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Analysis of the products of the anionic oligomerisation of a phosphaalkene using MALDI-TOF mass spectrometry†

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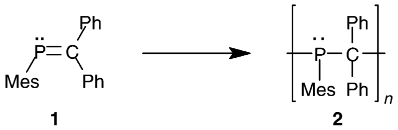
The first use of MALDI-TOF MS in the study of the products of RLi (R = Me, Bu) initiated oligomerisation of P=C bonds is reported. These studies may be considered as models for analogous polymerisation reactions. The detected linear products with R–P and C–H end-groups are consistent with a chain growth mechanism similar to that known for olefins. Interestingly, the results suggest that backbiting may compete with chain growth.

The addition polymerisation of olefins is one of the most important methods of polymer synthesis and forms the basis for the production of many commodity organic materials. There has been considerable interest in the synthesis and reactions of phosphaalkenes, and the remarkable parallels between P=C and C=C bonds in molecular chemistry.[1] We have been interested in expanding the so-called "phosphorus–carbon analogy" to polymer science, and have recently reported the high temperature polymerisation of phosphaalkene **1** to give poly(methylenephosphine) **2**.[2] The incorporation of inorganic elements into the polymer backbone is an active area of research and often leads to materials with novel properties.[3,4] Previously, addition polymerisation was often dismissed as unsuitable for inorganic systems. Now that **1** has been polymerised, one question that must be addressed is whether the initiation and propagation steps are analogous to those known for olefins. If so, by analogy with olefins, living polymers and novel block or end-functionalised polymers may be accessible. Knowledge of the structure of **2**, including end-groups, will provide insight into the mechanism of their formation. Here, we report the ambient temperature oligomerisation of **1** using anionic initiators and the detection of oligomers with up to 11 repeat units using MALDI-TOF MS. This work demonstrates that chain growth proceeds in solution without heating and the observation of end-groups confirms that the mechanism of anionic polymerisation for P=C bonds is analogous to that for olefins. To our knowledge, oligomeric phosphaalkenes larger than diphosphetaines have not previously been characterised by mass spectrometry.[5,6]

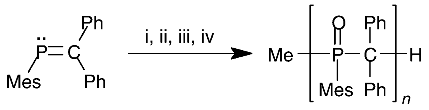


1 **2**

The emergence of soft ionisation (*i.e.* MALDI) mass spectrometric techniques to investigate high molecular weight (MW) macromolecules is revolutionising the field of synthetic polymers,[7] however their use is still relatively uncommon in the analysis of inorganic systems.[8] Importantly, MALDI-TOF MS gives absolute masses rather than relative (*i.e.* GPC) and usually only molecular ions are observed without fragmentation. We have been interested in analysing poly(methylenephosphine) **2** by MALDI-TOF MS. One objective is to obtain accurate MW's for **2** since laser light-scattering has shown that the MW is underestimated by GPC (*vs.* polystyrene standards).[2] Moreover, MALDI-TOF MS may provide mechanistic insight into this new polymerisation reaction by revealing endgroups which, thus far, have been undetectable by NMR spectroscopy. To date, we have not been able to successfully analyse polymeric samples of **2** by MALDI-TOF MS. Therefore, we attempted to synthesise small oligomers that might be easier to ionise using MALDI techniques.

Small oligomeric poly(methylenephosphine)s were prepared conveniently from the ambient temperature reaction of **1** (3 equiv.) with *in situ* generated Mes(Me)P–C(Ph)$_2$Li (δ ^{31}P = −45 ppm) in diethyl ether (Scheme 1). Our previous work on the polymerisation of **1** with MeLi (5%) in a minimum of solvent required a temperature of 150 °C.[2] Significantly, the present results suggest that in solution high temperatures may not be necessary. After oxidation and workup, analysis by ^{31}P NMR spectroscopy revealed that, analogous to oxidised **2**, only a broad signal (δ = 45 ppm) was observed. Interestingly, end-groups were not identified in the ^{1}H or ^{31}P NMR spectra and are possibly obscured by broad signals of the aryl and alkyl side-groups.

A sample for MALDI-TOF analysis was prepared with the matrix (2,5-dihydroxybenzoic acid) using the layer method.[7] A typical MALDI-TOF mass spectrum is shown in Fig. 1. Remarkably, a series of ions spaced by the mass of the monomer unit (332 Da) were observed that were assigned to linear oligomers $\mathbf{3_n}$ (n = 3–11). The masses of the oligomers were within experimental accuracy (±0.1%) of the calculated masses for protonated species ($\mathbf{3_n}$+H)$^+$. For example, inset A in Fig. 1 clearly shows an isotope pattern with lowest mass 1676 Da which is 1 less than ($\mathbf{3_5}$+H)$^+$ ($C_{111}H_{110}P_5O_5$; calcd. 1677 g mol^{-1}). The isotope pattern is consistent with that expected with the most intense ion due to the



1 $\mathbf{3_n}$

Scheme 1 *Reagents and conditions*: i, MeLi (1 equiv), Et$_2$O, −80 °C to 25 °C, 30 min; ii, **1** (3 equiv), 25 °C, 16 h; iii, H$_2$O (1 drop); iv, H$_2$O$_2$ (excess), CH$_2$Cl$_2$, 25 °C, 30 min, the higher oligomers were isolated by precipitation from a CH$_2$Cl$_2$ solution with hexanes, 54%.

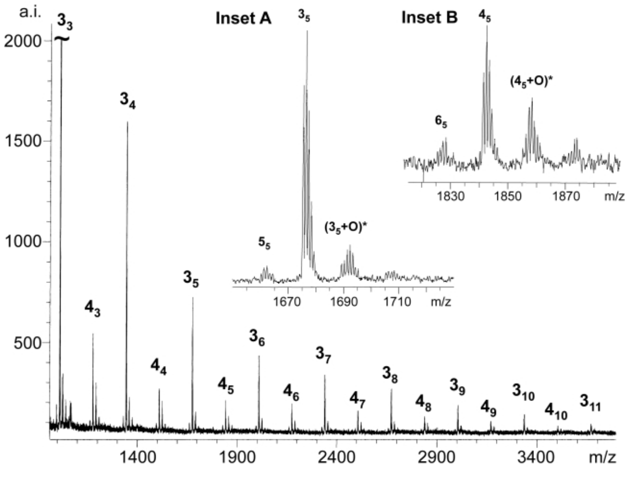


Fig. 1 MALDI-TOF MS of oligomer mixture. * tentative assignment.

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† Electronic supplementary information (ESI) available: experimental procedures and an additional figure. See http://www.rsc.org/suppdata/cc/b4/b406160h/

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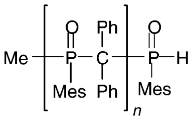
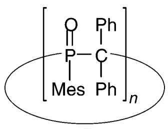
presence of 1 × ^{13}C (observed at 1677). Remarkably, oligomers of up to 11 repeat units [$(\mathbf{3_{11}}+H)^+$, 3669 Da; calcd., 3669 g mol^{-1}] were observed where the most intense ion was due to the presence of 2 × ^{13}C in the oligomer. The observation of ions consistent with the presence of CH_3 and H end-groups in $\mathbf{3_n}$ suggests that linear products are obtained and that the mechanism of chain growth is analogous to that for olefins. Confirmation of this postulate was obtained by varying the initiating species. Specifically, we have initiated oligomerisation of **1** with BuLi (0.5 equiv.) and quenched with H_2O. The MALDI-TOF mass spectra of the oligomers were consistent with linear species containing Bu and H end-groups, respectively. Oligomers with up to 6 repeat units were observed.

One puzzling feature of the MALDI-TOF mass spectra, regardless of whether MeLi or BuLi is used, is the unexpected presence of a second series of oligomers spaced by the monomer unit (332 Da). This second series can clearly be seen in Fig. 1. Remarkably, each peak in this series is situated exactly halfway (*i.e.* ±166 Da) between the ions assigned to the linear oligomers ($\mathbf{3_n}$). This observation suggested multiply charged species. However, after close inspection of the mass spectra this hypothesis was ruled out since the ions were spaced by integer mass units.[9] After further consideration, we assigned these signals to linear oligomers with an extra phosphorus group at the end of the chain ($\mathbf{4_n}$). Fig. 1, inset B, shows signals consistent with $\mathbf{4_5}$ with calculated mass of 1842 Da. Structures with an extra CR_2 and P–Me end-group are unlikely since a CPh_2–CPh_2 backbone linkage would be necessary to account for the observed masses.

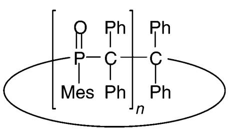
The reason for this second series of oligomers, is not obvious. It is possible that these species simply result from fragmentation of $\mathbf{3_n}$, however, this is relatively uncommon in polymer MALDI-TOF mass spectrometry.[7,10] Although if the P–C chains are easily fragmented during ionisation, $\mathbf{4_n}$ could be accounted for. However, if fragmentation during ionisation is facile, we should see oligomeric fragments in attempted MALDI analysis of polymer **2**. Under analogous MALDI conditions we have not observed any mass spectra for the polymer **2** (GPC $M_n = 5 \times 10^3 - 1 \times 10^4$ g mol^{-1}). In addition, oxidised **2** is thermally stable up to 320 °C as determined by TGA which seems to suggest a stable backbone not likely to fragment easily. Therefore, although we cannot rule out fragmentation of $\mathbf{3_n}$ as a source of $\mathbf{4_n}$, it is unlikely. If these are not fragments, these observations may have important implications on the proposed mechanism of anionic polymerization of **1**. This will now briefly be elaborated upon.



$\mathbf{4_n}$



$\mathbf{5_n}$



$\mathbf{6_n}$

We speculate that species $\mathbf{4_n}$ (n = 3–10), if not arising from fragmentation, could also result from backbiting during the polymerisation reaction. The proposed mechanism would involve nucleophilic attack of the growing carbanionic chain-end on either a P or C site in its own backbone – attack on C would give $\mathbf{4_n}$ after H_2O/H_2O_2 workup. Backbiting reactions of the type proposed are uncommon in olefin polymerisation. However, similar backbiting processes are very common in the anionic ring-opening polymerisation of cyclic trisiloxanes [$(R_2SiO)_3$].[3,11] A backbiting mechanism necessitates the formation of cyclic oligomers ($\mathbf{5_n}$, $\mathbf{6_n}$). Close inspection of Fig. 1 (inset A and B) show that ions are detected exactly 16 Da below $\mathbf{3_n}$ and $\mathbf{4_n}$, respectively. These signals could be due to a loss of oxygen or may also be assigned to cyclic oligomers $\mathbf{5_n}$ and $\mathbf{6_n}$. Moreover, cyclic species are observed in the analysis of BuLi initiated oligomers, confirming that they are $\mathbf{5_n}$ and $\mathbf{6_n}$ rather than linear minus oxygen. Cyclic species are only observed up to n = 5 for the MeLi initiated reaction. Further studies are underway to confirm whether backbiting is indeed involved and, if so, develop methods to minimise it. These results may provide a rationale for the relatively low MWs (*ca.* 10^4 g mol^{-1} by GPC) and isolated yields (*ca.* 30–40%) thus far obtained for polymer **2** and related polymers[12] prepared using anionic initiators.

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