Phosphonated Homopolymers and Copolymers via Ring Opening Metathesis Polymerization: T_g Tuning, Flame Resistance, and Photolithography

Xiaojuan Zhang,¹ Qian Zhang,¹ Chao Xie,² Aiting Gao,³ Zheng Chang,¹ Jung Kwon Oh,⁴ Peng Yang,³ Pengfei Li⁵

¹Department of Applied Chemistry, Xi'an University of Technology, No. 5 South Jinhua Road, Xi'an, Shaanxi, 710048, People's Republic of China

²Department of Oral Implantology, State Key Laboratory of Military Stomatology, School of Stomatology, the Fourth Military Medical University, No. 169 West Changle Road, Xi'an, Shaanxi, 710032, People's Republic of China

³Key Laboratory of Applied Surface and Colloids Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, No. 199 Chang'an South Road, Xi'an, Shaanxi, 710119, People's Republic of China ⁴Department of Chemistry and Biochemistry and Center for Nanoscience Research (CENR), Concordia University, 7141 Sherbrooke St. West, Montreal, Quebec, H4B 1R6, Canada

⁵Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University, No. 99 Yanxiang Road, Xi'an, Shaanxi, 710054, People's Republic of China

Correspondence to: Q. Zhang (E-mail: qzh@xaut.edu.cn) or P. Li (E-mail: lipengfei@mail.xjtu.edu.cn)

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ABSTRACT: Phosphonated and epoxy-containing norbornene based monomers were prepared by Diels–Alder reaction. They were then combined with three other commercial cyclic unsaturated monomers to synthesize phosphonated homopolymers and copolymers via ring opening metathesis polymerization (ROMP) using second-generation Grubbs catalyst. Glass transitions of these polymers were tunable in a broad range from –14 to 91 °C by varying the flexibility of comonomer. Interestingly, copolymerization with cyclopentene inhibited the crystallization of polycyclopentene, and instead, led to a copolymer with two $T_{\rm g}$ s. Paradoxically, results from thermogravimetric analysis (TGA) were not consistent with the followed flame-retarding experiment, implying that the early weight loss from

phosphonated moieties did not deleteriously affect the flameresistant property which actually depended more on the percentage of char residual after thermal degradation. In application studies, the norbornene derivative phosphonated polymer was tested for the first time as flame retarding material, and showed significant self-extinguishing ability. In a second study, photolithography was also successfully performed via thiol-ene "click" chemistry, which allowed the phosphonated polymer a promising negative photoresist. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1396–1408

KEYWORDS: flame resistance; photolithography; norbornene; phosphonate; ROMP

INTRODUCTION Phosphorus containing polymers (PCPs) have played versatile roles in shaping the world. Biologically, polyphosphate backbone upholds nucleic acids and insures inheritance of human beings.¹ In industry, PCPs are very promising as halogen-free flame retardants.^{2–6} They are also very good adhesives to bind metals due to potentially strong complexation abilities, which also found applications in dental and bone tissue engineering.^{7–9} In the development of highly efficient proton-conducting fuel-cell membranes, PCPs can compete with sulfonic acid materials for highly chemical and thermal stabilities.^{10–12} The great interest in these fields has stimulated the originality in exploring new chemical structures of PCPs, endeavors were made in this aim in the recent years.

Phosphate, phosphonate, and phosphinate were the most studied in literatures,⁷ other examples can be phosphazene derivatives.^{2,12} Free radical polymerization may be the most conventional method in obtaining PCPs. Since Kosolapoff observed polymerizability of vinylphosphonate, homopolymers and copolymers were prepared in free radical way till recently.¹³⁻²⁰ To achieve more control on the polydispersity and chemical structure, anionic polymerization,^{21,22} and controlled free radical polymerization^{23,24} were successfully developed. Rare-earth metal mediated polymerization has recently be employed to obtain high molecular weight polyvinylphosphonate,^{13,25-27} which presented exciting opportunities to obtain new macromolecular architectures despite of

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SCHEME 1 Monomers including some synthetic routes in the research.

a few limitations and the methodology is still under investigation.²⁸ Among the synthetic techniques, ring opening metathesis polymerization (ROMP) has seen an increasing interest in the synthesis of PCPs since 2009^{28,29} for some reasons: (1) novel norbornene-based structure (phosphorous on side chain)²⁸ and some unsaturate linear structure (phosphorous on backbone)^{8,30} can be obtained; (2) olefin methathesis catalysts are highly tolerant of functional groups and reaction conditions are milder (even in ionic liquids)³¹ compared to anionic and controlled radical polymerizations;²⁸ (3) living features and controllability are very good especially when the third generation Grubbs catalyst is used.^{8,28,30}

The current contribution targets at learning the thermal properties of PCPs via ROMP method on the homopolymer and copolymer of norbornene based polymers because these information are very important in applications,³² however, not paid much attention till now [except in Ref. (28)], especially when flexibility is tuned by adjusting the chemical structures of macromolecular backbones. Besides, an epoxy-containing norbornene monomer with rising potentials as a new crosslinker in resin industry was also used in this study.^{33,34} A second aim of this contribution is to test the flame retardance and photo resistance of PCPs for the promising industrial applications. Although phosphazene-based polymers have showed significant flameretarding property in halogen-free epoxy thermosetting systems,² PCPs from ROMP have not been reported for the same use so far. In this contribution, it is for the first time norbornene-based PCP homopolymer was tested for this purpose. On the other hand, polymers used as photoresist in lithography prepared via ROMP have proved very effective through thiol-ene click chemistry,³⁵ the current contribution is to verify this point using selected PCPs synthesized.

The monomers used are shown in Scheme 1. Monomer 1 and 2 were synthesized via Diels-Alder addition using either diethyl vinylphosphonate or glycidyl methacrylate with cylcopentadiene. Monomer 1 is a phosphonated component, 2 is epoxycontaining and showing increasing interest in the preparation of advanced epoxy curing resins.³³ Besides, the recent developed thiol-epoxy "click" chemistry by Khan and coll. is expected to be a very powerful tool for the postmodification of this monomer and its polymer, and would be very promising in the followed applications.^{36–39} Monomers **3** to **5** were from commercial sources. Monomer 3 has an anhydride moiety which can be transformed to carboxylic acid by hydrolysis and has general interest in applications. $^{\rm 28,40}$ Monomer 4 and 5 are less bulky, and were used to gain more flexibility in the chemical structures (note: monomer 5 incorporates linear structure with double bond, so should be more flexible than monomer **4**).

Polymers studied in the research were classified into homopolymers and copolymers, shown in Scheme 2. Statistical copolymers were prepared from equimolar monomers except **CP3** where less monomer **3** was used due to poor solubility of resulting polymers.

EXPERIMENTAL

Materials and Characterization

Materials were obtained from commercial sources and were used without further purification unless otherwise specified.





SCHEME 2 Synthetic routes of polymers in the research.

Triethyl phosphate (98%), methanol (AR), dimethyl sulfoxide (AR), benzene (GR), xylene (AR), and triethylamine (AR) were purchased from Sinopharm Chemical Reagent. 1,2-Dibromoethane (99%), dicyclopentadiene (97%, endo form, containing 100-200 ppm TBC as stabilizer), cyclopentene (96%), ethyl vinyl ether (98%, containing 0.1% KOH as stabilizer), bromotrimethylsilane (98%, containing Cu as stabilizer), *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (99%), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (Lucirin TPO, 97%) were from Aladdin Corp. Glycidyl methacrylate (GMA, 96%, containing 100 ppm MEHQ as inhibitor) and pentaerythritol tetra(3-mercaptopropionate) (PETMP, 90.0%) were from J&K Scientific. The Grubbs second generation catalyst, 1,3-bis(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene)(tricyclohexylphosphine)ruthenium (97%) was from Beijing HWRK Chem.

Tetrahydrofuran (THF) and dichloromethane (DCM) were all HPLC grade from Oceanpak and the DCM was degassed before use. HPLC acetonitrile was from Kermel inc. 2-Norbornene (>99.00%) was from TCI. The purification of triethylamine was according to reference.⁴¹

¹H-NMR spectra were recorded using a Bruker Advance III 400 MHz spectrometer equipped with autosampler. The CDCl₃ singlet at 7.26 ppm and DMSO-d₆ quintet at 2.5 ppm were selected as the reference standard. Spectral features

are tabulated in the following order: chemical shift (ppm); multiplicity (s, singlet; d, doublet; t, triplet; m, complex multiplet); number of protons.

Relative molecular weight (MW) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC, Malvern Viscotek 270MAX) from Malvern Instruments. It was equipped with a VE 3580 refractive index (RI) detector. Two PolyAnalytik columns (LT3000L and LT6000L) were used with THF as eluent at 35 °C at a flow rate of 1 mL/min.

The FTIR spectra of the samples were recorded on a Shimadzu Prestige-21 ATR spectrometer equipped with ZnSe crystal by single reflection in the range 4000-650 cm⁻¹.

Differential scanning calorimetry (DSC) was used to determine the temperature and enthalpy of transitions of the polymers protected in high purity N₂ using Mettler Toledo DSC 1. Samples were sealed in aluminum pans (40 μ L) and scanned at a heating rate of 20 °C/min and cooling rate of 10 °C/min.

Thermogravimetric analysis (TGA) was conducted using a Q50 thermogravimetric analyzer from TA Instruments. Samples were placed in platinum crucibles scanned from 100 to 600 °C under N₂ atmosphere at a heating rate of 20 °C/min.

Monomer Synthesis

Synthesis of Diethyl-5-norbornen-2-ylphosphonate (NBDEP, 1) First Step: Synthesis of Diethyl (β-Bromoethyl) Phosphonate

Arbuzov reaction was made in this step based on reference procedures.⁴² A round-bottom flask equipped with a reflux condenser was charged with 1,2-dibromoethane (5.515 mL, 64.00 mmol, 4.00 eq.) and triethylphosphite (2.716 mL, 16.00 mmol, 1.00 eq.). The mixture was then heated at 150–160 °C and stirred for 13 h. The product was finally obtained as colorless oil by vacuum distillation (2.651 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ : 4.12 (m, 4H), 3.53 (m, 2H), 2.42–2.33 (m, 2H), 1.33 (t, 6 H).

Second Step: Synthesis of Diethyl Vinylphophonate (DEVP)

The mixture of diethyl (β -bromoethyl)phosphonate (2.651 g, 10.82 mmol, 1.00 eq.), triethylamine (2.190 mL, 15.15 mmol, 1.40 eq.), and benzene (4.130 mL, 46.53 mmol, 4.30 eq.) was refluxed for 1 h. Then, the triethylamine hydrobromide was filtered off and benzene was removed in reduced pressure. The residue was further purified under reduced pressure to obtain pure product as colorless oil (1.610 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ : 5.70 (m, 1H), 5.11 (m, 2H), 4.01 (m, 4H), 2.50 (dd, 2 H), 1.22 (m, 6H).

Third Step: Synthesis of Monomer 1 (NBDEP)

Diethyl Vinylphophonate (5.225 mL, 34.00 mmol, 1.00 eq.) and freshly pyrolyzed cyclopentadiene (14.05 mL, 170.0 mmol, 5.00 eq.) were added to a round-bottom flask equipped with a condenser. 2,6-Di-tert-butyl-4-methylphenol (119.9 mg, 0.5440 mmol, 0.0160 eq.) was added and the mixture was refluxed for 14 h at 160-165 °C. At the end, the reaction mixture was cooled and concentrated under reduced pressure and purified by column chromatography (petroleum ether/ ethyl acetate = 7:3 v/v) to yield a yellowish oil (4.422 g, 56%). Endo: ¹H NMR (400 MHz, CDCl₃) δ : 6.14 (S, 1H), 6.07 (S, 1H), 4.05 (m, 4H), 3.16 (S, 1H), 2.94 (S, 1 H), 2.00 (m, 1H), 1.44 (t, 1H), 1.33–1.25 (m, 8H), 1.19 (d, 1H). Exo: ¹H NMR (400 MHz, CDCl₃) δ: 6.14 (S, 1H), 6.07 (S, 1H), 4.05 (m, 4H), 3.16 (S, 1H), 2.94 (S, 1 H), 2.30 (m, 1H), 1.44 (t, 1H), 1.33-1.25 (m, 8H), 1.19 (d, 1H). ELEM. ANAL. Calcd. for C₁₁H₁₉O₃P: C, 57.38%; H, 8.32%; C/H, 6.897. Found: C, 56.50%; H, 8.32%; C/H, 6.795.

Synthesis of 5-Methylbicyclo[2.2.1]hept-2-ene-5-Carboxylic Acid Glycidyl Ester (NBMGE, 2)

A round-bottom flask was charged with fresh cyclopentadiene (5.961 g, 90.18 mmol, 3.00 eq.) by pyrolysis of its dimer, GMA (4.273 g, 30.06 mmol, 1.00 eq.), and 7.420 mL xylene, then held at 140 °C for 10 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether as the eluent to get the pure product as a colorless oil (2.766 g, 44%). Endo: ¹H NMR (400 MHz, CDCl₃) δ : 6.19 (m, 1H), 6.05 (m, 1H), 4.43 (dd, 1H), 3.94 (m, 1H), 3.20 (m, 1H), 3.03 (s, 1H), 2.83 (m, 3H), 2.43 (dd, 1H), 1.42–1.34 (m, 2H), 1.11 (s, 3H), 0.86 (dd, 1H). Exo: ¹H NMR (400 MHz, CDCl₃) δ : 6.11 (m, 1H), 6.03 (m, 1H), 4.34 (m, 1H), 3.83 (m, 1H), 3.16 (m, 1H), 2.83 (m, 1H), 2.64 (m, 3H), 1.90 (dd, 1H), 1.55 (d, 2H), 1.42–1.34 (m, 1H). ELEM. ANAL. Calcd. for $C_{12}H_{16}O_{3}$: C, 69.21%; H, 7.74%; C/H, 8.942. Found: C, 70.23%; H, 7.69%; C/H, 9.137.

Synthesis of Homopolymers HP1-5

Monomer 1-5 was homopolymerized, respectively, via ROMP in the presence of second-generation Grubbs catalyst. In a typical polymerization, a vial was charged with monomer and a magnetic bar with the protection of argon. Then dry degassed DCM was added to the vial to obtain a 0.1M solution. Catalyst as a stock solution in DCM (0.5 mol% with respect to the monomer) was injected into the vial. The mixture was left to react at room temperature for 6.5 h. When reaction finished, ethyl vinyl ether (5 eq. to the monomer) was added to quench the reaction. The homopolymer HP1 and 3 were purified by precipitation in ethyl ether and acetone respectively, HP2, 4 and 5 were precipitated in methanol. The products were dried in vacuum for 24 h. HP1: ¹H NMR (400 MHz, CDCl₃) δ: 5.74-5.62 (b), 5.40-5.26 (b), 4.04 (b), 3.19 (b), 2.81 (b), 2.35 (b), 2.04 (b), 1.91 (b), 1.73 (b), 1.28 (b). HP2: ¹H NMR (400 MHz, CDCl₃) δ : 5.37–5.33 (b), 5.21 (b), 4.41 (b), 3.92 (b), 3.32-3.20 (b), 2.96 (b), 2.84 (b), 2.65 (b), 2.43 (b), 2.04 (b), 1.90 (b), 1.68 (b), 1.58 (b), 1.26-1.08 (b). **HP3**: ¹H NMR (400 MHz, DMSO-d₆) δ : 5.60 (b), 5.43 (b), 3.54 (b), 2.99 (b), 1.78 (b), 1.27 (b). **HP4**: ¹H NMR (400 MHz, CDCl₃) δ: 5.34 (b), 5.21 (b), 2.79 (b), 2.43 (b), 1.80 (b), 1.56 (b), 1.35 (b), 1.04 (b). HP5: ¹H NMR (400 MHz, CDCl₃) δ : 5.38 (b), 1.98 (b), 1.39 (b).

Synthesis of Statistical Copolymers CP2-5

To prepare CP2 typically, a flask was charged with 1 (252.4 mg, 1.10 mmol), 2 (228.1 mg, 1.10 mmol), DCM (0.725 mL), and stirred with a magnetic bar in nitrogen flow. Then, the second-generation Grubbs catalyst (9.490 mg, 11.2 μ mol in 0.500 mL DCM) was injected into the flask to start the reaction. The reaction was allowed to proceed at room temperature for 10 h. The polymerization was guenched by addition of excess of ethyl vinyl ether. The resulting polymer was isolated by precipitation in hexane. Similarly, 1 (275.3 mg, 1.20 mmol), 3 (28.05 mg, 0.170 mmol), DCM (0.700 mL), and catalyst (5.220 mg, 0.45 mol % relative to the total of monomers) were used. The mixture was stirred for 13 h at room temperature and then precipitated in acetone/diethyl ether (1:9) to obtain CP3. To prepare CP4, 1 (275.3 mg, 1.20 mmol), 4 (112.6 mg, 1.20 mmol), DCM (0.995 mL), and catalyst (12.49 mg, 0.60 mol % relative to total monomers) were used. The polymer was isolated by precipitation in hexane/diethyl ether (1:1) after being stirred for 10 h at room temperature. For the synthesis of CP5, the system with 1 (293.7 mg, 1.30 mmol), 5 (86.89 mg, 1.30 mmol), DCM (0.980 mL), and catalyst (13.13 mg, 0.60 mol % relative to total monomers) was stirred for 11 h. The polymer was isolated by precipitation in hexane/diethyl ether (1:1). **CP2**: ¹H NMR (400 MHz, CDCl₃) δ : 5.75–5.64 (b), 5.38-5.21 (b), 4.42 (b), 4.03 (b), 3.91 (b), 3.21 (b), 3.13-2.83 (b), 2.64 (b), 2.37 (b), 2.20-1.65 (b), 1.38-1.07 (b), 0.88 (b). **CP3**: ¹H NMR (400 MHz, CDCl₃) δ : 5.76–5.62 (b),





SCHEME 3 Schematic process for negative lithography. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

5.39–5.26 (b), 4.04 (b), 3.19 (b), 2.80 (b), 2.35 (b), 2.18–1.67 (b), 1.34–1.20 (b). **CP4**: ¹H NMR (400 MHz, CDCl₃) δ : 5.75–5.60 (b), 5.33–5.20 (b), 4.04 (b), 3.18 (b), 2.78 (b), 2.42 (b), 2.16–1.71 (b), 1.37–1.24 (b), 1.01 (b), 0.88 (b). **CP5**: ¹H NMR (400 MHz, CDCl₃) δ : 5.67 (b), 5.38 (b), 4.03 (b), 3.17 (b), 2.82 (b), 2.37 (b), 1.96 (b), 1.70 (b), 1.40–1.28 (b).

Hydrolysis of PCPs

Bromotrimethylsilane (0.3950 mL, 2.990 mmol, 8.00 eq. to the phosphonate ester group) was added dropwise to a solution of **HP1** (86.00 mg, 0.3740 mmol) in dry DCM (0.955 mL) in nitrogen flow. The reaction mixture was stirred for 24 h at room temperature. After removing excess bromotrimethylsilane under reduced pressure, methanol (1.515 mL) was added to the mixture and stirred for 24 h at room temperature, and then rotovaped to eliminate solvent and other volatile molecules to obtain the corresponding phosphonic acid functionalized polymers. Copolymers (**CP4** and **CP5**) were also hydrolyzed using the procedure similarly.



FIGURE 1 FTIR spectra for monomers 1 and 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flame-Resistant Experiment

Combustion experiments were carried out similar to UL-94 vertical burning experiments. A folded piece of print paper (140.0 \times 13.00 \times 0.090 mm, A4, 70 g/m²) was used as the testing substrate. Then, THF solution of polymer (100 mg/ mL) was used to apply a coating on the surface of the print paper followed by drying with heat blower and kept at room temperature for 18 h before use. The sample was ignited using a butane gas lighter 5 mm underneath. The combustion process was recorded with a digital camera. A blank without polymer coatings was also tested in parallel.

Photolithography

Preparation of the Polymer Thin Film

The substrates of glass slide (1 mm in thickness) and silicon wafer ([110] crystal plane, 0.43 mm in thickness) were cleaned with piranha acid $(H_2SO_4/H_2O_2 = 70/30 \text{ v/v})$ for 30 min at 80 °C (caution: Piranha acid reacts violently with organic materials, so must be handled with great care). And then they were washed with excess of deionized water, ethanol, and acetone for 15 min in sonicator. The cleaned silicon wafers were precoated 5 nm Cr adhesion layer and then 45 nm thick gold layer and cleaned in plasma cleaner (PDC-32G, Harrick) for 3 min. Solutions of polymer HP1 and CP4 (50 mg/mL) containing Lucirin TPO (10 wt % related to the polymer) as photoinitiator and PETMP ($\chi_{SH/C=C} = 4:1$ for glass slide, 6:1 for silicon wafer coated by gold) as crosslinker were freshly prepared in chloroform and protected from light. Then, thin films were prepared by spin coating (40 s, 2500 rpm) on the substrates just mentioned using a spin coater (WS-650MZ-23NPP80, Laurell Technologies) and dried in vacuum for 40 min at room temperature in dark before use.

Patterning

Photolithographic patterns were made in photochemical chamber (BL-GHX-V, Bilang Biotechnology) using a 1000 W mercury lamp as the UV-light source. The light intensity (10 mw/cm² at 254 nm) on the sample surface was maintained and tracked by spectroradiometer (Solatell, Sola Scope 2000^{TM}). Polymer films on substrates were placed in the



FIGURE 2 ¹H NMR spectra of the synthetic monomers and polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction chamber 40 cm underneath the lamp covered by a photomask preinscribed with patterned windows (Scheme 3). After exposure for a couple of minutes, the patterns were obtained after development in THF for less than 60 s. Then, the patterns of microarray were observed and pictured under an optical microscope (Eclipse Ti-U, Nikon, Japan).

RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization

Norbornene derivative species of monomer 1 and 2 were synthesized conveniently via Diels–Alder cycloaddition reaction from corresponding starting materials with cyclopentadiene freshly prepared by thermal cracking its dimer. The resulting phosphorus-containing monomer 1 and epoxy-containing monomer 2, having been subjected to rigorous vacuum distillation and column chromatography purification procedures, were highly pure, as confirmed by FTIR, NMR, and elemental analysis (Figs. (1 and 2)). Monomer 1 showed absorbance at 1022 and 957 cm⁻¹ that belonged to the asymmetric stretching of the P—O—C group in FTIR.^{12,43} The peak at 1215 cm⁻¹ corresponded to P=O stretching.^{43–45} Monomer **2** showed characteristic peak of epoxy at 912 cm⁻¹, and the peak at 1725 cm⁻¹ was attributed to C=O of the ester group.^{45,46} The isomers of endo and exo were calculated by NMR based on 1.8 ~ 2.4 ppm (monomer **1**) and 6.1–6.3 ppm (monomer **2**) respectively.^{33,40,47,48} It was found that the endo/exo ratio of monomer **1** was 1/1 and 2/1 for monomer **2**, which were consistent with the findings in references very well.^{33,40,48}

Polymerization of the monomers was performed using the second-generation Grubbs catalyst via ROMP method. The successful polymerization could be visually spotted by the increasing viscosity of the reaction mixture after a few hours. Pure polymers were collected by precipitation in a poor solvent followed by drying in vacuum. In copolymerization, the feeding ratio of two monomers was maintained at 1/1, except for CP3 which has higher content of monomer **1** for the fact that poor solubility was resulted when more monomer **3** was used. ¹H NMR spectra of the polymers were shown in Figure 2, corresponding well to spectra of their monomers. Relative molecular weight and PDI were shown in Table 1. The GPC chromatographs were shown in Supporting Information Figure S1. It may be noted that the seemingly higher PDI of HP2 than other polymers may raise the concern for the adsorption of polymer to column materials in GPC analysis, but in the separate experiment with varying injecting volumes, this possibility was ruled out.

Thermal Property

Thermal properties of the synthesized polymers were studied by DSC and TGA in nitrogen atmosphere. DSC thermographs were shown in Figure 3, the results were summarized in Table 1. Generally, all the polymers showed glass transitions above room temperature except HP5 and CP5. $T_{\rm g}$ of HP1 was found at 57 °C, higher than HP2 (51 °C) and HP4 (44 °C). HP3 showed no transition in the range of scanning temperature. This is consistent with its hard nature when pressing with spatula. It is noted that HP3 had very poor solubility in common organic solvents, such as acetone and THF except in highly polar solvents such as DMSO and DMF with actually still limited solubility, indicating high polarity so that the dipole-dipole interactions may severely interfere with the segments movement of polymer chain and consequently leading to high T_{g} . It may also be related to the hardly avoidable hydrolysis of small amount of anhydride to carboxylic acid, and the limited ionic characteristic may be the cause to increase chain rigidity, and thus lift T_g as found in ionic complexes.^{49,50} HP5 showed no glass transition, instead, a first order transition at lower temperatures, $T_{\rm m} = 1.2$ °C $(\Delta H_{\rm m} = -34.2 \text{ J/g})$. The transition peaks were both available during heating and cooling cycles with big supercooling of 36.8 °C. The results suggested melting and crystallization processes, which is not surprising for the highly flexible chain



Entry	M 1 Content ^a (%)	Time (h)	M _n	PDI	<i>T</i> _g (°C)	10 wt %loss in °C	Residual ^b wt %
HP1	100	7	$7.7 imes10^3$	1.59	57	331	31
HP2	0	9	$8.1 imes 10^4$	2.31	51	367	3
HP3	0	12	/	/	/	343	33
HP4	0	10	$4.6 imes10^4$	2.28	44	410	6
HP5	0	9	4.0×10^4	1.86	$T_{\rm m} = 1.2 \ ^{\circ}{\rm C}$ $\Delta H = 34.2 \ {\rm J/g}$	405	0
CP2	50	10	$4.6 imes10^4$	2.58	63	342	21
CP3	88	13	$1.0 imes 10^4$	1.36	91	331	34
CP4	50	10	$3.8 imes10^4$	2.24	52	335	27
CP5	50	11	$1.9 imes 10^4$	2.52	-14, 20	328	28

TABLE 1 Synthetic Parameters and Thermal Properties of Homopolymers and Copolymers

^a M 1 content = monomer 1/(monomer 1 + comonomer X).

structure of **HP5**. Copolymers with equimolar (except **CP3**) composition of monomer **1** and a comonomer **2**, **4–5** showed more interesting results. T_{gs} of **CP2** and **CP4** were at 63 and 52 °C, respectively, close to their corresponding homopolymers. The higher T_{g} of **CP2** than **CP4** was probably due to the bulky side group of monomer **2** compared to **4**. **CP3** showed an increased T_{g} at 91 °C, much higher than **HP1** by 34 °C. Considering the high T_{g} of **HP3** as explained above, the incorporation of monomer **3** by only 12% to **HP1** backbones hindered the movement of chain segments and so significantly increased T_{g} in the copolymer. In contrast, **CP5** showed much lower T_{g} than **HP1**. In addition, two T_{gs} (-14 and 20 °C, indi-



FIGURE 3 DSC traces of homopolymers and copolymers. Two glass transitions of **CP5** were indicated by arrows. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^b At 600 °C.

cated by arrows in Fig. 3) in broad temperature range (-25 to 40 °C) were found, and no melting was observed during heating in contrast to **HP5** because of the incorporation of monomer **1** to destroy the regularity in backbones. Such a broad $T_{\rm g}$ manipulation in PCPs can facilitate the design of new norbornene based PCPs via ROMP method, for example in shape-memory applications.⁵¹

TGA curves were shown in Figure 4 with the results summarized in Table 1. PCPs typically showed two steps of thermal degradation. The first step was from 313 to 331 °C and the second from 342 to 613 °C. The former step was mainly due to loss of ethylene and the second due to C—P bond according to reference.²⁸ **HP4** and **HP5** showed mainly one step process for their simplified C and H chemical compositions. The degradation starting temperatures (when comparing 10 wt % loss in Table 1) of phosphonate homopolymers and copolymers were mostly lower than **HP4** and **HP5** by 50–60 °C approximately. This is interesting, because PCPs were generally thought to be flame retardants instead of



FIGURE 4 TGA curves of polymer samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]



Crosslinked structure

SCHEME 4 Mechanism of hydrolysis of phosphonate and the resulting crosslinked structure of PCPs (modified based on reference 52).

HP4 and HP5 types of polymers made from C and H only. The paradox can be explained by the residual wt % after degradation. At 600 °C, the residual wt % of HP1 was 30%, much higher than HP4 and HP5 nearly at 0%. The corresponding copolymers CP4 and CP5 considerably increased residual wt % by more than 20%, indicating the significant effect from phosphonated monomer 1. The results for HP2 and CP2 were very similar to HP4, 5 and CP4, 5. With the results above, it may be found that thermal stability and flame resistance can have slightly different meanings in essence, the former was related to cleavage of chemical bonds and release of volatile

species, while the later was a practical consequence and mainly related to the ability to retain weight during degradation at high temperatures. However, the residual wt % of **HP3** was quite high, close to **HP1**. It can be due to the compact and rigid nature of **HP3** as seen by high T_{g} , which may delay the decomposition process by hindering the movement of highly reactive intermediate in matrix during degradation.

Hydrolysis

The PCPs were also tested in hydrolysis to yield phosphonic acid by treating with trimethylsilyl bromide in dry DCM to



FIGURE 5 FTIR of PCPs before and after hydrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yield trimethylsilyl esters, which were then cleaved in methanol to afford phosphonic acid. The mechanism is shown in Scheme 4, partly referring to reference.⁵² The successful hydrolysis of PCPs was confirmed by FTIR (Fig. 5). The broad band between 1060 and 905 cm⁻¹ appeared after hydrolysis was attributed to the stretching of P—OH.^{45,53,54} However, the solubility of the hydrolyzed samples was much decreased (Supporting Information Table S1) in contrast to their ester forms before hydrolysis in most organic solvents.²⁸ The reason could be due to the crosslink process where phosphonic acid reacted further to form phosphonic anhydride (Scheme 4).

Applications

Flame-Retarding Experiment

To study the flame-resistant property, the norbornene derivative PCPs synthesized from ROMP were for the first time subjected to flame retarding experiment. The results were shown in Figure 6. When bare print paper was used (blank test), the combustion was fast and stable till the end. Curling-up ash was left behind with little weight on. In contrast, when the paper was coated with HP1, the combustion was much slower, and the flame self-extinguished shortly [Fig. 7(a)]. To be more specifically, the average burning speed in air quickly decreased from 0.94 cm/s of the blank paper slip to 0.27 cm/s of the coated specimens. To confirm the efficiency of flame retardancy, limiting oxygen index experiment (LOI, according to EN ISO4589-2:1999 and ASTM D2863-13) was conducted. Blank paper slip quickly burned at LOI = 21% at a speed of 1.0 cm/s. In contrast, when coated with 40 wt % HP1 on the surface, LOI increased and approached 25% with a much decreased burning speed <0.1 cm/s. At oxygen concentration = 35%, the burning speed was still below 0.5 cm/s which is half of the value of blank paper. The results indicated that HP1 coating did retard the flame by an LOI increase of 19% compared to the



FIGURE 6 Digital photographs of the combustion process of print paper without (a) and with (b) **HP1** coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 Digital photograph of the paper coated with HP1 after combustion (a) and the SEM image (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blank sample. Considering that the specimen was a coated paper slip with thin HP1 layer on top, and the high inflammability of blank paper, the result should be an averaged reflection of blank paper and HP1. After complete combustion, the paper slip kept its original shape very well, and had enough hardness after combustion when pressed (Fig. 7). Examination of the burned paper showed a clear char layer on top [Fig. 7(a)], which is typically found in phosphorouscontaining materials indicating the formation of phosphoric acid and consequently shielding the materials from oxygen.⁵⁵ SEM showed more morphological details in Figure 7(b). A gassy surface with many pores breaking through was observed, indicating the typical intumescent char formation.² Copolymers showed less flame-retarding efficiency than **HP1** because of the lower phosphorous content, and so, cyclotriphosphazene of high phosphorous content and should be anticipated more effective.² It is interesting to see from literatures that aryl-substituted PCPs are the most studied up to date besides cyclotriphosphazene-based polymers,² such as arylphosphinate,^{56–58} phenylphosphonate,^{59,60} phenyl phosphate,⁶¹ and phenyl-phosphorous amide⁶² where phosphorous was incorporated into the resin of epoxy^{56,60,62} or novolacs⁵⁷ to act as flame-retarding component. Most of these mentioned PCPs showed LOI from 22 to 40%, except for a thiol-containing polyphosphonate with a reported high LOI = 60% in Ref. 59. It has been known that LOIs of PCPs are typically proportional to the phosphorus contents (*P*%),⁵⁷ for example, polystyrene with phosphate pending groups showed typical increase of LOI from 25 to 41% with *P*% increasing from 4.97 to 12.79% by weight.⁶¹ In a



SCHEME 5 The reactive mechanism of photo-induced crosslink in **HP1** via thiol-ene click chemistry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 Optical microscopic photographs of the arrays formed after UV irradiation using a photo mask. The films were tested for **HP1** (a) and **CP4** (b) on glass slide substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

second example, LOI increased from 24.5 to 34.0% with P % from 1.50 to 5.20%.⁵⁷ Nevertheless, P % may not be the only factor to impact on LOI. In the just mentioned two examples, $T_{\rm g}$ s are mostly above 100 °C because of the steric aryl substitutions and especially after complete curing. In another example, pheynyl-phosphorous amides of lower T_{g} showed lower LOIs than the just mentioned two examples, that is, LOI = 28% at P% = 5.23% with $T_{\rm g}$ = 60 °C.⁶² In this contribution, P % of HP1-coated paper slip is 5.4% which resulted in LOI = 25%, a little lower then reference 62, where $T_{\rm g}$ s are relatively close. Take all these results into consideration, it may reach a conclusion that LOI of norbornene-based polyphosphonates is a little lower than aryl-substituted PCPs probably because the flexible olefinic backbone of HP1 would be less hindered than aromatic backbones towards highly reactive intermediates during combustion on molecular levels.

Photolithography

A second application study was to investigate the ROMP derived PCPs as photoresists. In recent years, ROMP derived polymers showed increasing interests in photomicro manufacturing area, taking advantage of the highly efficient thiolene click chemistry.³⁵ Recently, it was also successfully applied in making fine 3D microstructures using two-photon induced thiol-ene reactive process.⁶³ The convenience of copolymerization with maleic anhydride derivatives, such as monomer **3**, was regarded as a benefit to obtain high performance photoresist.⁴⁰ So in this contribution, we for the first time tested the PCP polymer, **HP1**, as negative photoresist via thiol-ene click chemistry. The mechanism is illustrated in Scheme 5, and the result in Figure 8.

The features of the inscribed micro-structure after development on the thin film of **HP1** were visualized by optical microscopy using a transmission set-up. Periodic arrays with sharp contrast can be observed on the film, indicating the successful photo-crosslink process. The results were also very positive on gold wafers (not shown).

CONCLUSIONS

A series of phosphonated norbornene based homopolymers and copolymers were synthesized, and their chemical structures were confirmed by NMR and FTIR. By using comonomers with epoxy and anhydride moieties, or purely comonomer of norbornene or cyclopentene, the glass transition temperatures of the copolymers could be tuned in a broad temperature range from -14 to 91 °C in this study. The $T_{\rm g}$ of phosphonated homopolymer **HP1** was at 57 °C, and increased significantly to 91 °C by copolymerization with anhydride comonomer 3 (only 12% by content). However and interestingly, when the phosphonated monomer was copolymerized with equimolar cyclopentene, two glass transitions were observed with the lower one only at -14°C. The results suggest that glass transitions of PCPs can be conveniently tuned by adjusting the flexibility of comonomer to meet the needs in specific applications. Thermal degradation in nitrogen atmosphere indicated that phosphonated polymers started to lose weight 50 °C lower than polycyclopentene and polynorbornene. This contradicted with PCPs' known superior flame-resistant performance paradoxically. By measuring the residual weight at 600 °C after degradation, it can be explained by less weight loss in PCPs, indicating more char generated in PCPs to prevent combustion. In the followed application studies, norbornene derivative PCPs showed significant flame-retarding property, and proved to be a promising negative photoresist via thiol-ene click chemistry.

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