Mass spectrometric characterization of oligomeric phosphaalkenes

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Mass spectrometric characterization of oligomeric phosphaalkenes

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In honour of Reg Mitchell, scientist and bon vivant.

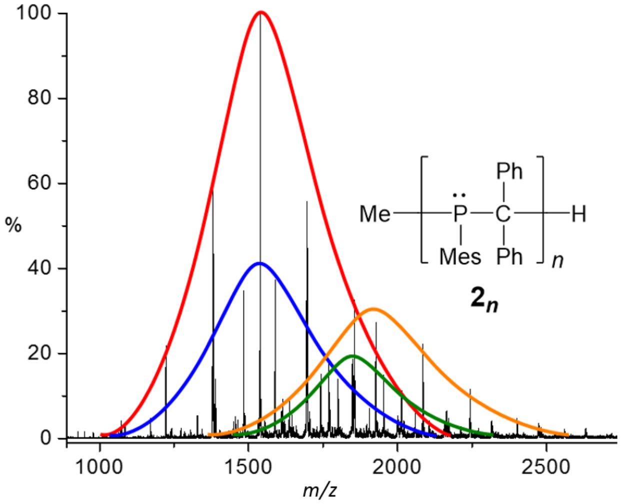
Keywords

mass spectrometry, phosphorus, polymer, electrospray ionization, oligomers

Abstract

Oligomeric phosphalkenes are readily characterized using electrospray ionization mass spectrometry (ESI-MS). The high affinity of phosphines for silver ions permits the detection of the unadulterated polymer as $[M + xAg]^{x+}$ ions ($x = 2$-3). When the oligomers are oxidized using H_2O_2, the resulting phosphine oxide polymer may be treated with sodium ions to produce $[M + xNa]^{x+}$ ions ($x = 2$-3). Both methods predict a similar distribution of oligomers: M_n values of 3450±100 Da and a PDI of 1.09±0.01 cover both analyses. This distribution represents oligomers of the general formula $Me(PMesCPh_2)_nH$ from $n = 4$-20 and maximizing at $\sim n = 10$.

Graphical abstract



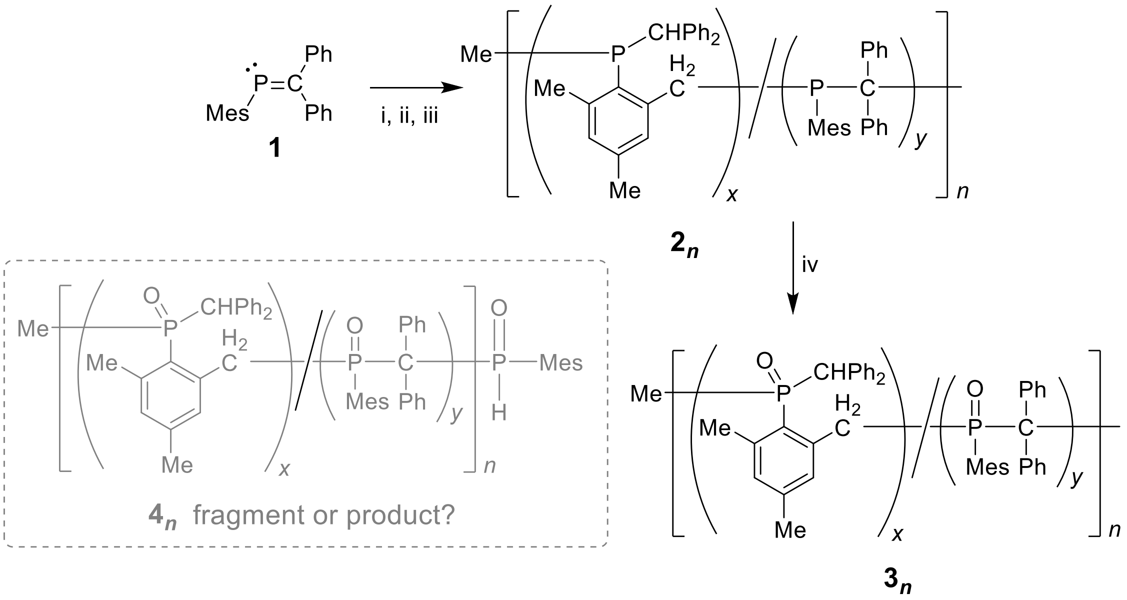
Introduction

The development of phosphorus-containing polymers is motivated by the prospect of discovering new materials with unique properties, structures and chemical functionality [1-5]. Despite the widespread importance of polyphosphazenes [6, 7], developments in phosphorus polymer chemistry is hindered by the lack of general synthetic methods to incorporate phosphorus atoms into long chains. Recently, there have been numerous advances in the synthesis of phosphorus macromolecules [8].

The addition polymerization of olefins is perhaps the most widely applicable and general method of organic polymer synthesis. By contrast, the polymerization of heavier-element-containing multiple bonds remains largely unexplored, even being dismissed for heavy element multiple bonds (e.g. Si=Si) [9]. Over the past decade, our group and the group of Baines have successfully developed a polymerization chemistry for the P=C bonds [4], and Si=C or Ge=C bonds [10, 11]. For phosphaalkenes, we have developed routes to homo- and co-polymers using radical and living anionic methods of polymerization and have shown that the resultant poly(methylenephosphine)s have unique properties and potential applications as: supports for metal-catalyzed organic transformations, flame retardants, templates for the self-assembly of gold nanostructures, and turn-on sensor materials [12-23]. Recent work has shown that the radical polymerization of **1** proceeds via an unprecedented addition-isomerization mechanism whereby the *o*-Me group of Mes is activated and serves as the propagating species (see: **2** where x >> y) [24]. Although still under investigation, we believe that the anionic polymerization of P-Mes phosphaalkenes may follow a similar pathway.

Although these recent mechanistic investigations involved multinuclear one- and two-dimensional NMR spectroscopy, we earlier studied the MALDI-TOF MS of oligomers derived from the anionic oligomerization of MesP=CPh$_2$ with MeLi or BuLi (25 mol%) [25]. Oligomerization of **1** (Scheme 1) leads to a mixture of oligomeric species (**2*n***) that can be characterized by MALDI-TOF MS as the phosphine oxides (**3*n***) after oxidation with H$_2$O$_2$. These results revealed oligomers stretching out to

~3500 Da, with an exponential decay in intensity beyond the trimer. The oligomers were of two types: the expected oligomeric series $[\mathbf{3}_n + \mathrm{H}]^+$, and an additional series $[\mathbf{4}_n + \mathrm{H}]^+$, which appeared as though it might arise either through fragmentation during the ionization process or via genuine chemistry during polymerization. MALDI-TOF has been used previously to characterize phosphorus-containing dendrimers up to generation 4, with a variety of fragmentation processes observed [26]. Oligomers with phosphonium end-groups have been characterized by both MALDI and ESI-MS [27]. The use of ESI-MS to characterize inorganic polymers has been fairly limited. Poly(aminoboranes) have been shown to be detectable by ESI-MS up to n = 49 [28]; we are not aware of any previous studies characterizing poly(methylenephosphine)s by ESI-MS.



Scheme 1. Reagents and conditions: i, MeLi (1 equivalent), Et_2O, -80 to 25 °C, 30 minutes; ii, **1** (3 equivalents), 25 °C, 16 h; iii, H_2O quench (1 drop); iv, H_2O_2 (excess), CH_2Cl_2, 25 °C, 30 min. The higher oligomers were isolated by precipitation from a CH_2Cl_2 solution with hexanes.

Results and Discussion

Herein, we describe the analysis of oligomeric models for polymer **2** by using ESI-MS methods [29], both with and without oxidation of the oligomeric products. The oligomers, **2_n**, were prepared following the identical procedure to that described previously for the earlier MALDI-TOF analyses (Scheme 1) [25]. ESI-MS is a powerful tool for the examination of inorganic materials [30, 31]. ESI-MS relies on being able to analyze ions, so examining neutral compounds such as those under study requires the addition of a cation, whose identity is best selected based on the affinity of the neutral compound for different cations. Before oxidation, the mixture of oligomers **2_n** has phosphorus sites in the backbone with a free lone pair that has high affinity for soft metal ions such as silver. So the initial analysis involved adding a drop of $AgNO_3$ solution to an acetonitrile solution of the oligomer mixture [32, 33]. The resulting mass spectrum was complicated but entirely tractable to assignment, as ~99% of the total ion current could be attributed to reasonable species that had acquired charge through cationization (Figure 1).

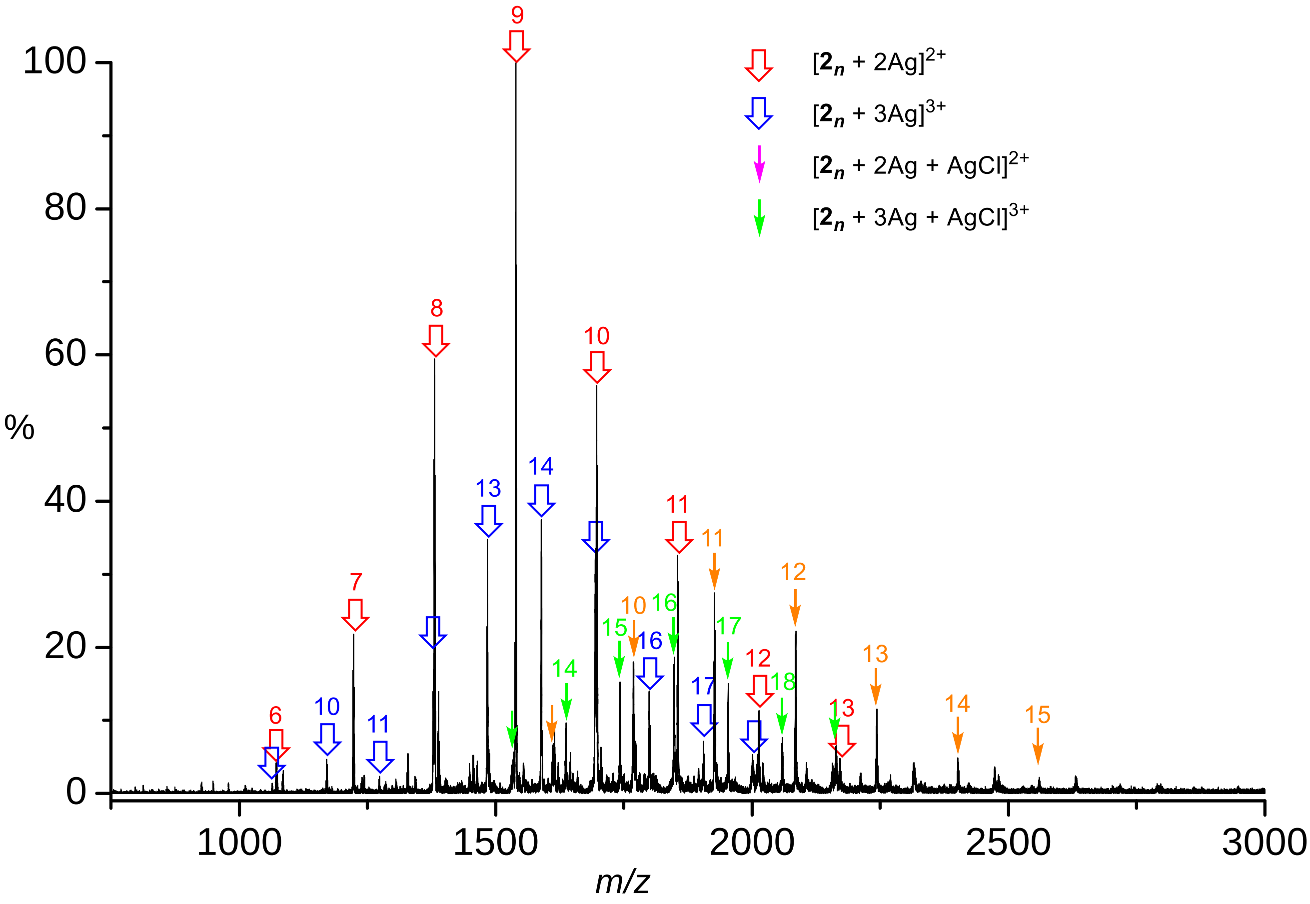


Figure 1. Positive ion ESI-MS of oligomerized phosphaalkene **1** to make oligomeric mixture **2**$_n$, recorded in acetonitrile with the addition of AgNO$_3$.

None of the species observed were monocations. All of the oligomers were bound to at least two silver ions. The most prominent series consisted of the dications $[\mathbf{2}_n + 2\mathrm{Ag}]^{2+}$, which provided a distribution between $n = 6$ and $n = 13$, with $n = 9$ being most abundant. The fact that the peaks in the isotope pattern are m/z 0.5 apart readily identifies the dicationic nature of these species. The next highest series was $[\mathbf{2}_n + 3\mathrm{Ag}]^{3+}$, appearing between $n = 9$ and $n = 18$, and peaking at $n = 14$ (all have peaks in the isotope pattern m/z 0.33 apart). Unsurprisingly, the more phosphorus in an oligomer, the more likely it is to associate with more silver ions. Two smaller series also appear as a manifestation of the high affinity of silver ions for chloride ions, the di- and tricationic species $[\mathbf{2}_n + 3\mathrm{Ag} + \mathrm{Cl}]^{2+}$ ($n = 9 – 15$) and $[\mathbf{2}_n$ + 4Ag

+ Cl]$^{3+}$ (n = 13 – 19). While chloride was not directly involved in the analysis at any point, it is one of those ions that is almost impossible to exclude from the instrument entirely, and the oligomers had been in contact with CH_2Cl_2.

Making the approximation that the area of each peak is proportional to the abundance of that species, we can sum the contributions of each mass spectrometrically observed series to the overall distribution (Figure 2). No oligomers below n = 4 or above n = 20 were observed, and the distribution maximises at n = 9. The M_n and M_w were calculated at 3550 and 3800 Da, respectively, giving a polydispersity index of 1.07.

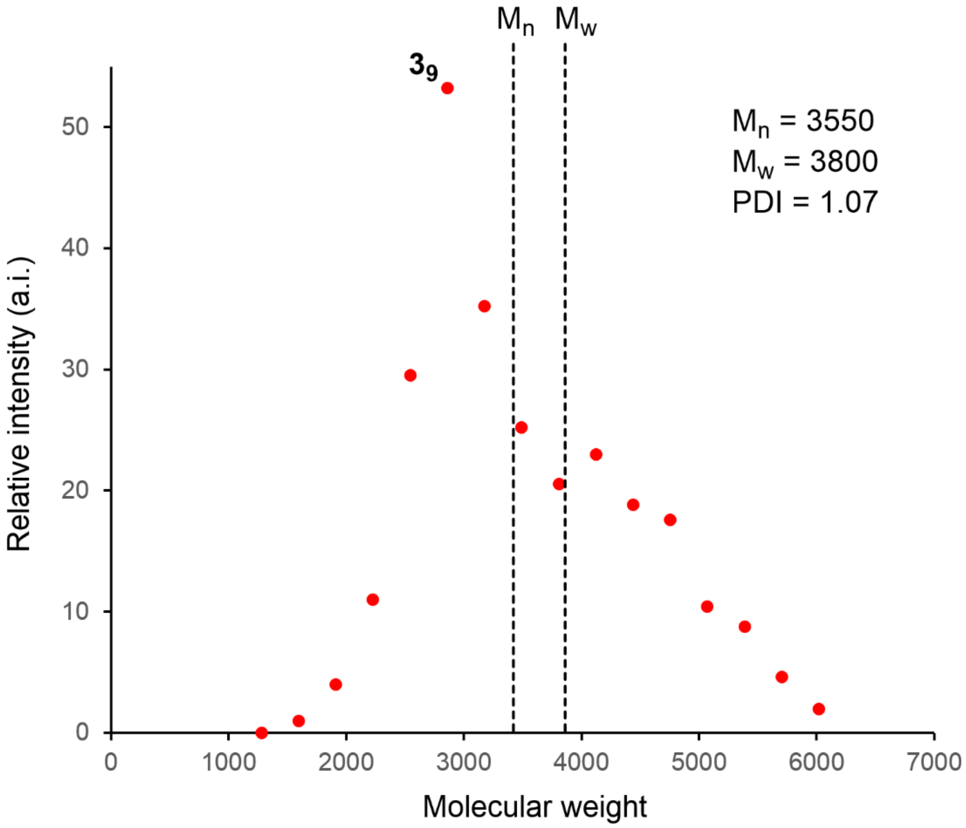


Figure 2. Oligomeric distribution generated by combining contributions from all of the $\mathbf{2}_n$ series observed in Figure 1.

A sample of the same oligomer was then oxidized with H_2O_2, converting all phosphines into phosphine oxides. The affinity of the oxygen for Ag^+ is low, but is good for the harder Na^+, so sodium ions were used as the ionization aid in this analysis [34]. Overall, the signal was considerably weaker than for the previous experiment, resulting in a noisier baseline (Figure 3).

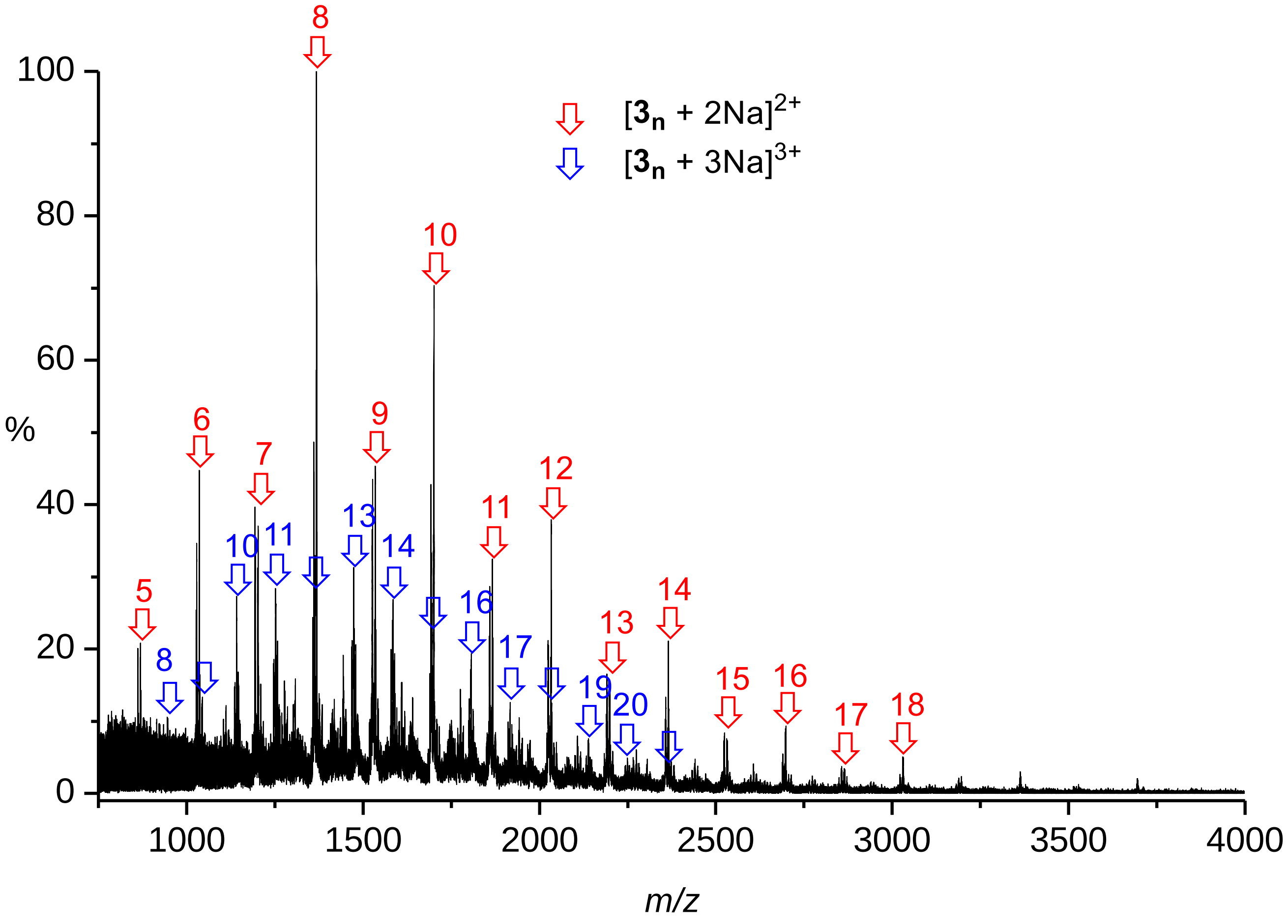


Figure 3. Positive ion ESI-MS of oligomerized and oxidized phosphaalkene **1** to make oligomeric mixture $\mathbf{3}_n$,, recorded in acetonitrile with the addition of NaI.

Just as in the unoxidized oligomeric mixture, no monocations were observed. There were two principal series present, the most prominent series being the dications $[\mathbf{3O_n} + 2Na]^{2+}$, which provided a distribution between *n* = 5 and *n* = 18, with *n* = 8 being most abundant. The dicationic nature of these species is given away by the peaks in the isotope pattern being *m/z* 0.5 apart. The next highest series was [$\mathbf{3O_n}$ + 3Na]$^{3+}$, appearing between *n* = 8 and *n* =20, and peaking at *n* = 13 (all have peaks in the isotope pattern *m/z* 0.33 apart). Some additional complexity appears because oxidation is not complete. Thus, some peaks appear at intervals of *m/z* 8 (*m/z* 5.33 for the 3+ species) below the completely oxidized oligomers.

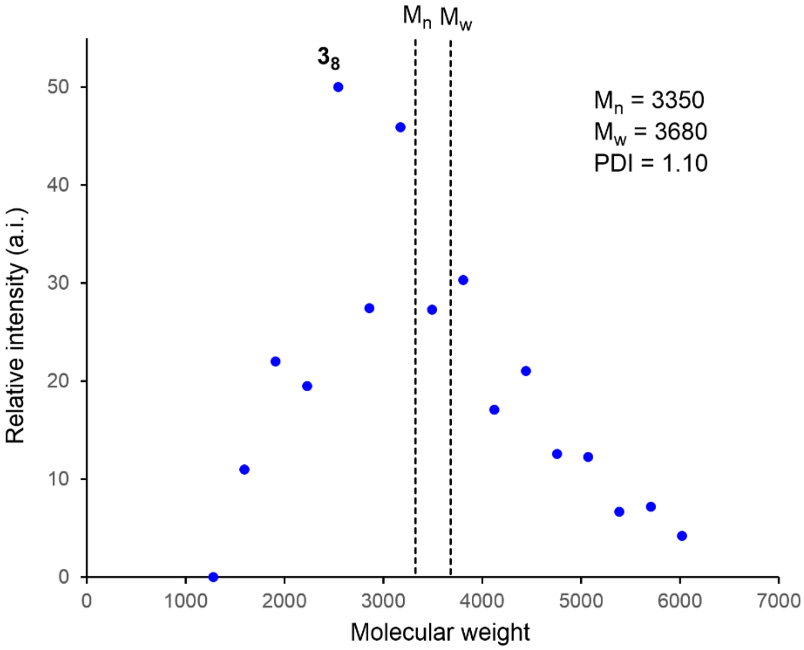


Figure 4. Oligomeric distribution generated by combining contributions from all of the $\mathbf{3}_{\boldsymbol{n}}$ series observed in Figure 3.

No oligomers below *n* = 4 or above *n* = 20 were observed, and the distribution maximises at *n* = 8 (Figure 4). The M_n and M_w were calculated at 3350 and 3680 Da, respectively, giving a polydispersity index of 1.10. This distribution was very similar to that observed for the unoxidized polymer, giving confidence that the results are meaningful. M_n values of 3450±100 Da and a PDI of 1.09±0.01 covers both observed distributions, despite the fact the polymers are chemically distinct and the ionization mechanisms are quite different from one another. As such, we combined together both sets of results in an averaged plot (Figure 5), which suggests the molecular weights of the oligomers form a pattern that is quite close to a normal distribution. The fact that the estimated degree of polymerization ($DP_n \approx 10$) is larger than that expected for an oligomer generated from a [M]:[I] ratio of 4:1 (e.g. $DP_n = 4$) is not unexpected since monomer **1** was not purified to the extent required for a "living" anionic polymerization nor was the initiator (n-BuLi) titrated prior to use. For these reasons, the actual degree of polymerization of $\mathbf{2_n}$ or $\mathbf{3}_n$ is expected to be higher than the calculated molecular weight from the [M]:[I] ratio, as observed. Another possible explanation is that the higher molecular weight oligomers have higher ionization efficiencies than the lower members of the series, regardless of the source of ionization (Ag^+ or Na^+).

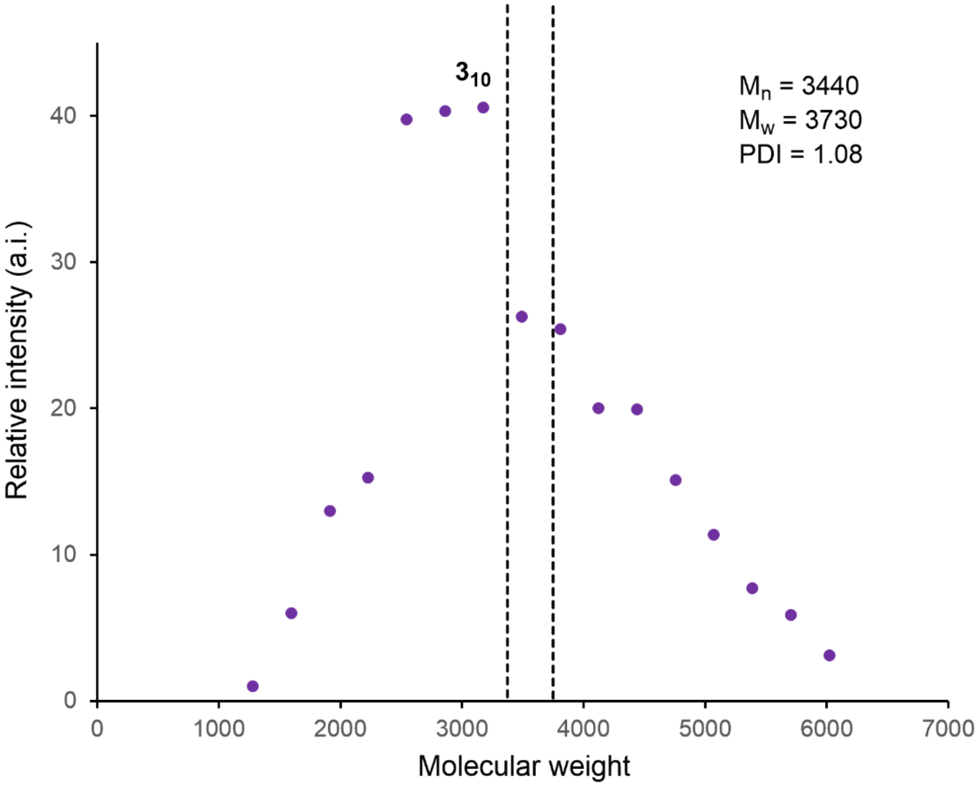


Figure 5. Oligomeric distribution generated by averaging the contributions from all of the $\mathbf{2}_n$ series observed in Figure 1 and the $\mathbf{3}_n$ series observed in Figure 3.

Failure to observe any oligomers of the form $\mathbf{4}_n$ suggests that the appearance of these species in the MALDI-TOF MS of $\mathbf{3}_n$ is a result of fragmentation. Although MALDI is generally a soft ionization technique, it does of course involve intense laser ablation and this oligomer contains a high proportion of aromatic rings that will absorb UV light effectively. Further evidence that fragmentation is happening in MALDI can be gathered by examining the distribution of oligomers – it peaks at $\mathbf{3}_3$, which by ESI does not exist in appreciable quantities at all in solution. It does seem that the fragmentation observed is somewhat selective, as the fragments observed are primarily generated through cleavage of a P-C backbone bond (as opposed to the P-C_{mesityl}, C-C, C-H or P=O bonds).

Experimental

ESI-MS data were collected on a Waters Micromass Q-Tof *micro* mass spectrometer with Z-spray electrospray source. Samples were infused from a 250 μL gas-tight syringe at 10–40 μL min^{-1} via syringe pump. Instrument settings: capillary voltage 2900 V, cone voltage 20 V, source temperature 100 °C, desolvation gas temperature 200 °C. Nitrogen was used as the desolvation gas.

Conclusions

ESI-MS appears to be an effective way of characterizing inorganic oligomers with phosphorus in the backbone. Addition of Ag^+ provided a suitable means of cationizing the phosphorus with available lone pairs, and Na^+ proved to have a strong affinity for phosphine oxides. Therefore, this approach should be generally useful to analyze oligomeric materials provided the choice of cation is judicious. One might expect, for example, that if the oligomers were transformed into phosphine sulfides that silver ions would be a better choice than sodium ions. The reverse would be true for a phosphazene oligomer. Like all such materials, as the average molecular weight of the polymeric compound rises the analysis will become more challenging; there will be more species with greater degrees of charging. Furthermore, the overlap of signals increasingly become a problem and the ions will be distributed across many more values of *m/z*, hence degrading the signal-to-noise ratio. We plan to explore these limits in future work – how many repeat units can be added while still preserving reasonable data quality?

Acknowledgements

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References

(1) Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. *Chem. Soc. Rev.* **2016,** *45*, 922.
(2) Caminade, A. M.; Majoral, J. P. *New J. Chem.* **2013,** *37*, 3358.
(3) Ren, Y.; Baumgartner, T. *Dalton Trans.* **2012,** *41*, 7792.
(4) Bates, J. I.; Dugal-Tessier, J.; Gates, D. P. *Dalton Trans.* **2010,** *39*, 3151.
(5) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006,** *106*, 4681.
(6) Allcock, H. R. *Dalton Trans.* **2016,** *45*, 1856.
(7) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*, Wiley, Hoboken, 2003.
(8) For recent work, see: (a) Womble, C. T.; Coates, G. W.; Matyjaszewski, K.; Noonan, K. J. T. *ACS Macro Lett.* **2016**, *5*, 253. (b) Rawe, B. W.; Gates, D. P. *Angew. Chem. Int. Ed.* **2015**, *54*, 11438. (c) Marquardt, C.; Jurca, T.; Schwan, K. C.; Stauber, A.; Virovets, A. V.; Whittell, G. R.; Manners, I.; Scheer, M. *Angew. Chem. Int. Edit.* **2015**, *54*, 13782. (d) Schäfer, A.; Jurca, T.; Turner, J.; Vance, J. R.; Lee, K.; Du, V. A.; Haddow, M. F.; Whittell, G. R.; Manners, I.; *Angew. Chem. Int. Ed.* **2015**, *54*, 4836. (e) Guterman, R.; Kenaree, A. R.; Gilroy, J. B.; Gillies, E. R.; Ragogna, P. J. *Chem. Mater.* **2015**, ***27***, 1412. (f) Wolf, T.; Steinbach, T.; Wurm, F. R. *Macromolecules*, **2016**, *48*, 3853. (g) Tian, Z. C.; Chen, C. Allcock, H. R. *Macromolecules* **2014**, *47*, 1065. (h) Matano, Y.; Ohkubo, H.; Honsho, Y.; Saito, A.; Seki, S.; Imahori, H. *Org. Lett.* **2013**, *15*, 932. (i) Wang, X.; Cao, K.; Liu, Y.; Tsang, B.; Liew, S. *J. Am. Chem. Soc.* **2013**, *135*, 3399. (j) He, X.; Woo, A. Y. Y.; Borau-Garcia, J.; Baumgartner, T. *Chem. Eur. J.* **2013**, *19*, 7620. (k) Greenberg, S.; Gibson, G. L.; Stephan, D. W. *Chem. Commun.* **2009**, 304.
(9) Mark, J. E.; Allcock, H. R.; West, R., *Inorganic Polymers*. 2nd ed.; Oxford University Press: Oxford, 2005.

(10) Pavelka, L. C.; Holder, S. J.; Baines, K. M. *Chem. Commun.* **2008**, 2346.

(11) Pavelka, L. C.; Milnes, K. K.; Baines, K. M. *Chem. Mater.* **2008,** *20*, 5948.

(12) Tsang, C. W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003,** *125*, 1480.

(13) Tsang, C. W.; Baharloo, B.; Riendl, D.; Yam, M.; Gates, D. P. *Angew. Chem., Int. Ed.* **2004,** *43*, 5682.

(14) Noonan, K. J. T.; Gates, D. P. *Angew. Chem., Int. Ed.* **2006,** *45*, 7271.

(15) Noonan, K. J. T.; Patrick, B. O.; Gates, D. P. *Chem. Commun.* **2007**, 3658.

(16) Noonan, K. J. T.; Feldscher, B.; Bates, J. I.; Kingsley, J. J.; Yam, M.; Gates, D. P. *Dalton Trans.* **2008**, 4451.

(17) Gillon, B. H.; Patrick, B. O.; Gates, D. P. *Chem. Commun.* **2008**, 2161.

(18) Noonan, K. J. T.; Gillon, B. H.; Cappello, V.; Gates, D. P. *J. Am. Chem. Soc.* **2008,** *130*, 12876.

(19) Noonan, K. J. T.; Gates, D. P. *Macromolecules* **2008,** *41*, 1961.

(20) Dugal-Tessier, J.; Serin, S. C.; Castillo-Contreras, E. B.; Conrad, E. D.; Dake, G. R.; Gates, D. P. *Chem. Eur. J.* **2012,** *18*, 6349.

(21) Rawe, B. W.; Chun, C. P.; Gates, D. P. *Chem. Sci.* **2014,** *5*, 4928.

(22) Priegert, A. M.; Siu, P. W.; Hu, T. Q.; Gates, D. P. *Fire Mater.* **2015,** *39*, 647.

(23) Serin, S. C.; Dake, G. R.; Gates, D. P. *Dalton Trans.* **2016,** *45*, 5659.

(24) Siu, P. W.; Serin, S. C.; Krummenacher, I.; Hey, T. W.; Gates, D. P. *Angew. Chem., Int. Ed.* **2013,** *52*, 6967.

(25) Gillon, B. H.; Gates, D. P. *Chem. Commun.* **2004**, 1868.

(26) Blais, J.-C.; Turrin, C.-O.; Caminade, A.-M.; Majoral, J.-P. *Anal. Chem.* **2000,** *72*, 5097.

(27) Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci (A)* **1999,** *36*, 653.

(28) Metters, O. J.; Chapman, A. M.; Robertson, A. P. M.; Woodall, C. H.; Gates, P. J.; Wass, D. F.; Manners, I. *Chem. Commun.* **2014,** *50*, 12146.

(29) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Mass Spectrom. Rev.* **1990,** *9*, 37.

(30) Henderson, W.; McIndoe, J. S., *Mass Spectrometry of Inorganic and Organometallic Compounds: Tools - Techniques - Tips*. John Wiley & Sons: Chicester, 2005.

(31) Yunker, L. P. E.; Stoddard, R. L.; McIndoe, J. S. *J. Mass Spectrom.* **2014,** *49*, 1.

(32) Henderson, W.; Nicholson, B. K. *J. Chem. Soc.-Chem. Commun.* **1995**, 2531.

(33) Öberg, E.; Orthaber, A.; Santoni, M.-P.; Howard, F.; Ott, S. *Phosphorus, Sulfur, and Silicon* **2013,** *188*, 152.

(34) Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 519.