

An expanded range of catalysts for synthesising biodegradable polyphosphonates

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In this paper we expand the scope of catalysts able to mediate the ring opening polymerisation of the phosphonate monomer 2-methyl-1,3,2-dioxaphosphalane-2-oxide. A range of nitrogen bases efficiently catalyse the reaction, each with pK_a s of 19 or above; lower pK_a bases do not ring open the monomer. Aluminium based catalysts supported by salen and salan ligand frameworks also afford exceptional control, with conversions in excess of 99% and dispersities under 1.1. Together, these studies significantly expand the scope of catalysts to prepare this biodegradable, non-toxic, water soluble polymer. Additionally, we report efforts to expand the monomer scope for these catalysts, showing that altering ring structure and substitution can strongly inhibit productive ring opening.

1. Introduction

Phosphorus containing polymers are a robust area of academic and industrial research, with some also representing a promising family of new biodegradable polymers. Phosphorus containing polymers are prevalent in nature (i.e. DNA),¹ as synthetic biodegradable and biocompatible polymers,² and in more applied research in dentistry,³ tissue engineering,⁴ drug delivery,⁵ and high refractive index polymers.^{6,7} Phosphorus polymers are conventionally synthesised through polycondensation reactions, offering little to no control over molecular weights and dispersities while preventing the synthesis of more complicated macrostructures. More recently, ring opening polymerisations (ROPs) of cyclic phosphorus based monomers have accessed controlled molecular weights and dispersities. Penczek and co-workers pioneered this work, showing alkyl aluminum compounds affected the ROP of 6-membered cyclic phosphates.⁸ These phosphate monomers were later polymerized by Sn(Oct)₂,⁹ lanthanides (as copolymers with ϵ -caprolactone),¹⁰ and organocatalysts.¹¹ While bases like 1,8-diazabicycloundec-7-ene (DBU) are effective, the dual activating organocatalysts like 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) requires shorter reaction times.¹²

While the products of these ROPs, polyphosphoesters and the related polyphosphoramidates, have been extensively explored, there is a paucity of investigations into the analogous monomers that feature a phosphorus-carbon bond. The preparation of polyphosphonates by ROP was only recently discovered by Wurm and co-workers,^{13,14} despite previous polycondensations producing polymeric fire retardants,¹⁵ and optical materials.^{16,17} Wurm reported the DBU catalyzed ROP of monomer **1** to afford polymers with narrow dispersities, producing a greener, water soluble,

non-toxic polymer (Figure 1).¹³ The group has since prepared a series of novel polyphosphonates, catalysed by DBU and TBD, with good control over molecular weights and dispersities.¹⁴ The P-C bond is more resistant to cleavage relative to the P-O bond of polyphosphates, while also lowering the electrophilicity of the diphosphoester, minimizing transesterification and controlling degradation.¹³

While catalyst design has had a transformative effect on the ROP of cyclic esters,¹⁸ little effort to explore this chemical space has been reported. Catalysts may further control transesterification, increase monomer scope and facilitate copolymerizations of these promising monomers. Early lessons learned could later be applied to tacticity control of chiral phosphonates, as in lactide polymerizations.^{19,20} In this contribution, we significantly expand the catalyst scope for the ROP of phosphonate monomers and also show limitations to this ROP in the synthesis and screening of novel aromatic and bicyclic phosphonate monomers (Figure 1).

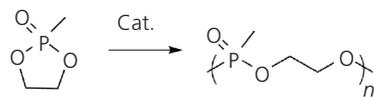
2. Experimental

2.1 Procedures and materials

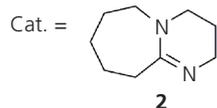
All experiments involving moisture- and air-sensitive compounds were performed under a nitrogen atmosphere using an MBraun LABmaster sp glovebox system equipped with a -35°C freezer and [H₂O] and [O₂] analysers or using standard Schlenk techniques. Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL min⁻¹ on a Malvern Instruments Viscotec 270 GPC Max with 2 \times mixed bed styrene/divinylbenzene columns (300 \times 7.5 mm), calibrated by standard polystyrene samples. ¹H NMR spectra were recorded using BrukerAsance (400 or 500 MHz) spectrometers and tetramethylsilane as the reference.

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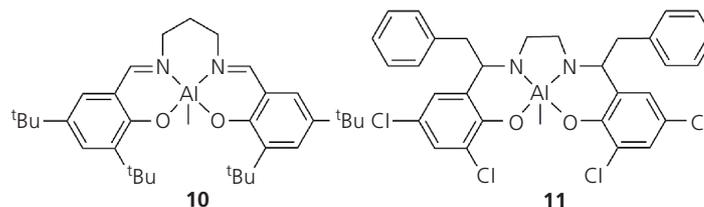
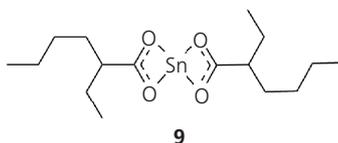
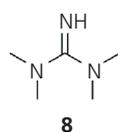
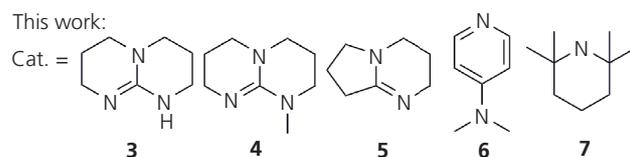
Reaction scheme:



Previous work:



This work:



New monomers:

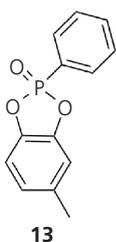
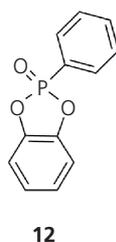


Figure 1. Ring-opening polymerisation of phosphonate monomers and catalyst scope

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a BrukerAsance (at 202 MHz) spectrometer referenced to 80% H_3PO_4 . All spectra were recorded at room temperature. 2-Methyl-1,3,2-dioxaphospholane 2-oxide,¹³ $\text{MeAl}[\text{salen}]^{\text{BuBu-Pr}}$,²¹ and $\text{MeAl}[\text{salan}]^{\text{ClCIBn-Et}}$,²² were prepared via literature procedures, with catalyst preparations modified by refluxing overnight instead of for 3 hr. 2-(Benzyloxy) ethanol was distilled from sodium prior to use. Triethylamine (TEA), dichloromethane (DCM), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 2,2,6,6-tetramethylpiperidine (TMP), 1,1,3,3-tetramethylguanidine (TMG), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MeTBD) and pyridine were purchased from Sigma-Aldrich and dried over calcium hydride and distilled before use. 4-(Dimethylamino)

pyridine (DMAP) was purchased from Merck and used as received while 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), methylphosphonic dichloride, catechol, phenylphosphonic dichloride, trans-1,2-cyclohexanediol and 4-methylcatechol were purchased from Sigma-Aldrich and used as received.

2.2 Representative polymerisation

Reagent ratios for polymerisations were $[\text{Monomer}]_0:[\text{Initiator}]_0:[\text{Catalyst}]_0 = 100:1:1.5$ unless otherwise stated. A solution of monomer and initiator were made up in 1.5 mL of DCM. The mixture was freeze-thaw degassed three times. The catalyst in 0.3 mL of DCM was added to the monomer initiator solution at 0°C. The reaction was then terminated by addition of excess

formic acid in DCM and the polymer precipitated into cold hexane. The precipitate was then filtered and dried under vacuum to give poly(ethylene methylphosphonate) as a white solid. ^1H NMR (DMSO- d_6 , ppm): δ 7.42–7.21 (m, 5H, Ar), 4.39–4.05 (m, 373H, O-CH₂-CH₂-O), 1.57–1.49 (m, 279H, P-CH₃). ^{31}P NMR (DMSO- d_6 , ppm): δ 31.5. GPC characterisation *vide infra*.

2.3 Monomer Synthesis

12: A solution of catechol (2.79 g, 0.025 mol), pyridine (4.00 mL, 0.050 mol) in THF (15 mL) was added at -20°C to a stirred solution of phenylphosphonic dichloride (4.87 g, 0.025 mol) in THF (20 mL). The mixture was then allowed to warm to room temperature and stirred for 6 hr. It was then filtered and the solvent removed and the white solid dried under vacuum to give 1,3,2-benzodioxaphosphole,1-phenyl-2-oxide. Yield: 4.29 g (74%). ^1H NMR (C₆D₆, ppm): δ 7.74–7.58 (m, 2H, Ar-H), 7.01–6.92 (m, 1H, Ar-H), 6.82 (q, $J = 7.6$, 2H, Ar-H), 6.72–6.63 (m, 2H, Ar-H), 6.55 (dt, $J = 5.9$, 3.7 Hz, 1H, Ar-H). ^{13}C NMR (C₆D₆, ppm): δ 145.64, 134.06 (d, $^4J_{\text{CP}} = 3.3$ Hz), 132.55 (d, $^3J_{\text{CP}} = 11.5$ Hz), 125.44 (d, $^1J_{\text{CP}} = 187.5$ Hz), 123.77, 112.78 (d, $^2J_{\text{CP}} = 10.4$ Hz). ^{31}P NMR (C₆D₆, ppm): δ 34.87. FTIR (cm⁻¹): 1298 (P=O). HRMS ([MCH₃]⁺) m/z calculated: 232.03, found: 232.03.

13: A solution of 4-methylcatechol (3.10 g, 0.025 mol), pyridine (4.00 mL, 0.050 mol) in THF (15 mL) was added at -20°C to a stirred solution of phenylphosphonic dichloride (4.87 g, 0.025 mol) in THF (20 mL). The mixture was then allowed to warm to room temperature and stirred for 6 hr. It was then filtered and the solvent removed. The white solid was then dried under vacuum to give 1,3,2-benzodioxaphosphole-6-methyl, 2-phenyl-2-oxide. Yield: 5.35 g (87%). ^1H NMR (C₆D₆, ppm): δ 7.77–7.65 (m, 2H, Ar-H), 7.02–6.93 (m, 1H, Ar-H), 6.89–6.80 (m, 2H, Ar-H), 6.62 (d, $J = 8.1$ Hz, 1H, Ar-H), 6.52 (s, 1H, Ar-H), 6.38 (d, $J = 8.1$ Hz, 1H), 1.89 (s, 3H, CH₃). ^{13}C NMR (C₆D₆, ppm): δ 145.54, 143.53, 134.02 (d, $^4J_{\text{CP}} = 3.4$ Hz), 133.82, 132.51 (d, $^3J_{\text{CP}} = 11.4$ Hz), 128.96 (d, $^3J_{\text{CP}} = 16.1$ Hz), 125.70 (d, $^1J_{\text{CP}} = 123.95$ Hz), 123.95, 113.52 (d, $^2J_{\text{CP}} = 10.4$ Hz), 112.21 (d, $^2J_{\text{CP}} = 10.4$ Hz), 20.98. ^{31}P NMR (C₆D₆, ppm): δ 35.27. FTIR (cm⁻¹): 1289 (P=O). HRMS ([MCH₃]⁺) m/z calculated: 247.05, found: 247.05.

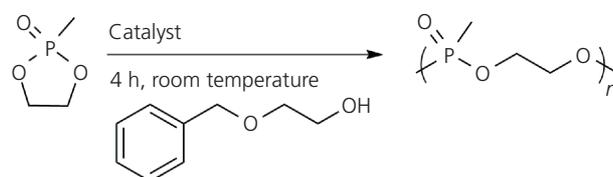
14: A solution of *trans*-1,2-cyclohexanediol (2.90 g, 0.025 mol), pyridine (4.00 mL, 0.050 mol) in THF (15 mL) was added at -20°C to a stirred solution of methylphosphonic dichloride (3.30 g, 0.025 mol) in THF (20 mL). The mixture was then allowed to warm to room temperature and stirred for 6 hr. It was then filtered and the solvent removed and the white solid was dried under vacuum to give 1,3,2-benzodioxaphosphole, hexahydro-2-methyl-2-oxide. Yield: 3.17 g (72%). ^1H NMR (C₆D₆, ppm): δ 3.65–3.59 (m, 1H, CH), 3.18–3.07 (m, 1H, CH), 1.64 (d, $J = 14.0$ Hz, 1H, CH₂), 1.19 (d, $J = 17.3$ Hz, 3H, CH₃), 1.15–1.06 (m, 3H, CH₂), 0.89 (qd, $J = 11.8$, 3.7 Hz, 1H, CH₂), 0.66–0.52 (m, 2H, CH₂). ^{13}C NMR (C₆D₆, ppm): δ 83.83, 81.61, 29.62 (d, $^2J_{\text{CP}} = 10.5$ Hz), 29.40 (d, $^2J_{\text{CP}} = 9.2$ Hz), 23.36, 23.33, 11.86 (d, $^1J_{\text{CP}} = 134.3$ Hz). ^{31}P NMR (C₆D₆, ppm): δ 41.21. FTIR (cm⁻¹): 1256 (P=O). HRMS ([MH]⁺) m/z calculated: 176.06, found: 176.07.

3. Results and discussion

The only catalyst reported to ring-open monomer 1 is DBU.¹³ To expand the catalyst scope, we screened a range of nitrogen containing organocatalysts in phosphonate ROP (3–8, Scheme 1) for 4 hr at room temperature. 2-(benzyloxy)ethanol was chosen as an initiator to easily determine M_n of the polymer produced by ^1H NMR and has the possibility for post polymerisation modification. A clear relationship between pK_a of the catalyst and conversion is observed (Table 1), measured by integration of the new ^{31}P NMR signal relative to monomer; the phosphorus in the polymer is shielded compared to the monomer due to release of ring strain and a concomitant increase in bond angle.²³ An increase in pK_a increases the catalyst's ability to make the chain end more nucleophilic, with a more nucleophilic chain end propagation of the polymerisation is more successful hence an increase in conversion is observed. Catalysts with a pK_a of 14 and below (TMP and TEA) gave little to no polymerisation and 2,2,6,6-tetramethylpiperidine ($pK_a = 19$) only produced low molecular weight oligomers, suggesting these catalysts are not being basic enough for polymerisation to occur. At particularly low conversions, accurate molecular weights could not be determined. Of these poor catalysts, 6 shows a broadened D , suggesting that poor performance may be a combination of slower initiator activation by the less basic catalysts combined with less activation of the propagating chain.

Catalysts 2–5 demonstrate very good control over the polymerisation ($D < 1.07$), with NMR molecular weights in good agreement with those expected from monomer conversion. Figure 2a confirms a linear relationship between conversion and pK_a . However, TBD gives a much higher conversion than expected; this “dual activating” catalyst activates both monomer (increasing its electrophilicity) and chain end (increasing its nucleophilicity) to promote polymerisation (Figure 2b). This dual mode of activation also brings the reactants into closer proximity. Finally, the amino acids serine and proline gave conversions of 44 and 24 respectively. As the pK_a s of these amino acids are below 14 and thus too low to activate the initiator/chain end, the amino acids must work by activation by the carboxylic acid moiety, suggesting that phosphonates can also undergo predominantly cationic ROP. The observed molecular weight and ^1H NMR spectrum of the amino acid catalysed polymerisations suggests a single end group, indicating immortal initiation from the amino acid catalysts is negligible.

The polymerisation was then explored using three Lewis acid based catalysts common in cyclic ester ROP (Table 2). Sn(Oct)₂



Scheme 1. Polymerisation of 2-methyl-1,3,2-dioxaphospholane-2-oxide using a variety of catalysts

Catalyst	pK _a	Conversion: % ^a	M _n ^{theob}	M _n ^{calcc}	D ^d
3	26	91	11 100	10 400	1.04
4	25	66	8050	7900	1.06
2	24	56	6800	6100	1.02
5	23	47	5700	4000	1.07
6	21	33	4000	4200	1.28
7	19	13	—	—	—
8	14	3	—	—	—
9	11	0	—	—	—
Serine	2/9	44	5400	5000	1.19
Proline	2/11	24	—	—	—

^a Calculated by phosphorus-31 NMR

^b Molecular weight of repeat unit × conversion

^c Calculated by hydrogen-1 NMR spectroscopy

^d Determined by GPC

Table 1. Polymerisation data catalysed by organocatalysts

proved to be a poor catalyst for the ROP under the conditions tested. Aluminium salen and salan, however, was effective under the same conditions as the organocatalysts, reaching conversions above 70% and having narrow dispersities of 1.05 and 1.07. Increasing the reaction time to 6 hours provided quantitative yields with no loss of control.

While the high levels of control certainly depend upon catalyst composition, the low *D* is easily accessible due to the inherent nature of this new monomer. In polyphosphonates, transesterification can occur by intra- and inter-molecular mechanisms, as shown in Figure 3a. Polyphosphates have an additional reactive site in the alkoxide side group. Transesterification at that site (see Figure 3b) provides both an additional mechanism of transesterification and also produces a free alcohol that can participate in chain exchange reactions and immortal polymerisation, preventing reaction control and broadening *D*.^{12,13} While the monomer choice impacts the prevalence of these second reactions, catalyst choice is still essential to limiting in-chain transesterification.

Finally, we explored other potential monomers to complement those previously explored by Wurm and coworkers.¹⁴ Novel aromatic and bicyclic phosphonate monomers were synthesised using the synthetic route shown in Scheme 2. The potential monomers were prepared in one step from commercially available reagents via a condensation reaction between the chosen diol and phosphonic dichloride and each was easily purified by filtration of precipitated product. All monomers are stable in air at ambient temperatures for several months. Our motivation for targeting aromatic-containing monomers was to produce polymers with quite different thermal and mechanical properties and significantly increased refractive indices⁶ while targeting the cyclohexyl monomer raised the potential of generating tactic microstructures into polyphosphonates.

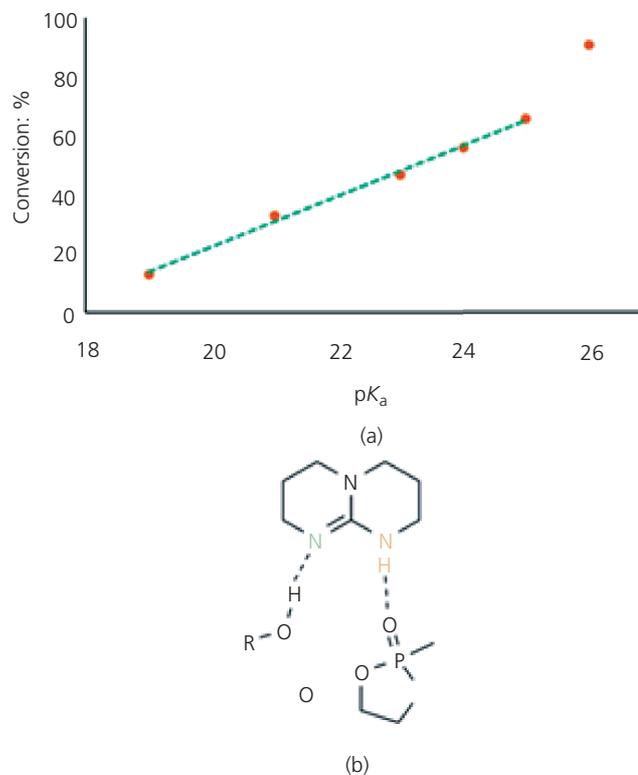


Figure 2. (a) Conversion vs pK_a, (b) TBD as a dual activating catalyst

¹H, ¹³C, and ³¹P NMR spectroscopy confirmed the synthesis of **12**. In the ¹H NMR the proton environments in the side chain appear at a much higher chemical shift relative to the proton from the catechol substituent. A single sharp peak at δ34.87 in the ³¹P NMR confirms formation of the monomer, both spectra are shown in Figure 4.

Similar results were obtained for **13** and **14** (Figures 5 and 6). For monomer **13**, the splitting pattern in the ¹H NMR is now resolved to two sets of doublets and a singlet on the catechol moiety due to the presence of the methyl group. A single ³¹P resonance is

Catalyst	Time: h	Conversion: % ^a	M _n ^{theob}	M _n ^{calcc}	D ^d
9	4	25	3000	2700	1.11
10	4	71	8600	9200	1.05
11	4	73	8900	9000	1.07
10	6	>99	12 000	11 200	1.06
11	6	>99	12 000	11 100	1.07

^a Calculated by phosphorus-31 NMR

^b Molecular weight of repeat unit × conversion

^c Calculated by hydrogen-1 NMR

^d Determined by GPC data

Table 2. Polymerisation data catalysed by common metallic catalysts

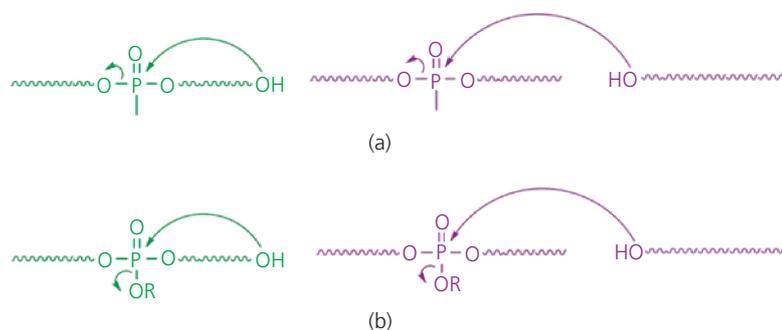
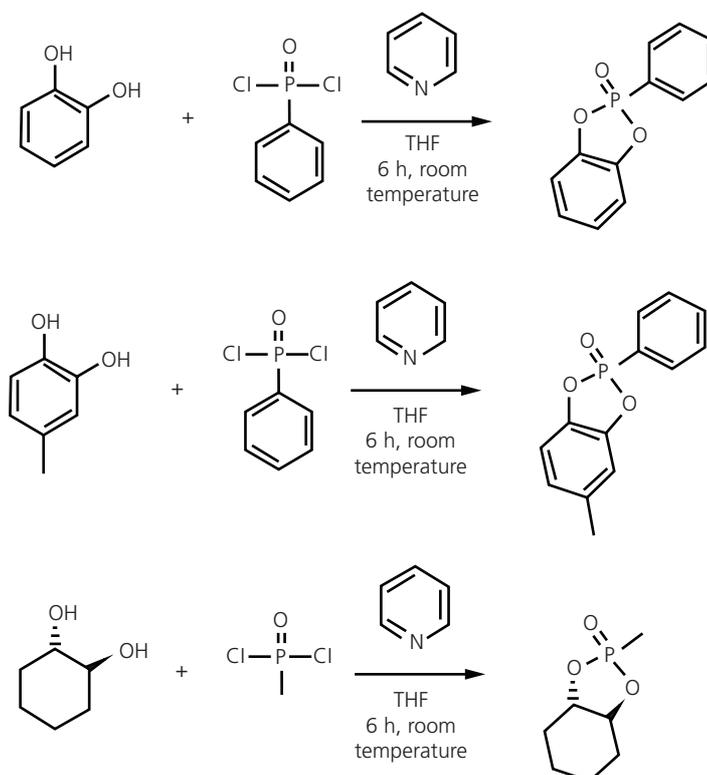


Figure 3. Intramolecular (green) and intermolecular (purple) transesterification of (a) polyphosphonates and (b) polyphosphates

observed at a similar chemical shift. In the ^1H NMR of **14** the complexity of signal splitting increased within the cyclohexane substituent, probably due the non-planar nature of the ring causing multiple environments. **14**'s ^{31}P NMR chemical shift increased as the side group is now methyl group.

Under the same conditions and with the same catalysts that polymerised **1**, no change in the ^1H and ^{31}P spectra of monomers **12**, **13** and **14** were observed, indicating no productive polymerisation. Harsher conditions including higher temperatures and longer reaction times also resulted in no observed reaction.

Initiators of different $\text{p}K_{\text{a}}$ s did not promote polymerisation. Copolymerisations were also attempted with the above monomers. Using the same conditions and catalysts, copolymers were tested with lactide, ϵ -caprolactone and ethylene ethyl phosphate. All reactions gave no incorporation of cyclic phosphates **12**, **13** or **14**, producing solely homopolymers of the second monomer. This is somewhat expected: the phosphoryl bond in the aromatic monomers is much stronger than **1**, as evidenced by their stretching frequencies 1298 (**12**) and 1289 cm^{-1} (**13**) compared to 1255 cm^{-1} (**1**). This bond is expected to break and reform when the initiator/chain end attacks the electrophilic phosphorus center.



Scheme 2. Synthetic route to aromatic and bicyclic phosphonate monomers

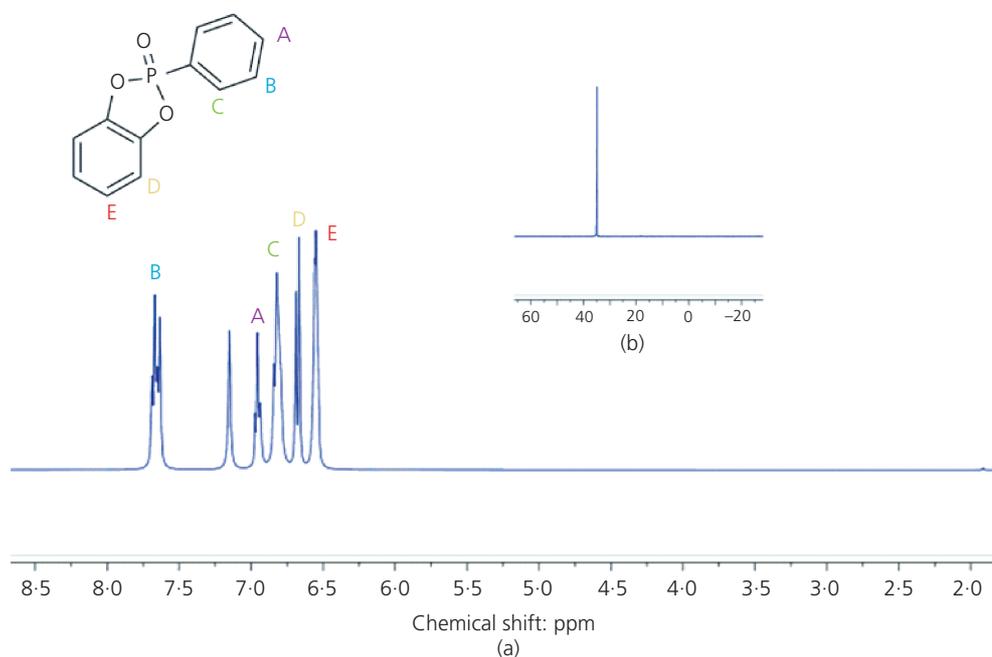


Figure 4. (a) ^1H NMR and (b) ^{31}P NMR spectra of **12**

If this bond is stronger it may prevent polymerisation, favoring the ring closed form. Other phosphonate monomers that have successfully been polymerised are shown in Table 2 along with their P=O stretching frequencies, with each successful monomer having a stretching frequency within 10 cm^{-1} of the parent monomer (Figure 7).¹⁴

However, and somewhat surprisingly, the P=O stretch of **14** is at a similar frequency to **1**: 1256 cm^{-1} , suggesting a strong potential for ring opening. Wurm recently published a cyclic phosphonate monomers that contains a cyclohexyl side group, that successfully under goes ROP with excellent control over molecular weight and distribution.²⁴ It is likely when connected to the five-membered

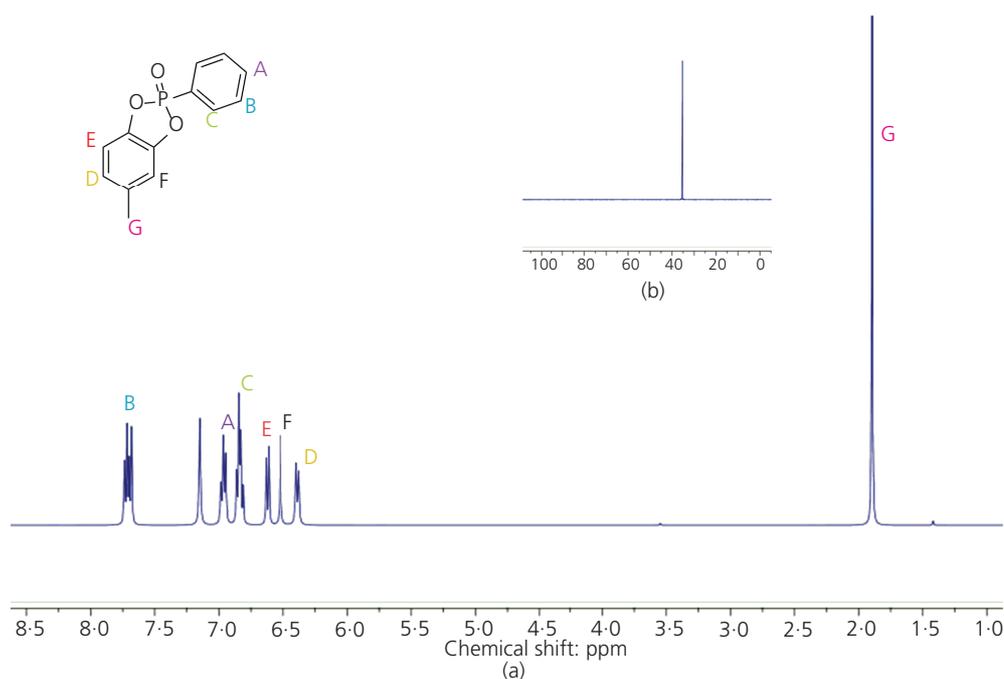


Figure 5. (a) ^1H NMR and (b) ^{31}P NMR spectra of **13**

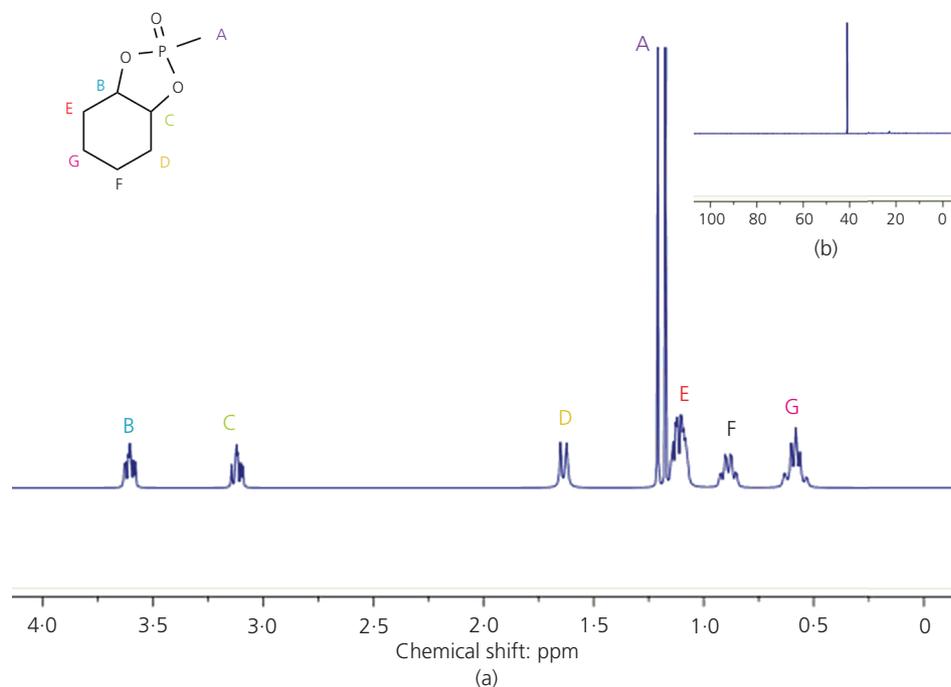


Figure 6. (a) ¹H NMR and (b) ³¹P NMR spectra of **14**

dioxaphospholane ring the cyclohexyl ring adopts a conformation to relieve strain so that there is insufficient ring strain to make ROP favorable, a hypothesis we continue to explore. These observations of the polymerisations of **12–14** suggest that a fine balance in monomer reactivity is needed to promote productive polymerisation and produce these new polymers. This study shows that these monomers were not successful at polymerising under the conditions and catalysts outlined. It may be possible that these monomers are capable of polymerising using other known catalysts, outside the scope of this publication. We, and others, continue to explore new monomer frameworks with the caveat that the syntheses be accessible, robust and scalable to address polymer supply needs.

Monomer	15	16	17
n(P=O): cm ⁻¹	1265	1244	1259

Table 3. Stretching frequencies of phosphonate monomers

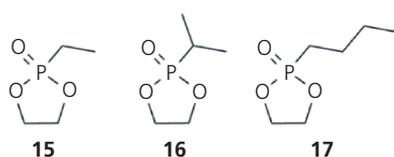


Figure 7. Phosphonate monomers capable of ring-opening polymerisation

4. Conclusions

We have expanded the catalyst scope of ROP of phosphonates to include a range of nitrogen containing bases and the first report of efficient aluminum based catalysts. Fast polymerizations, low dispersities and excellent control of molecular weight were obtained. Organocatalyst performance correlated with the pK_a of the base, while aluminum performance matched that of the organocatalysts and offer significant opportunity to tune the reaction in the future, including in tacticity control of chiral phosphonates. Three novel phosphonate monomers were also successfully synthesised, however, their ability to undergo ROP under the conditions tested was unsuccessful due to lower activation of the heterocycles.

Acknowledgments

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