to yield the resultant bridge-like polymer, consisting of the non-conjugated polyolefin backbone and the separated double-stranded PNBI. According to the TGA test, the amount of residual carbonaceous mass also increased with the molecular weight of the resultant polymers, indicating excellent thermal stability. The micro-scale combustion calorimetry and limiting oxygen index tests also displayed superior flame-retardant performance.

KEYWORDS: Metathesis polymerization; one-pot process; ladder-like polymer; bridge-like polymer; phosphate linker

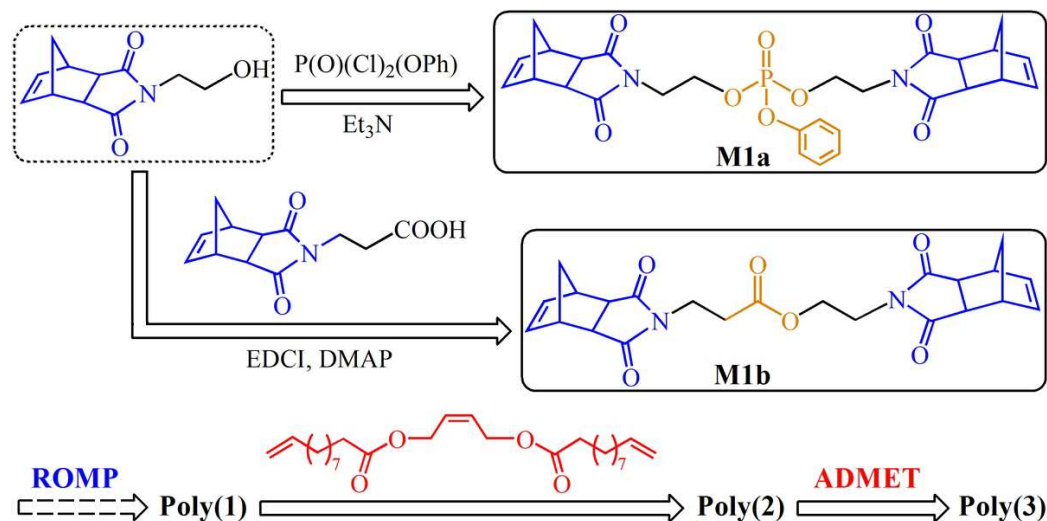
Introduction

Precisely controlled the size of polymer chain, meanwhile, reduced the complexity and cost of synthesis is the main target for more complex polymer synthetic efforts.¹ Among various complex macromolecule structures, ladder-like polymers, which have two strands connected by covalent dative or ionic bonds, provide greater resistance to linear polarized ultraviolet light irradiation as well as thermal and chemical degradation in comparison to their single-stranded counterparts.² Besides, ladder-type arrays should have planar and rigid π - π stacked structures that facilitate electron delocalization and enhance conjugation.³ Luh reported a series of double-stranded polynorbornenes by ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) of the corresponding monomers having a range of planar aromatic pendants or linkers.⁴ More recently, a novel double-stranded polyacetylene with a perylene bisimide bridge has been efficiently synthesized by metathesis cyclopolymerization (MCP) of bis(1,6-heptadiyne) derivatives.⁵ All above design involved a suitable monomer that contains two polymerizable groups linked by a relatively rigid spacer, few bearing a flexible linker.

In recent years, there have been more and more investigations into much better flame retardants and phosphorus-containing polymers have been given increased attention.^{6,7} A very interesting subclass are poly(phosphate)s, which were used as flame retardant materials, are one of the most versatile class of materials due to their modular synthesis and broad range of possible applications.^{6e} The chemical versatility of the monomeric phosphate allows the design of functional materials with tunable and complex architectures and many different properties. The combination of phosphorus chemistry with metathesis allows tailoring of the polymer functionality due to the high functional group tolerance of modern ruthenium metathesis

catalysts.⁸⁻¹² However, poly(phosphate)s are only scarcely found in recent studies in spite of some highly promising flame-retarding properties.

Consequently, building upon our experience with metathesis polymerization, herein, we designed a bis(norbornene dicarboximide) (NBI) derivative as monomer (**M1**) for ROMP, for the first time, to generate a novel double-stranded PNBI with ladder-like architecture using phosphate or ester as linker (poly(**1**)). When ROMP was terminated by the symmetrical α,ω -alkenyl *cis*-olefinic ether, a new type of double-stranded PNBI with telechelic reactive long chain end alkenes (poly(**2**)) was obtained, which can be utilized as a macromonomer in subsequent ADMET polymerization, producing a bridge-like polymer (poly(**3**)) (Scheme 1, Fig. 1). To the best of our knowledge, this is the first report of the fundamental preparation of ladder- and bridge-like polymers containing a phosphate-linked double-stranded PNBI by one-pot tandem ROMP and ADMET polymerization, and this type of polymer is envisioned to have high thermal stability and excellent flame-retardant property.



Scheme 1 Schematic representation for synthesis of ladder- and bridge-like polymers via combination of ROMP and ADMET polymerization in one-pot process.

2. Experimental Part

Materials

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (first generation Grubbs catalyst, **C1**), benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst, **C2**), Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) (third generation Grubbs catalyst, **C3**), acrylic acid (99%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI·HCl, 99%), 5-norbornene-*endo,endo*-2,3-dicarboxylic anhydride (>98%), ethanolamine (99%), undecenoic acid (98%), phenyl dichlorophosphate (99%), oxalyl chloride ((COCl)₂, 98%), *cis*-1,4-butanediol (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 was freshly distilled and dried by sieves.

Characterization

UV–vis absorption spectra were measured on a Cary 60 spectrometer. Elemental analysis (EA) was conducted with an Elementar Vario EL. Gas chromatography (GC) was measured by Agilent 6890 series GC system instrument equipped with a flame ionization detector and a capillary column (HP–5. 0.25 mm × 30 m), using decane as an internal standard. T_{inj} 280 °C, T_{detec} 280 °C, T_{init} 50 °C (10 °C/min), carrier gas: N₂. High–resolution mass spectrometry (HRMS) data were recorded on a Waters GCT Premier mass spectrometer with electron ionization mode. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ on a Bruker DPX spectrometer. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Waters 1500 Isocratic HPLC pump, a Waters 2414 refractive

index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 μm bead size; 10³, 10⁴, and 10⁵ 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. The microscale combustion calorimeter test (MCC, Govmark Organization) was carried out according to the standard ASTM D 7309. The sample (5–10 mg) was heated under a nitrogen stream flow in a pyrolyzer at a certain heating rate (typically 1 °C/s) and suffered thermal decomposition. Limiting oxygen index (LOI) values were measured on a Stanton Redcroft instrument provided with an oxygen analyser in vertical tests, and LOI values were taken as the average of three measurements.

Polymerizations were carried out in Schlenk tubes under dry nitrogen atmosphere.

Synthesis of bis(norbornene dicarboximide) derivative monomer (M1a)

To a dried round bottom flask, 1.5 mL (2.11 g, 10 mmol) of phenyl dichlorophosphate dissolved in 50 mL of dry CH₂Cl₂ with stirring was added under nitrogen atmosphere. The solution was cooled to 0 °C and then 2.2 equiv of the appropriate alcohol (4.55 g, 22 mmol) and 2.2 equiv of Et₃N (2.22 g, 22 mmol) were added to the solution via syringe. The reaction was stirred overnight at room temperature. The crude mixture was washed with aqueous 1 M HCl and deionized water. The organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated in vacuum, and purified by column chromatography over silica using CH₂Cl₂ as an eluent (R_f = 0.50) to give a colorless viscous liquid with a yield of 80.3%. ¹H NMR (CDCl₃): δ (ppm) 7.39–7.24 (m, 2H, *m*-ArH), 7.23–7.04 (m, 3H, *o*-ArH + *p*-ArH), 6.36–6.24 (s, 4H, CH=CH), 3.83–3.67 (m, 8H, NCH₂CH₂O), 3.58–3.49 (m, 4H, CHCON), 3.28–3.17 (m, 4H, CHCH₂CH), 1.80–1.73 and 1.71–1.52 (d, 4H, CHCH₂CH). ¹³C NMR (CDCl₃): δ (ppm) 176.5, 153.8, 138.4, 131.1, 122.3, 117.6, 63.4, 47.8, 46.0, 40.9, 38.6. GC: single peak was

observed. EI/HRMS: Calcd. For $C_{28}H_{29}O_8N_2P$: 552.5171; found: 552.5208. Anal. Calcd for C: 60.87, H: 5.29, O: 23.17; Found C: 60.88, H: 5.26, O: 23.19.

Synthesis of bis(norbornene dicarboximide) derivative monomer (M1b)

Under a nitrogen atmosphere, $(COCl)_2$ (13 mL, 150 mmol) was added by syringe to N-2-carboxyl-ethyl-norbornene-dicarboximide (7.05 g, 30 mmol) at room temperature with rapid stirring. After 6 h, the excess $(COCl)_2$ was removed in vacuum, which was then added by syringe to the solution of the appropriate alcohol (6.21 g, 30 mmol) in 80 mL of CH_2Cl_2 and 6 mL (45 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 further purified by column chromatography over silica using methylene chloride/petroleum ether (5/1) as an eluent ($R_f = 0.45$) to give a colorless viscous liquid with a yield of 72.7%. 1H NMR ($CDCl_3$): δ (ppm) 6.26–6.22 (s, 4H, $CH=CH$), 4.28–4.23 (m, 2H, CH_2OCOCH_2), 3.87–3.59 (m, 12H, $NCH_2CH_2O + CHCON$), 3.26–3.20 (m, 4H, $CHCH_2CH$), 2.55–2.50 (m, 2H, CH_2OCOCH_2), 1.58–1.52 and 1.50–1.47 (d, 4H, $CHCH_2CH$). ^{13}C NMR ($CDCl_3$): δ (ppm) 176.8, 171.7, 139.2, 67.1, 47.8, 45.9, 36.3, 35.6, 32.4. GC: single peak was observed. EI/HRMS: Calcd. For $C_{23}H_{24}O_6N_2$: 424.4326; found: 424.4228. Anal. Calcd for C: 65.08, H: 5.70, O: 22.62; Found C: 65.08, H: 5.72, O: 22.61.

Representative ROMP procedure for syntheses of ladder-like polymer (Poly(1))

In a nitrogen-filled Schlenk tube, a solution of Grubbs catalyst (4 μ mol) in $CHCl_3$ (0.5 mL) was degassed with three freeze–vacuum–thaw cycles and then added to a degassed (with the same procedure as above) solution of **M1** (0.1 mmol) in $CHCl_3$ (40 mL) under vigorous stirring at 30 °C for 1 h. The reaction mixture was concentrated

and poured into an excess of methanol. The precipitate was isolated and dried under vacuum for 24 h to give the colorless ladder-like poly(**1**). For poly(**1a**), ^1H NMR (CDCl_3): δ (ppm) 7.41–7.02 (m, ArH), 6.03–5.84, 5.61–5.39 (d, CH=CH), 3.92–3.60 (m, $\text{NCH}_2\text{CH}_2\text{O}$), 3.55–3.23 (m, $\text{CHC}=\text{ON}$ + CHCH_2CH), 1.82–1.47 (m, CHCH_2CH). ^{13}C NMR (CDCl_3): δ (ppm) 177.4, 161.2, 139.8, 132.3, 130.7, 129.9, 128.5, 127.6, 122.4, 118.0, 64.3, 49.7, 47.8, 40.9, 38.6, 35.1. For poly(**1b**), ^1H NMR (CDCl_3): δ (ppm) 7.38–7.22 (m, ArH), 6.08–5.92, 5.71–5.47 (d, CH=CH), 4.32–4.24 (m, $\text{CH}_2\text{OCOCH}_2$), 3.88–3.57 (m, $\text{NCH}_2\text{CH}_2\text{O}$ + CHCON), 3.35–3.22 (m, CHCH_2CH), 2.61–2.46 (m, $\text{CH}_2\text{OCOCH}_2$), 1.77–1.49 and 1.48–1.37 (m, CHCH_2CH). ^{13}C NMR (CDCl_3): δ (ppm) 176.7, 171.6, 141.2, 135.8, 129.6, 128.4, 127.9, 127.2, 114.5, 65.1, 46.0, 39.7, 36.9, 36.4, 31.3.

Typical one-pot synthesis of alkene-terminated telechelic macromonomer (Poly(2)) and bridge-like polymer (Poly(3))

In a nitrogen-filled Schlenk tube, Grubbs third generation catalyst, **C3** (0.025 mmol) in CHCl_3 (5 mL) was added to the solution of monomer (0.25 mmol) in CHCl_3 (45 mL) via a syringe under vigorous stirring at 30 °C, which was degassed with three freeze-vacuum-thaw cycles. After confirming the monomer conversion by TLC (about 10 min), an excess of terminating agent, TA (0.25 mmol) was added as a solution in CHCl_3 in 1 mL. The reaction mixture was allowed to stir for 12 h. Then the solution was concentrated to about 10 mL, a first aliquot of the solution was taken out from the reaction mixture by syringe and the polymerization was stopped, and then the content was poured into an excess of methanol. The precipitate was isolated by filtration, dried under vacuum for 24 h to give the double-stranded poly(**2**) in a nearly quantitative yield. For poly(**2a**), ^1H NMR (CDCl_3): δ (ppm) 7.43–7.00 (m, ArH), 5.96–5.71, 5.68–5.42 (m, CH=CH + $\text{CH}_2=\text{CH}$), 5.01–4.96 (m, $\text{CH}_2=\text{CH}$),

4.77–4.69 (m, $\text{CH}_2\text{OCOCH}_2$), 4.04–3.75 (m, $\text{NCH}_2\text{CH}_2\text{O}$), 3.64–3.25 (m, CHCON + CHCH_2CH), 2.19–2.02 (m, $\text{CH}_2\text{OCOCH}_2$ + $\text{CH}_2=\text{CHCH}_2$), 1.80–1.53 (m, CHCH_2CH), 1.51–1.24 (m, $\text{CH}_2(\text{CH}_2)_6\text{CH}_2$). ^{13}C NMR (CDCl_3): δ (ppm) 177.4, 161.2, 139.8, 132.3, 130.7, 129.9, 128.5, 127.6, 122.4, 118.0, 64.3, 49.7, 47.8, 40.9, 38.6, 35.1. For poly(**2b**), ^1H NMR (CDCl_3): δ (ppm) 7.31–7.20 (m, ArH), 6.04–5.83, 5.77–5.59 (d, $\text{CH}=\text{CH}$ + $\text{CH}_2=\text{CH}$), 5.02–4.95 (m, $\text{CH}_2=\text{CH}$), 4.34–4.08 (m, $\text{CH}_2\text{OCOCH}_2$), 4.04–3.81 (m, $\text{NCH}_2\text{CH}_2\text{O}$ + CHCON), 3.37–3.21 (m, CHCH_2CH), 2.68–2.43 (m, $\text{CH}_2\text{OCOCH}_2$), 2.17–2.03 (m, $\text{CH}_2\text{OCOCH}_2$ + $\text{CH}_2=\text{CHCH}_2$), 1.56–1.41 (m, CHCH_2CH). ^{13}C NMR (CDCl_3): δ (ppm) 178.9, 176.3, 162.5, 141.0, 134.8, 132.7, 129.5, 128.1, 127.2, 126.4, 125.7, 118.6, 115.9, 70.1, 64.7, 41.8, 34.7, 30.2, 29.4, 27.3, 25.2.

After that, the residual solvent (CHCl_3) in above ROMP system was removed in vacuum to yield a macromonomer. Then, a solution of **C1** (0.5 mol% to macromonomer) in CHCl_3 (1 mL) degassed with the same procedure was added to this ROMP system to make the polymerization transform into ADMET polymerization, and the reaction mixture was stirred at 60 °C for 24–72 h under a slow purge of nitrogen to drive off the ethylene condensate. A fresh batch of **C1** (0.5% mol to macromonomer) was then added to the reaction vessel at about 24 h intervals. The polymerization was finally quenched by adding ethyl vinyl ether with stirring for 30 min. The mixture was poured into an excess of methanol and the precipitate was isolated by filtration, dried under vacuum for 24 h to give the bridge-like poly(**3**). For poly(**3a**), ^1H NMR (CDCl_3): δ (ppm) 7.46–7.02 (m, ArH), 6.01–5.73, 5.69–5.40 (m, $\text{CH}=\text{CH}$ on ROMP polymer chain + $\text{CH}_2=\text{CH}$), 5.34–5.23 (m, $\text{CH}=\text{CH}$ on ADMET polymer chain), 4.03–3.72 (m, $\text{NCH}_2\text{CH}_2\text{O}$), 3.59–3.03 (m, $\text{CHC}=\text{ON}$ + CHCH_2CH), 2.11–1.93 (m, $\text{CH}_2\text{OCOCH}_2$ + $\text{CH}_2=\text{CHCH}_2$), 1.55–1.20 (m,

$\text{CH}_2(\text{CH}_2)_7\text{CH}_2$). ^{13}C NMR (CDCl_3): δ (ppm) 177.8, 175.7, 163.2, 140.5, 137.2, 134.1, 133.4, 129.8, 128.3, 125.5, 118.2, 70.8, 62.9, 44.8, 38.3, 33.9, 32.5, 31.7, 31.1, 30.5, 29.8, 24.4. For poly(**3b**), ^1H NMR (CDCl_3): δ (ppm) 7.37–7.21 (m, ArH), 6.02–5.88, 5.75–5.47 (d, $\text{CH}=\text{CH}$ on ROMP polymer chain + $\text{CH}_2=\text{CH}$), 5.34–5.22 (m, $\text{CH}=\text{CH}$ on ADMET polymer chain), 4.40–4.16 (m, $\text{CH}_2\text{OCOCH}_2$), 4.01–3.57 (m, $\text{NCH}_2\text{CH}_2\text{O}$ + CHCON), 3.43–3.08 (m, CHCH_2CH), 2.62–2.43 (m, $\text{CH}_2\text{OCOCH}_2$), 2.19–2.01 (m, $\text{CH}_2\text{OCOCH}_2$ + $\text{CH}_2=\text{CHCH}_2$), 1.58–1.44 (m, CHCH_2CH). ^{13}C NMR (CDCl_3): δ (ppm) 177.6, 170.1, 140.0, 137.7, 137.1, 132.9, 132.3, 130.5, 129.6, 128.9, 128.0, 122.8, 118.4, 70.3, 62.7, 40.6, 38.2, 34.9, 32.7, 31.9, 31.2, 30.8, 24.6.

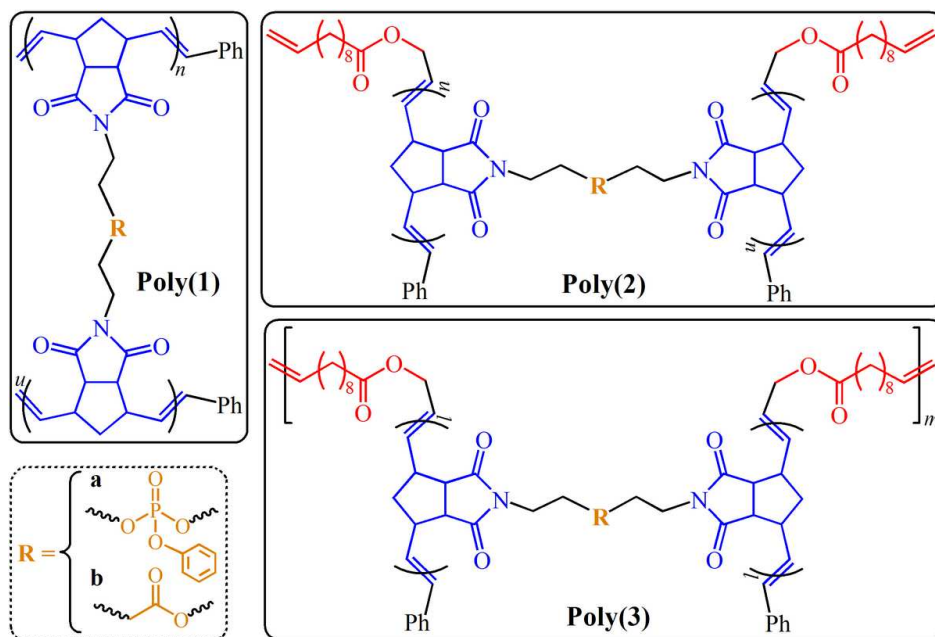


Fig. 1 The chemical structure of polymers synthesized in this study.

Results and Discussion

The functional monomer, a bis(NBI) derivative bearing two polymerizable norbornene rings and one phosphate moiety, was first synthesized by one-step esterification reaction with phenyl dichlorophosphate in CH_2Cl_2 solution. The crude product was further purified by column chromatography on silica gel using CH_2Cl_2 as

eluent to give monomer as a colorless viscous liquid. ATR-IR, NMR, GC or LC/MS, and elemental analysis were employed to verify the chemical composition, structure and purities of compound and monomer (Fig. S1-S6).

Polynorbornene-based double- and triple-stranded ladderphanes have recently been disclosed by Ru-catalyzed ROMP of the corresponding bis and tris(norbornene) monomers connected by a rigid linker in CH_2Cl_2 .⁴ In sharp contrast to the desired results, polymerization of **M1a** under the similar conditions (high concentration and long reaction time) led to the formation of organically insoluble polymer (precipitated out from the solvent during the polymerization process) in the short reaction time (about 20 min). The reason may be that the π - π interaction between the rigid segments during the course of polymerization could restrict the rigid moiety aligned to the same direction, which would finally be beneficial to the stereo-selectivity to guarantee the formation of expected ladder-like structures. Simultaneously, the π - π stacking interaction between conjugated bonds along the longitudinal axis of polymers, and van der Waals interaction between the neighboring polymeric backbones in the second dimension may also be responsible for such long ordered patterns.⁵ However, for **M1a** containing two polymerizable norbornene rings and one flexible phosphate moiety, crosslinking reaction is prone to occur under general ROMP conditions. Thus, only the highly dilute solution with the short reaction time may prevent crosslinking reaction effectively and obtain desired structure. Treatment of **M1a** with 10-30 mol% of the diverse Grubbs catalysts afforded, in high yields, the double-stranded poly(**1a**), which were soluble in CHCl_3 , CH_2Cl_2 , and THF. After a screening of various parameters as reported in Table 1, the optimum conditions for the polymerization were found (Fig. S7 and S8). The ^{13}C NMR spectrum of poly(**1a**) matched nicely that of monomer and the signals of poly(**1a**) were relatively sharp (Fig.

S9a), which was consistent with it having a double-stranded structure.

Table 1 Analytical data for ladder-like polymers prepared via ROMP^a

Entry	Polymer	Catalyst	t (h)	Temp (°C)	[M]: [C]	Yield ^b (%)	$M_{n,MALLS}^c$	M_w/M_n^c
1	Poly(1a)	C1	1	30	10: 1	92	4300	1.41
2	Poly(1a)	C1	1	50	10: 1	94	5100	1.52
3	Poly(1a)	C2	1	30	10: 1	96	6900	1.58
4	Poly(1a)	C2	0.5	50	10: 1	99	Insoluble	–
5	Poly(1a)	C3	1	30	10: 1	94	5800	1.44
6	Poly(1a)	C3	1	30	20: 1	96	12400	1.47
7	Poly(1a)	C3	1	30	30: 1	95	17600	1.49
8	Poly(1b)	C3	1	30	10: 1	95	4500	1.49
9	Poly(1b)	C3	1	30	30: 1	93	13700	1.51

^a ROMP reaction conditions for preparation of ladder-like polymers **1**: [**M1a** or **M1b**]: [C] = 10: 1~30: 1, [**M1**] = 10⁻³ mol/L, reaction temperature = 30~50 °C, reaction time = 0.5~1 h.

^b Obtained gravimetrically from the dried polymer.

^c Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were obtained from multiangle laser light scattering analysis.

Once the ROMP conditions were established, we decided to prepare the telechelic polymer via adding terminating agent (TA) to above ROMP system. Xie recently prepared a telechelic double-stranded polyacetylene with two terminal alkenyl groups through the **C1**-mediated chain terminating MCP of bis(1,6-heptadiyne), in the presence of a symmetrical triolefinic ether acted as a functional TA.¹³ In this case, to obtain the telechelic poly(**2a**) with relatively low molecular weight, ROMP was initiated by **C3** with the monomer to catalyst ratio of 10: 1. After full consumption of monomer, monitored by TLC (about 30 min), the residual solvent in the system was concentrated in vacuum (about 10⁻² mol/L), then excess TA was added and the mixture was further stirred for 12 h to ensure the full replacement of the ruthenium–alkylidene end group on the growing polymer chain by the olefinic group

of TA, giving the telechelic double-stranded poly(**2a**) bearing two long chain alkenyl groups. GPC trace of poly(**2a**) in Fig. 2 displayed monomodal peak with relatively moderate molecular weight distribution (1.52) and low molecular weight ($M_{n, \text{GPC}}$) of 5900, which was in accordance with the feed ratio of 10: 1 (Table 2).

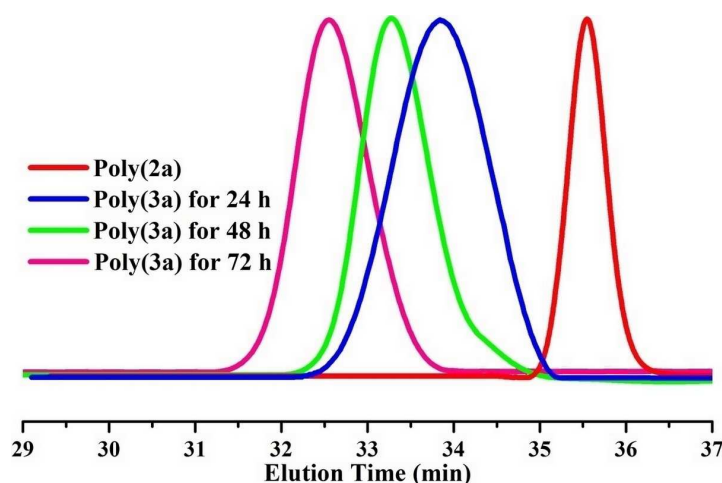


Fig. 2 MALLS–GPC traces for ladder-like poly(**2a**) and bridge-like poly(**3a**).

Table 2 Characteristics of ladder-like polymers by ROMP^a and bridge-like polymers via ADMET polymerization^b in one-pot process

Polymer	t (h)		[M]: [C]	Yield ^c (%)	$M_{n, \text{MALLS}}^d$	M_w/M_n^d	TGA		LOI ^e
	ROMP	ADMET					T_d^c (°C)	Char ^f (%)	
Poly(2a)	0.5/12	–	10: 1	92	5900	1.52	358/524	10.9	29.1
		24	50: 1	96	21300	2.03	366/535	14.2	30.4
Poly(3a)	–	48	50: 1	92	39800	1.97	–	–	33.6
		72	50: 1	94	78500	1.85	379/551	18.6	39.8
Poly(2b)	0.5/12	–	10: 1	93	4700	1.55	356	2.8	19.0
		24	50: 1	92	25300	2.06	365	2.7	–
Poly(3b)	–	48	50: 1	96	43400	1.99	–	–	–
		72	50: 1	94	82600	1.87	378	2.7	19.0

^a ROMP reaction conditions for preparation of ladder-like polymers **2**: [**M1a** or **M1b**]: [**C3**]: [**TA**] = 10: 1: 10, [**M1**] = 10^{-3} – 10^{-2} mol/L, reaction temperature = 30 °C, reaction time = 0.5 h + 12 h.

^b ADMET polymerization reaction conditions for synthesis of bridge-like polymers **3**: [**Poly(2)**]:

[**C3**] = 50: 1, [**Poly(2)**] = 10^{-1} ~1 mol/L, polymerization temperature = 60 °C, polymerization time = 24–72 h.

^c Obtained gravimetrically from the dried polymer.

^d Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were obtained from multiangle laser light scattering analysis.

^e Start degradation temperatures determined by TGA.

^f Residual quantity at 800 °C.

^g LOI values were taken as the average of three measurements.

The structure of poly(**2a**) was determined by NMR spectroscopy. For comparison, the ¹H NMR spectrum of double-stranded poly(**1a**), obtained by ROMP without a terminating reaction, showed two peaks at 6.03–5.72 and 5.70–5.38 ppm due to the protons on the conjugated *trans* and *cis* double bonds of poly(**1a**), and the *trans/cis* ratio is nearly 1: 1 based on the calculation of peak areas (Fig. 3a). After ROMP of **M1a** fully proceeded and was terminated by TA, as expected, the resonances of the telechelic alkenyl protons of poly(**2a**) at 5.92–5.71 and 5.68–5.43 ppm were observed from the ¹H NMR spectrum (Fig. 3b), which is deemed as an evidence for the newly-incorporated long alkenyl end groups from TA at the two living chain ends of the poly(**2a**) precursor. Additionally, by comparing the peak integration areas of methylene protons on each phosphate core at 4.06–3.77 ppm (S_{e+f} , 8H) with that of the terminal alkene protons at 5.02–4.95 ppm (S_j , 4H), the number-average molecular weight of poly(**2a**) was determined: $M_{n,NMR} = [(S_{e+f}/8)/(S_j/4)] \times M_{(M1a)} + M_{(TA)} + 2 \times M_{(Ar-CH)} = 6100$, which was close to that of 5900 from the GPC curve. Besides, the poly(**2a**) showed two peaks for the newly formed terminal alkenes at nearly 139 and 114 ppm in ¹³C NMR spectrum (Fig. S9b). All these observations confirmed that the double-stranded poly(**2a**) with telechelic alkenyl groups has successfully been synthesized by ROMP accompanied with the terminating reaction.

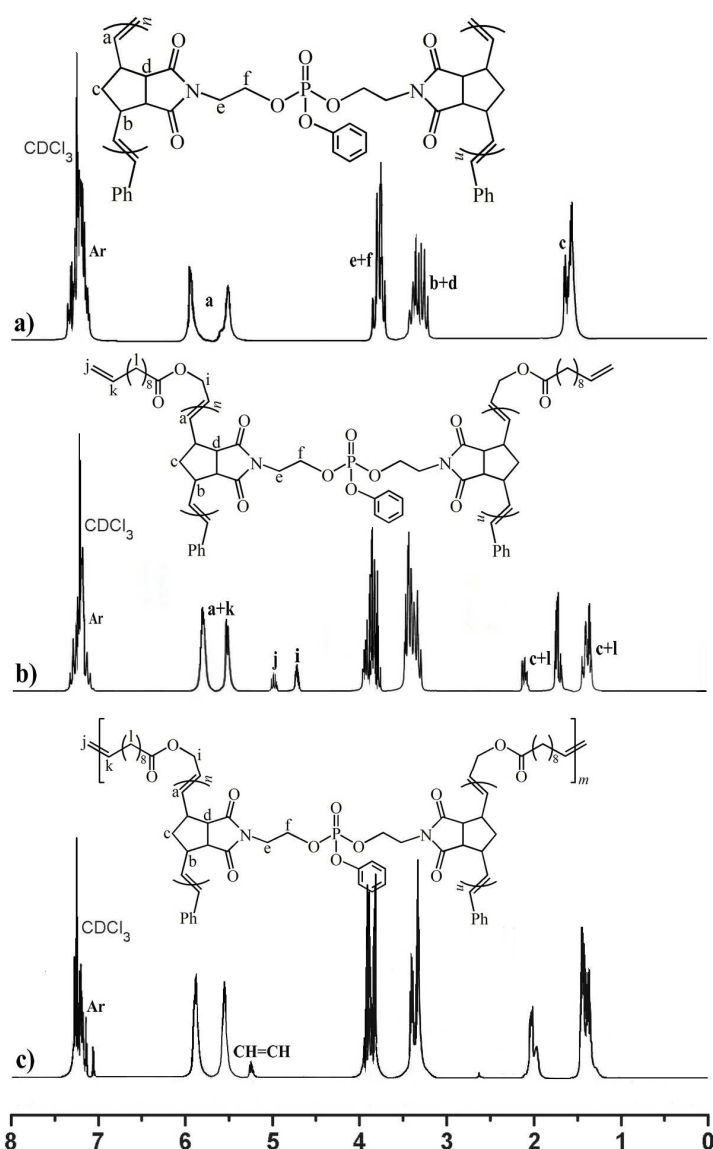


Fig. 3 ^1H NMR spectra for (a) double-stranded poly(**1a**), (b) telechelic double-stranded poly(**2a**), and (c) bridge-like poly(**3a**).

The obtained functional telechelic double-stranded poly(**2a**) with two reactive alkenyl groups could be acted as a macromonomer in subsequent ADMET polymerization. Followed by addition of **C3** to the rest of above-mentioned ROMP mixture in an opened reaction system, as expected, ADMET polymerization of macromonomer is actually promoted and gradually formed bridge-like poly(**3a**). The effect of reaction time on the molecular weight of the resultant polymer was then investigated, and the results were listed in Table 2. Considering the length of the

catalyst's lifetime in the reaction solution, a fresh batch of 0.5 mol equivalent of **C1** was then added to the reaction vessel at about 24 h intervals to ensure the effectiveness of prolonging the polymerization time past 72 h.¹⁴ GPC traces of poly(**3**) obtained from different polymerization times are shown in Fig. 2. With evolution of ADMET polymerization, the elution curves were gradually shifted to much higher molecular weight region and molecular weight distribution also became broad as compared to those of macromonomer poly(**2a**), indicating longer polymerization time could increase the molecular weight and polymer chain length. ¹H NMR spectrum of poly(**3a**) (Fig. 3c) with extending the polymerization time to 72 h showed undetectable signals of the terminal olefins 5.92–5.71 and 5.68–5.43 ppm, and the new formed peak at 5.36 ppm arose from the protons of the internal double bonds on the backbone after ADMET polymerization. These data also provided indirect evidence for the correctness of the double-stranded structure of poly(**2a**) with two telechelic end groups.

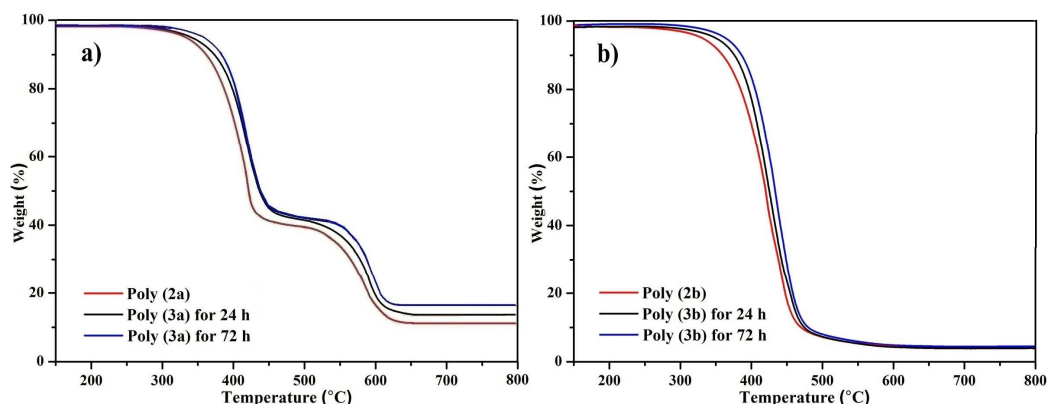


Fig. 4 TGA curves of ladder-like poly(**2**) and bridge-like poly(**3**).

The thermal stability of poly(**2a**) and poly(**3a**) with different molecular weights was systematically studied by TGA under a nitrogen atmosphere. According to the previous study, phosphonated or phosphonic acid functional single-stranded PNBI

degraded in two steps under nitrogen atmosphere.¹⁵ The first step (for the 5% weight loss) occurred between 300 and 330 °C, and then the second degradation step occurred between 340 and 500 °C. On the contrary, from the results shown in Fig. 4a and Table 2, it can be seen that the initial decomposition temperature (T_d) of poly(**2a**) is 358 °C, while the second degradation step started at 524 °C, which has increased significantly compared to the single-stranded polymer materials, and is due to the special ladder-like structure. After ADMET polymerization, the T_d values of poly(**3a**) with different molecular weights are higher than that of poly(**2a**). Besides, all the polymers did not degrade completely. From 360 °C to 450 °C, the mass decreased at a relatively mild rate. In the second period of temperature from 500 °C to 620 °C, the phosphonate groups play an important role for the thermal stability, and it was mainly due to the unusual high thermal stability of the P–O–C bond. The thermal degradation would lead to the formation of the phosphorus-containing char, which acted as a protective layer for the polymer surface.¹⁶ Therefore, the residues obtained at 800 °C increase as the molecular weight does. Although TGA experiments cannot directly reflect the flame retardant properties of materials, these experiments usually are applied for the studies of thermal stability and thermal degradation of polymers. As char production is an important and a well-known mechanism for reducing the flammability of polymers, it is important to reproduce the necessary conditions leading to char formation in order to have a practical significance. The final residual char significantly increased up to 19% with the highest molecular weight of 78500. Except for the objective double-stranded poly(**2a**) and bridge-like poly(**3a**), poly(**2b**) and poly(**3b**) without phosphate as linker was also prepared for comparison (Scheme 1, Fig. 1, and Fig. S11–S13). As shown in Fig. 4b and Table 2, the TGA curve exhibited a one-step degradation process, and the initial decomposition temperatures

were in accord with double-stranded poly(**2a**) and poly(**3a**), respectively.

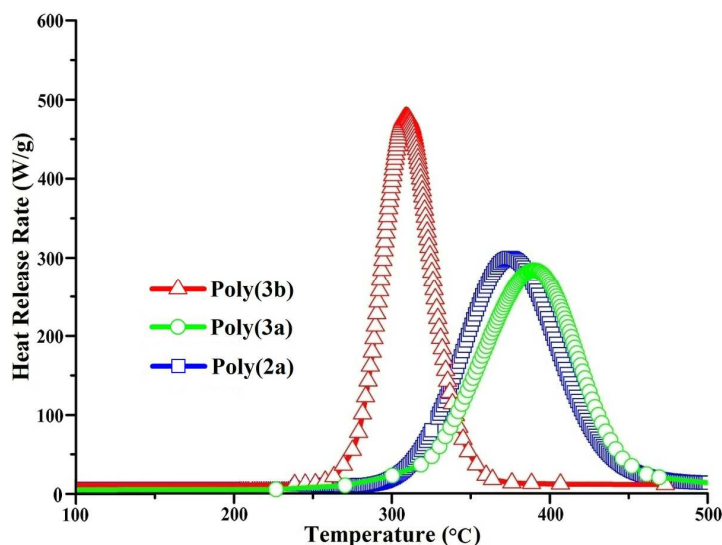


Fig. 5 MCC curves of ladder-like poly(**2**) and bridge-like poly(**3**).

The flame retardant properties of the resultant polymers were evaluated using the limiting oxygen index (LOI) test. LOI indicates the minimum oxygen concentration which supports the flaming combustion of a certain material. Usually, a material is considered to have no flame retardant property when the LOI value is less than 21.¹⁷ The LOI values of poly(**2a**) and poly(**3a**) with different molecular weights were tested using a method similar to that reported by Meier⁹ for estimating their flame retardancy, and then were listed in Table 2. A distinct and steady increase of the LOI with increasing the molecular weight was observed, and reaching a maximum value of 39.8, indicating an improved significantly flame retardant property. Moreover, flame retardant properties of the polymers have been evaluated by MCC measurement. For double-stranded poly(**2a**), poly(**2b**), and bridge-like poly(**3a**), the results of heat release rate (HRR) from MCC are shown in Fig. 5. Obviously, there is a significant difference between three samples. Usually, HRR or the peak of HRR (PHRR) is an important parameter in determining the fire hazard of materials. The higher the HRR,

the faster the heat decomposition rate of materials, which also means more volatile organic compounds would be generated. Consequently, it will speed up the flame propagation and bring a higher fire risk.^{7b,18} In the case of poly(**2b**), the curve shows a sharp HRR peak, and the value of PHRR is 490 W/g. The temperature corresponding to the PHRR is 315 °C, which means that the maximum fuel produced by poly(**2b**) decomposition at this temperature. However, it can be seen from Fig. 4 that the HRR curves of poly(**2a**) and poly(**3a**) are significantly different from that of poly(**2b**). The shape of HRR curves of poly(**2a**) and poly(**3a**) look a bit gentle compared with the sharp curve of poly(**2b**), meaning that the decomposition process of poly(**2a**) and poly(**3a**) have been changed by introducing phosphate into the double-stranded polymer. More importantly, the PHRR values of poly(**2a**) and poly(**3a**) are 295 and 278 W/g, and the temperature is increased considerably to 375 and 396 °C. All these results indicated that such resultant materials have a good flame retardant performance and could reduce the potential fire risk of practical materials evidently.

Conclusion

We have demonstrated a new strategy to prepare a bridge-like polymer with a nonconjugated polyolefin backbone and a unit of conjugated double-stranded PNBI with a phosphate linker through tandem ROMP and ADMET polymerization in a one-pot procedure. The double-stranded poly(**2a**) with telechelic alkenyl end groups was obtained first from ROMP of bis(NBI)-based monomer bearing a phosphate linker by using the catalyst **C3** and trifunctional *cis*-olefinic TA, which then can be used as a macromonomer in subsequent ADMET polymerization, yielding the resultant bridge-like poly(**3a**). GPC analysis showed that the double-stranded poly(**2a**) has a low molecular weight of 5900 with a narrow PDI of 1.52, and bridge-like poly(**3a**) has a relatively high molecular weight of 21300–78500 and a reasonable PDI

value of 2.03–1.85. In addition, the resultant double-stranded ladder-like and bridge-like polymers exhibited the good thermal stability with higher decomposition temperature (from 350 °C to 380 °C) and final residual carbonaceous mass (char) (up to 19%). Meanwhile, LOI values up to 39.8 and much lower pHRR value (278 to 295 W/g) were obtained indicated that such type of polymers may have a great potential to be used as fire proofing materials.

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Ladder- and bridge-like polynorbornene with phosphate linker: facile one-pot synthesis and excellent property

Liang Ding,^{*,†} Junmei Zhang,[‡] Lingfang Wang,[†] Chengshuang Wang[†]

A novel telechelic double-stranded polymer with two terminal alkenyl groups was first prepared through ROMP of the corresponding monomer having a phosphate linker, and was then utilized as a macromonomer in subsequent ADMET polymerization to yield the resultant bridge-like polymer.

