

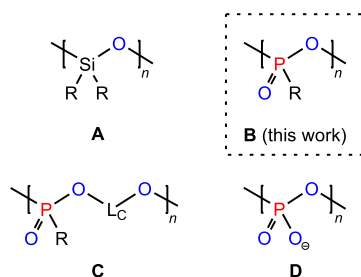
Ring-Opening Polymerization of Cyclic Phosphonates: Access to Inorganic Polymers with a P^V–O Main ChainMarius I. Arz,[†] Vincent T. Annibale,[†] Nicole L. Kelly,^{‡,§} John V. Hanna,[‡] and Ian Manners^{*,†,||}[†]School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom[‡]Department of Physics, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, United Kingdom[§]MAS CDT, Senate House, University of Warwick, Coventry CV4 7AL, United Kingdom^{||}Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada

Supporting Information

ABSTRACT: We describe a new class of inorganic polymeric materials featuring a main chain consisting of P^V–O bonds and aryl side groups, which was obtained with >70 repeat units by ring-opening polymerization of cyclic phosphonates. This monomer–polymer system was found to be dynamic in solution enabling selective depolymerization under dilute conditions, which can be tuned by varying the substituents. The polymers show high thermal stability to weight loss and can be easily fabricated into self-standing thin films. Structural characterizations of the cyclic 6- and 12-membered ring precursors are also described.

The development of new polymers based on p-block elements is of continued interest due to the possibility to find materials with unique properties which may lead to new applications in polymer and material science.^{1,2} For example, polysiloxanes [SiRR'–O]_n (A, Chart 1) evolved from their

Chart 1. Different Types of Inorganic Polymers Relevant to This Work^a



^aL_c = carbon-based linker.

early discovery as a laboratory curiosity to widely used versatile materials, mainly resulting from the fruitful interplay of the unique features imposed by the Si–O main chain and the tunable carbon-based (organic) side chains.³ In this context, polymers consisting of a main chain of alternating P–O bonds with modifiable organic side chains such as polyphosphonates of type [–P(O)R–O]_n (B, Chart 1) may as well exhibit interesting properties, but have only been briefly noted in the literature.

An early report from 1963 described the insoluble material obtained from dehydrochlorination of MePOCl₂ and MePO(OH)₂ as polymeric [–P(O)Me–O]_n, but no characterization was provided.⁴ The formation of poorly characterized polymers of type B as decomposition products of transiently generated dioxophosphoranes (RPO₂) under pyrolytic conditions was also mentioned.⁵ Polyphosphonates B can be regarded as hybrids between polyphosphoesters [–P(O)R–O–L_c–O–] (C, Chart 1; L_c = carbon-based linker), an emerging class of flame-retardant polymers recently recognized for their promising biomedical applications,^{6,7} and ionic polyphosphates [PO₃]_n[–] (D, Chart 1), which are applied in diverse areas ranging from cation sequestering, fertilizers, flame retardants and in biomedicine.⁸ Analogies with polynucleotides, which also possess P–O units in the main chain, are also intriguing. These considerations all suggest that polyphosphonates B are interesting synthetic targets with potentially useful properties.

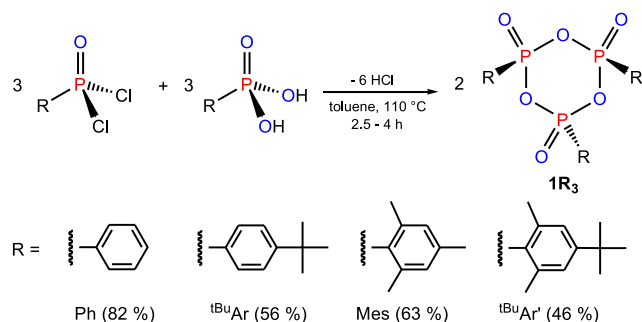
The polymers of type B are polymeric derivatives of cyclic phosphonates, which remained surprisingly unexplored since the early discovery of “PhPO₂” by Michaelis and Rothe in 1892.⁹ Only two cyclic phosphonates, specifically the six-membered rings (tBuPO₂)₃¹⁰ and [(2-MeO–C₆H₄)PO₂]₃,¹¹ have been previously structurally characterized by single-crystal X-ray diffraction analysis (XRD). Notably, (nPrPO₂)₃ (T3P) is used as a particularly mild dehydration reagent for various synthetic applications,¹² but little is known about the structure of this reagent.^{9h} The related polyphosphates [–P(OR')(O)–O–]_n (so-called “Langheld esters” with R' = alkyl or silyl group) also find use as mild dehydration reagents, but consist of complex mixtures of short-chain cycles and oligomers.¹³ Herein, we demonstrate that the ring-opening polymerization (ROP) of cyclic phosphonates leads to high molar mass polyphosphonates of type B with >70 repeat units.

ROP of inorganic heterocycles provides an important route to high molar mass polymers based on p-block elements.^{1–3,14} As a prerequisite to an exploration of a ROP route to polyphosphonates using sterically demanding substituents, we synthesized the cyclic monomers (RPO₂)₃ [1R₃; R = Ph (1Ph₃), 4-tBu–C₆H₄ (1^{tBu}Ar₃), Mes (1Mes₃), 4-tBu-2,6-Me₂–C₆H₂ (1^{tBu}Ar'₃)] via the dehydrochlorination of phosphonic

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dichlorides RPOCl_2 and phosphonic acids $\text{RPO}(\text{OH})_2$ in refluxing toluene (Scheme 1). After workup, the compounds

Scheme 1. Synthesis of the Cyclic Phosphonates $\mathbf{1R}_3$ ^a



^aYields are given in brackets.

$\mathbf{1R}_3$ were isolated as hydrolytically sensitive, colorless solids and fully characterized by solution NMR spectroscopy, single-crystal XRD, ESI-MS, FT-IR spectroscopy and elemental analysis (see SI, section 3).¹⁵

Single crystal XRD analyses of $\mathbf{1Mes}_3$, $\mathbf{1}^{\text{tBu}}\text{Ar}_3$ and $\mathbf{1}^{\text{tBu}}\text{Ar}'_3$ confirmed that these cyclic phosphonates consist of six-membered $(\text{PO})_3$ rings in the solid state, which adopt boat conformations with one aryl substituent in *trans* orientation (Figure 1a). In contrast, crystallization of $\mathbf{1Ph}_3$ yielded reproducibly minor quantities of single crystals consisting of the 12-membered ring $\mathbf{1Ph}_6$ (Figure 1b), which represents the

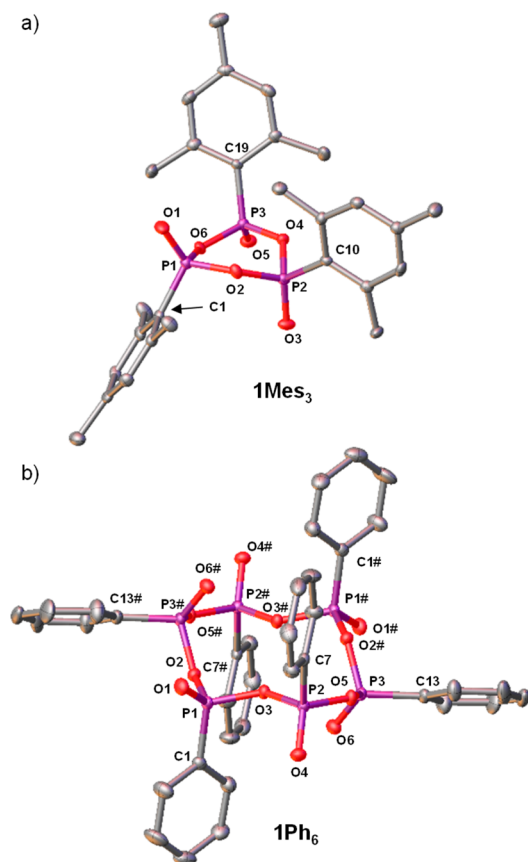


Figure 1. Molecular structures of $\mathbf{1Mes}_3$ (a) and $\mathbf{1Ph}_6$ (b) by single-crystal XRD; H atoms omitted for clarity.

first example of a neutral $(\text{PO})_n$ ring with $n > 3$ [ionic cyclophosphates $(\text{PO}_3)_n^{n-}$ (“metaphosphates”) were structurally characterized for ring sizes up to $n = 12$].¹⁶

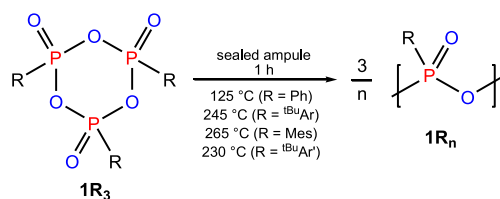
^1H , ^{13}C and ^{31}P NMR spectroscopy in CDCl_3 and toluene- d_8 revealed that all cyclotriphosphonates $\mathbf{1R}_3$ consist of six-membered rings with time-averaged C_s symmetry in solution, leading to diagnostic AB_2 patterns in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in the range of 0.8–4.1 ppm. Minor signals of low intensity (<10%) were also visible in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in several instances (see SI, section 3), which could be attributed to oligomeric $\mathbf{1R}_n$ species. We speculate that one of these species could be the cyclohexaphosphonate $\mathbf{1R}_6$, which was also found in the single crystal structure of $\mathbf{1Ph}_6$. This is corroborated by the ESI-MS spectra obtained from CH_2Cl_2 solutions of $\mathbf{1R}_3$, which showed the expected ion peaks for the cyclotriphosphonates $\mathbf{1R}_3$ and also intense ion peaks for the cyclohexaphosphonates $\mathbf{1R}_6$.

The dynamic covalent chemistry of the cyclotriphosphonates $\mathbf{1R}_3$ in solution was further investigated by mixing $\mathbf{1Ph}_3$ and $\mathbf{1Mes}_3$ in CDCl_3 , which led to highly complex $^{31}\text{P}\{^1\text{H}\}$ NMR spectra after ca. 24 h at ambient temperature, suggesting that ring-opening/ring-closure equilibria occur in solution leading to substituent scrambling, as further confirmed by ESI-MS (see SI, section 3.5). In comparison, variable temperature ^1H and ^{31}P NMR spectroscopy of 0.5 M solutions of $\mathbf{1R}_3$ in CDCl_3 revealed no significant changes in the temperature range of -60 to $+52$ $^\circ\text{C}$.

Studies of the cyclic precursors $\mathbf{1R}_3$ by differential scanning calorimetry (DSC) suggested that melting of $\mathbf{1R}_3$ is accompanied by thermally induced ROP leading to the polymers $\mathbf{1R}_n$. In each case, the first heating cycles of $\mathbf{1R}_3$ displayed an intense endothermic signal characteristic of a melting of the material, and a small ROP exotherm was discernible (except for $\mathbf{1}^{\text{tBu}}\text{Ar}'_3$). The melting transition was absent in the subsequent heating cycles and instead a new deflection associated with a change in gradient emerged, which is diagnostic of a glass transition, providing an indication for the formation of polymeric $\mathbf{1R}_n$. The glass transition temperatures (T_g) of the materials differed significantly depending on the aryl group [$T_g = 66$ ($\mathbf{1Ph}_n$), 103 ($\mathbf{1}^{\text{tBu}}\text{Ar}_n$), 133 ($\mathbf{1Mes}_n$), 140 $^\circ\text{C}$ ($\mathbf{1}^{\text{tBu}}\text{Ar}'_n$)], whereby higher degrees of substitution lead to larger T_g values, probably due to enhanced rigidity of the polymer chains.¹⁷

The preparative synthesis of the polymers $\mathbf{1R}_n$ was achieved by thermal ROP of the cyclic precursors $\mathbf{1R}_3$ (Scheme 2). The

Scheme 2. Synthesis of the Polymers $\mathbf{1R}_n$ via Thermal ROP of $\mathbf{1R}_3$



monomers were heated slightly above the temperature of melting of $\mathbf{1R}_3$ as previously determined by DSC, which led to a considerable increase of the viscosity of the melt. After keeping the materials under thermal ROP conditions for 1 h and cooling to ambient temperature, glassy solids were obtained. These solids showed only the previously observed

glass transitions for $1R_n$ in the DSC analysis and distinct changes were observed for the $\nu(P-O)$ absorption bands in the ATR FT-IR spectra, which can be explained by the changes in the P–O bond energies due to ROP (see SI, section 4). Slow decomposition to the corresponding phosphonic acids occurred upon exposure of the polymers $1R_n$ to atmospheric moisture, but the materials were found to be indefinitely stable under a dry nitrogen atmosphere at ambient temperature.

The polymer $1Ph_n$ was found to be insoluble in common organic solvents, whereas $1^{tBu}Ar_n$ readily dissolved in $CDCl_3$, toluene or hexane, but rapidly depolymerised in solution to the cyclic precursor $1^{tBu}Ar_3$ according to 1H and ^{31}P NMR spectroscopy, preventing further analysis of these materials by solution-based techniques. By contrast, the 1H and ^{31}P NMR spectra of the polymers $1Mes_n$ and $1^{tBu}Ar'_n$ (data discussed below) containing sterically more congested side chains with methyl groups in the *ortho* positions showed only slow depolymerization to the cyclic precursors $1Mes_3$ and $1^{tBu}Ar'_3$ in solution ($t_{1/2} > 15$ days), suggesting that these polymers are kinetically trapped in solution by the presence of the bulkier side groups. The identity of the polymers $1Ph_n$ and $1^{tBu}Ar_n$ was further corroborated by their solid state ^{31}P CP-MAS NMR spectra (Figure 2a), showing broad isotropic ^{31}P

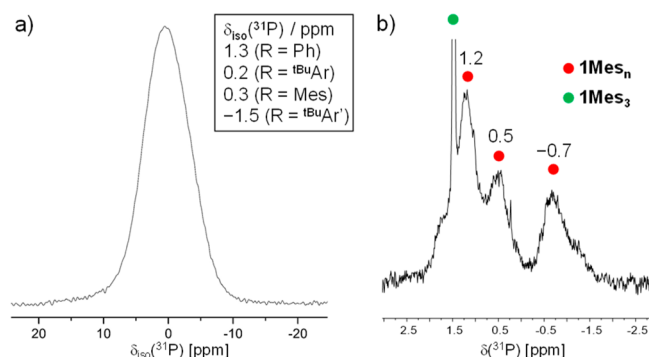


Figure 2. (a) Representative ^{31}P CP-MAS NMR spectrum of $1^{tBu}Ar'_n$; the inset shows the isotropic ^{31}P NMR chemical shifts of all materials. (b) $^{31}P\{^1H\}$ NMR spectrum of $1Mes_n$ in $CDCl_3$.

resonances at 1.3 and 0.2 ppm, respectively. These signals are similar to the ^{31}P NMR signals of $1Mes_n$ and $1^{tBu}Ar'_n$ in the solid state [$\delta_{iso} = 0.3$ ppm ($1Mes_n$), -1.5 ppm ($1^{tBu}Ar'_n$)]. In $CDCl_3$ solution, the polymers $1Mes_n$ and $1^{tBu}Ar'_n$ give rise to broad resonances in the 1H and $^{13}C\{^1H\}$ NMR spectra and three broad signals are observed in the $^{31}P\{^1H\}$ NMR spectra ($\delta = -1.3$ – 1.5 ppm) with a rough intensity distribution of 2:1:1 (Figure 2b). These were assigned to rm/mr and either mm or rr triads, respectively, suggesting the presence of stereoirregular atactic polymer chains, as expected from the forcing conditions of the thermal ROP.¹⁸ Notably, the much broader ^{31}P NMR signals of the polymers $1R_n$ appear in a similar spectral region to those of the cyclic monomers $1R_3$ in $CDCl_3$ (0.8–4.1 ppm).

Further evidence for the assigned structure for $1Ph_n$ was provided by treatment of a suspension of $1Ph_n$ in $CDCl_3$ with 4-dimethylaminopyridine (4-dmap), leading to complete dissolution of all insoluble material due to selective formation of (4-dmap)PhPO₂ (**2Ph**; Figure 3),¹⁹ which is the Lewis base adduct of the transient dioxophosphorane PhPO₂,^{5c,20,21} i.e. the monomer unit of $1Ph_n$. The adduct **2Ph** as well as its derivative (4-dmap)MesPO₂ (**2Mes**) were subsequently syn-

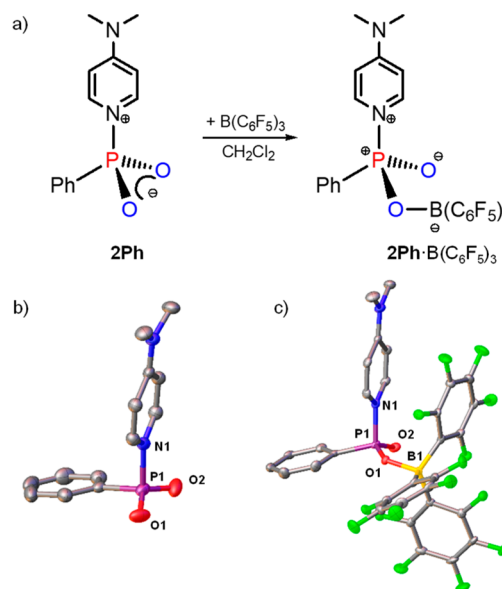


Figure 3. (a) Reaction of **2Ph** with $B(C_6F_5)_3$ to give **2Ph**· $B(C_6F_5)_3$. (b) Molecular structures by single crystal X-ray diffraction of (b) **2Ph** and (c) **2Ph**· $B(C_6F_5)_3$ (H atoms omitted for clarity).

thesized from $1R_3$ and 4-dmap and fully characterized by XRD, NMR and elemental analysis (for details see SI, section 5). Remarkably, the adducts **2R** (R = Ph, Mes) exist in a dissociative equilibrium with $1R_3$ and free 4-dmap in $CDCl_3$ solution. The estimated equilibrium constants derived by NMR spectroscopy amount to $K = 1.11 \cdot 10^{-7}$ (**2Ph**) and $3.49 \cdot 10^{-4}$ mol L⁻¹ (**2Mes**). Attempts to abstract the 4-dmap substituent from **2R** with the Lewis-acidic boranes BPh₃ or $B(C_6F_5)_3$ resulted in either mixtures of mainly the six-membered rings $1R_3$ and (4-dmap)·BPh₃ or the “push-pull” adduct (4-dmap)PhPO₂[$B(C_6F_5)_3$] [**2Ph**· $B(C_6F_5)_3$, Figure 3], which was also isolated and fully characterized, but no formation of polymeric $1R_n$ was detected during these reactions by NMR spectroscopy.

Analysis of dilute solutions of $1Mes_n$ and $1^{tBu}Ar'_n$ in CH_2Cl_2 by dynamic light scattering (DLS) revealed the presence of particles with average hydrodynamic radii of 3.1 and 3.3 nm, respectively. These values corroborate the presence of polymeric material and can be roughly compared to polystyrene particles of similar size, which possess weight-average molecular weights (M_w) of 14 400 or 16 100 g mol⁻¹, corresponding to degrees of polymerization (DP_w) for $1Mes_n$ and $1^{tBu}Ar'_n$ of ca. 79 and 72 repeat units. These molecular weights are reasonably consistent with the MALDI-ToF mass spectra of $1Mes_n$ and $1^{tBu}Ar'_n$ (Figure 4a), which suggest an upper limit to the degree of polymerization of >70, corresponding to molecular weights of ca. 12 900 and 17 300 g mol⁻¹, respectively. A significant decrease of intensity toward high molar masses was observed in the MALDI-ToF mass spectra, which indicates that short-chain molecules are preferably ionized and the measured intensity distribution does not reflect the molecular weight distribution determined by DLS.

Thermal gravimetric analysis (TGA) revealed a high thermal stability to weight loss for the polymers $1R_n$ with high $T_{5\%}$ loss values, which range from ca. 310 to 380 °C (see SI, section 4). TGA also revealed low ceramic yields (ca. 10%), indicating an almost complete thermal decomposition and vaporization of

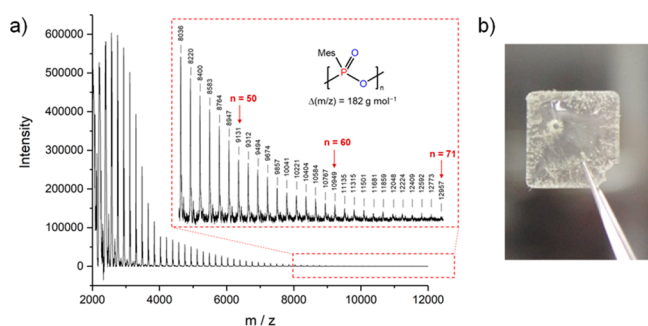


Figure 4. (a) Representative MALDI-ToF mass spectrum of **1Mes_n**, showing the presence of high molecular weight polymer; for details on the MALDI-ToF mass spectra of **1Mes_n** and **1^{tBu}Ar'_n**, see SI, sections 4.3 and 4.4. (b) Free-standing film (12 mm × 12 mm) of **1Mes_n**, prepared by drop-casting from 1,2-dichloroethane solution.

the materials at 575 °C. Initial studies aiming at the fabrication of the polymers revealed that self-standing films of **1Mes_n** can be prepared by drop-casting of a concentrated solution in 1,2-dichloroethane onto a Teflon mold (Figure 4b), providing evidence for the promising processability properties of these materials.

In summary, we have established synthetic access to novel polymers consisting of a P–O main chain and aryl groups at phosphorus via ROP of cyclic phosphonates. The relatively small ROP exotherms detected by DSC suggest that ΔH_{ROP}^0 is low for these materials, as expected for monomers with bulky substituents, rationalizing that ROP only occurs at high monomer concentration, i.e. in the melt phase. Careful adjustment of the side groups leads to significant changes in the properties of the polymers, including the solubility and the stability in solution toward depolymerization. This tunable reversible depolymerization behavior in solution, which can be furthermore chemically triggered as demonstrated by the depolymerization upon addition of a Lewis-base, suggests potential for the development of recyclable materials.²² The simple fabrication, the high thermal stability and the large diversity of possible organic side groups opens up a large scope for future explorations of these new inorganic soft materials.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b13435.

Details of syntheses, characterization and analytical data of starting materials, cyclic monomers and polymers including single-crystal XRD studies (PDF)

Crystallographic data for MesPOCl₂, MesPO(OH)₂, **1Ph₆**, **1Mes₃**, **1^{tBu}Ar'₃**, **1^{tBu}Ar'₃**, **2Ph**, **2Mes** and **2Ph-B(C₆F₅)₃** (CIF)

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Notes

The authors declare no competing financial interest.

Crystallographic data have also deposited with Cambridge Structural Database under the deposition numbers CCDC 1882836–1882844.

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