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Characterization of Oligo(vinyl phosphonate)s by High-Resolution Electrospray Ionization Mass Spectrometry: Implications for the Mechanism of Polymerization

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ABSTRACT: Dimethyl vinyl phosphonate, diethyl vinyl phosphonate, and diisopropyl vinyl phosphonate were polymerized at 60 °C via free radical polymerization to give oligomers. High-resolution electrospray ionization−mass spectrometry was used to analyze the resulting oligo(vinyl phosphonate)s in order to elucidate their polymerization mechanism. The resulting mass spectra showed no evidence of polymer chains capped with initiator derived fragments as end groups. Instead, the mass spectra indicated that transfer reactions generate activated monomer species (i.e., a monomeric radical), which then act as initiators in the polymerizations. Additionally, these studies indicate that termination takes place by chain transfer to monomer.

Introduction

Copolymers of vinyl phosphonates[1] find use in the electrical, transportation, and construction industries due to their flame-retardant properties;[2] however, relatively few investigations into the homopolymerization of vinyl phosphonates have been reported. The few reports found in the literature have investigated the free radical polymerization of diethyl vinyl phosphonate (DEVP),[3] diisopropyl vinyl phosphonate (DISP),[4] and dimethyl vinyl phosphonate (DMVP).[5,6] Kosolapoff et al. indicated the reluctance of DEVP to polymerize,[3] and Pike et al. suggested that chain transfer may play an important role in the hompolymerization of DEVP and DISP.[4] The failure of vinyl phosphorus monomers to homopolymerize to high molecular weight products was explained invoking significant steric effects that retard the propagation reaction with regard to termination and chain transfer processes.[7] However, vinyl phosphonic acid can be polymerized to high molecular weight products by free radical polymerization as was recently demonstrated.[6]

A significant challenge regarding the study of oligo(vinyl phosphonate)s is the characterization of oligomers in terms of their molecular weights. Size exclusion chromatography cannot be used to obtain the weight-averaged molecular weight, M_w, n, or polydispersity of poly(vinyl phosphonate)s, since narrow molecular weight distribution standards are not available for calibration. Moreover, static light scattering is difficult to apply to determine the M_w of poly(vinyl phosphonate)s of only oligomeric nature.

Mass spectrometry is another technique capable of obtaining molecular weight information, and the capability of mass spectrometric techniques, such as electrospray ionization−mass spectrometry (ESI-MS), in the analysis of synthetic oligomers has been outlined in numerous publications.[8−12] ESI-MS is a soft ionization method capable of detecting the exact masses of individual oligomer chains with limited tendency toward end-group fragmentation.[8−10,12] It thus appears to be well suited to the characterization of poly(vinyl phosphonate)s and specifically its oligomers. However, to the best of our knowledge, until today there is no report on a mass spectrometry study of poly(vinyl phosphonate)s.

The aim of the current contribution is to investigate the details of the free radical polymerization mechanism of vinyl phosphonates to better understand the reasons for their sluggish polymerization behavior. At the onset of this work, there was a strong hint that transfer to the monomer plays an important role in the polymerization,[13] and this gave the reason to test the following monomers: $CH_2{=}CH{-}P(O)(OCH_3)_2$ (DMVP), $CH_2{=}CH{-}P(O)(OCH_2CH_3)_2$ (DEVP), and $CH_2{=}CH{-}P(O)(OCH(CH_3)_2)_2$ (DISP).

Experimental Section

Materials. All chemicals were used as received unless otherwise noted. DMVP (Aldrich, 85%) and DEVP (Aldrich, 97%) were distilled under reduced pressure. DISP was synthesized following the procedure described in the literature.[4] 2,2′-Azobis(2-methylpropionitrile) (AIBN; Fluka, 98%) and 4,4-azobis(4-cyanovaleric acid) (CVA; Aldrich, 98%) were used as initiators.

Polymerization of DISP. DISP (1.0 mL, 5×10^{-3} mol) and initiator (AIBN (0.5 mg, 3.0×10^{-3} mmol) (0.5 g/L) or CVA (0.9 mg, 3×10^{-3} mmol) (0.85 g/L)) were put in a Schlenk flask, which was evacuated and backfilled with nitrogen prior to the polymerization. The reaction mixture was heated to 60 °C for 12.5 h. The conversion was 35% as determined by ^{1}H NMR by comparing the intensities of the signal of the methine (OCH) protons of oligo(DISP) with that of the double bonds left in the reaction medium in the ^{1}H NMR spectrum after polymerization.

Polymerization of DEVP. DEVP (1.0 mL, 6.5×10^{-3} mol) and AIBN (0.64 mg, 3.88×10^{-3} mmol) (0.64 g/L) were put in a Schlenk flask, which was evacuated and backfilled with nitrogen prior to the polymerization. The synthetic procedure was the same as described for DISP. The conversion was found as 17% by ^{1}H NMR by comparing the intensities of the signal of the methylene (OCH_2) protons of oligo(DEVP) with that of the double bonds left in the reaction medium in the ^{1}H NMR spectrum after polymerization.

Polymerization of DMVP. DMVP (1.0 mL, 8.4×10^{-3} mol) and AIBN (0.82 mg, 4.9×10^{-3} mmol) (0.82 g/L) were put in a

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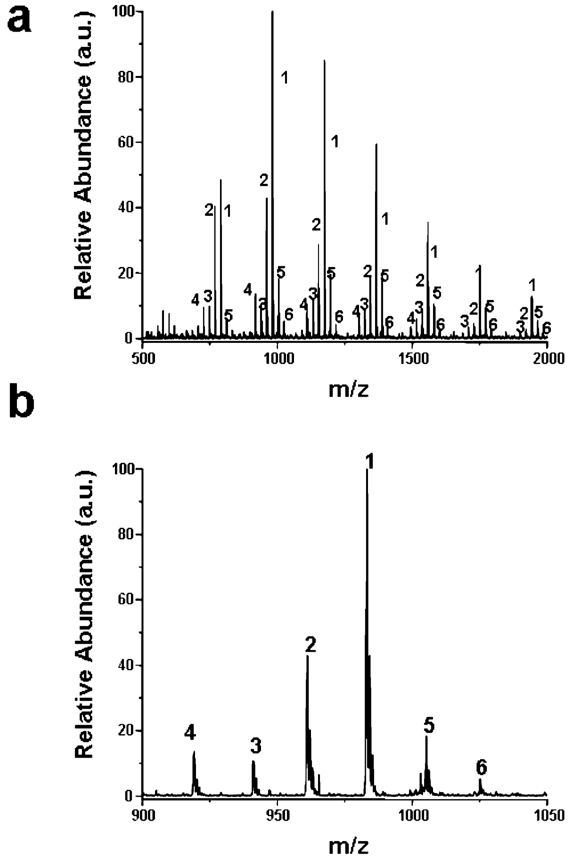


Figure 1. Electrospray ionization−mass spectrum obtained on a Thermo Finnigan LCQ Deca ion trap mass spectrometer using 0.1 mM sodium acetate in methanol as eluent from a sample of oligo(diisopropyl vinyl phosphonate) synthesized in the presence of 0.06 mol % 2,2′-azobis(2-methylpropionitrile) as initiator in bulk (a) shown over a full *m*/*z* scan range and (b) shown over a *m*/*z* range corresponding to a single diisopropyl vinyl phosphonate repeat unit.

Schlenk flask, which was evacuated and backfilled with nitrogen prior to the polymerization. Reaction time and temperature were 12.5 h and 60 °C, respectively. ^{1}H NMR revealed the conversion as 27% by comparing the intensities of the signal of the methine (OCH) protons of oligo(DMVP) with that of the double bonds left in the reaction medium in the ^{1}H NMR spectrum after polymerization.

Characterization. The product species present in unpurified oligo(vinyl phosphonate) samples were characterized using electrospray ionization−mass spectrometry (ESI-MS). Two soft-ionization ESI instruments were employed in the mass spectroscopic studies: a Thermo Finnigan LCQ Deca ion trap mass spectrometer (Thermo Finnigan, San Jose, CA) and an Ultima hybrid quadrupole time-of-flight (Q-TOF) instrument (Micromass, Altrincham, Cheshire, UK). All theoretical molecular weights were calculated using the exact mass as provided by the program package CS ChemDraw 6.0 for the first peak in any given isotopic peak pattern.

The LCQ Deca ion trap instrument was equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode and was used in positive ion mode. Mass calibration was performed using caffeine, MRFA, and Ultramark 1621 (Aldrich) in the mass-to-charge (*m*/*z*) range 195−1822 Da. All spectra were acquired within the *m*/*z* range of 150−2000 Da with spray voltages ranging from 3 to 6 kV, capillary voltages ranging from 10 to 45 V, and a capillary temperature of 275 °C. Nitrogen was used as sheath gas (flow: 50% of maximum), and helium was used as auxiliary gas (flow: 5% of maximum). Typical *m*/*z* value errors were observed to be ±0.3 Da. Theoretical isotopic peak patterns were generated using the Xcalibur software.

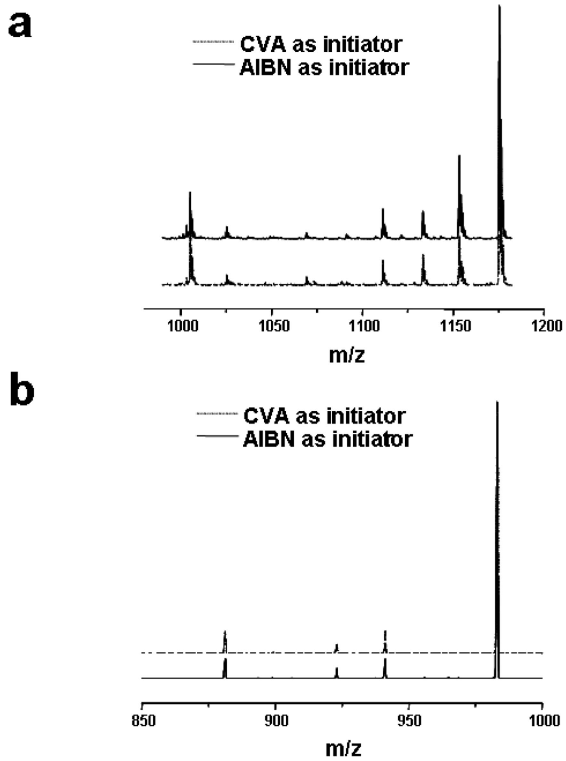


Figure 2. Electrospray ionization−mass spectra obtained on a Thermo Finnigan LCQ Deca ion trap mass spectrometer using 0.1 mM sodium acetate in methanol as eluent from samples of oligo(diisopropyl vinyl phosphonate) synthesized in the presence of 0.06 mol % 2,2′-azobis-(2-methylpropionitrile) and 4,4-azobis(4-cyanovaleric acid) as initiator in bulk, shown over *m*/*z* ranges corresponding to a single diisopropyl vinyl phosphonate repeat unit.

The Q-TOF instrument was equipped with a ZSpray sample introduction system in a nanoflow electrospray ion source and was used in positive ion mode with a source temperature of 200 °C. Mass calibration was performed using the fragment ions of Glu-fibrino peptide. Samples were delivered into the ion source from nanospray emitters (Proxeon, Odense, Denmark). The cone voltage offset was set at 35 V, and the system was operated with capillary voltages ranging from 800 to 1200 kV. All spectra were acquired via the TOF analyzer and were integrated every 2.4 s within the *m*/*z* range 50−2000 Da. Typical *m*/*z* value errors were observed to be ±0.06 Da. Theoretical isotopic peak patterns were generated using the MassLynx software, version 4.0.

Two-stage mass spectrometry (MS/MS) experiments were conducted upon precursor ions of interest in order to gain additional structural information from the resulting fragmentation patterns. All spectra were acquired using identical source conditions to the single-stage mass spectrometry experiments. Typical normalized collision energies ranged from 25 to 30% for MS/MS experiments conducted using both the ion trap and Q-TOF instruments.

Three different eluents were employed in the ESI-MS studies: methanol with a sodium acetate concentration of 0.1 mM; methanol with a potassium iodide concentration of 0.03 mM; and methanol with a lithium iodide concentration of 0.03 mM.

^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker spectrometer operating at 300 MHz.

Results and Discussion

Vinyl phosphonates were homopolymerized in the presence of 0.5 mol % of AIBN (or CVA as radical initiators) at 60 °C for 12.5 h in bulk. The resulting oligomers were analyzed by ESI-MS in order to gain insight into structure of the products and more specifically to the end groups. The end-group characterization of the various oligo(vinyl phosphonate)s are presented below.

Characterization of Oligo(DISP). An ESI-MS ion trap mass spectrum obtained from oligo(DISP) synthesized in the presence

Table 1. Peak Assignments for the Mass Spectrum Obtained from Oligo(diisopropyl vinyl phosphonate) Shown in Figure 1 Obtained Using a Quadrupole Ion Trap Detector

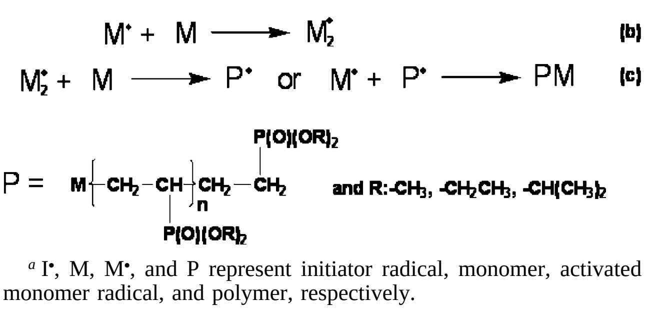
peak	ion assignment	$m/z_{\mathrm{theoretical}}$	$m/z_{\mathrm{experimental}}$	error (m/z)
1	$[\mathbf{P} + \mathrm{Na}]^+$	983.44	983.44	0.00
2	$[\mathbf{P} + \mathrm{H}]^+$	961.46	961.20	0.26
3	$[(\mathbf{P}\text{-1 ester group}) + \mathrm{Na}]^+$ or $[\mathbf{P_2} + \mathrm{Na}]^+$	941.39	941.30	0.09
4	$[(\mathbf{P}\text{-1 ester group}) + \mathrm{H}]^+$ or $[\mathbf{P_2} + \mathrm{H}]^+$	919.40	919.20	0.20
5	$[(\mathbf{P}\text{-1H} + \mathrm{Na}) + \mathrm{Na}]^+$	1005.43	1005.30	0.07
6	$[\mathbf{P_1} + \mathrm{Na}]^+$	1025.48	1025.27	0.21

of AIBN is depicted in Figure 1. Six adduct species (**1**−**6**) were observed within each repeat unit. Signals labeled with the same number in different repeat units are separated by 192.09 mass-to-charge (*m*/*z*) units, which corresponds to the exact mass of the monomer. Theoretical and experimental *m*/*z* values used in the assignment of the mass spectrum of oligo(DISP) are given in Table 1.

Each main peak (labeled **1** in Figure 1a) of the distribution corresponds to a chain with the expected structure **P** (Scheme 1) for a chain growth where an activated monomer species formed via transfer from an AIBN radical acts as the initiator, and termination occurs by a chain transfer reaction. For instance, the *m*/*z* of the most abundant peak in the observed distribution, 983.44, corresponds to a singly charged sodiated adduct formed from a oligo(DISP) 3-mer chain with a monomer unit at both ends (Table 1). In addition to these sodium adducts, protonated adducts formed from chains of **P** were identified as well. The signal belonging to the protonated adduct formed from this oligomeric species is labeled **2** in Figures 1a,b. Experimental and simulated isotopic pattern distributions for the proposed chemical structure are in excellent agreement.

To confirm that the monomer radical does indeed initiate the homopolymerization of DISP, the synthesis of oligo(DISP) was repeated in the presence of another initiator with a similar half-life compared to AIBN at the same polymerization temperature, namely CVA. Since decomposition constants of AIBN and CVA in the same solvent were not available at 60 °C, the half-lives of the two initiators were compared with the aid of data already present in the literature at 80 °C and in similar solvents. AIBN and CVA have a half-life of 1.24 h at 80 °C in toluene or at 78 °C in dimethylacetamide, respectively.[13] ESI ion trap mass spectra of oligo(DISP) prepared with two different initiators are given in Figure 2a, where a single repeat unit is depicted. Clearly, the spectra of oligo(DISP) synthesized with AIBN and CVA are identical. In other words, mass spectra obtained from oligo(DISP) synthesized in the presence of AIBN and CVA did not reveal the signature of the initiator fragments as the end group, since end groups arising from different initiators would lead to a differences in the *m*/*z* of the individual oligomers. Two stage mass spectrometry (MS/MS) experiments were also conducted with two oligo(DISP) samples synthesized with the different initiators in order to gain additional structural information for selected signals from the resulting fragmentation patterns. A comparison of the spectra of the signals observed at *m*/*z* 983.44 in the two oligo(DISP) samples revealed the same fragmentation products, confirming the absence of initiator fragments as end groups. The mass losses observed during fragmentation correspond to the masses of propene and water, which are formed from oligo(DISP) upon elimination of the isopropyl ester moiety and formation of cyclic anhydrides, respectively. In other words, the chemical structures observed in oligo(DISP) samples synthesized in the presence of two different initiators are identical. These results confirm that the homopolymerization of DISP proceeds via chain transfer from an initiator radical to monomer, which then acts as the true initiating species in the polymerization (Schemes 1a,b). Mass spectra also indicate that the termination step of the polymerization takes place via chain transfer (Scheme 1c). Chain transfer either to monomer or to polymer can terminate the polymerization of DISP. Termination via chain transfer to polymer would lead to a branched polymer; however, evidence for such a branched polymer has yet to be observed.

Scheme 1. Suggested Mechanism for Free Radical Polymerization for Vinyl Phosphonates[a]



[a] I•, M, M•, and P represent initiator radical, monomer, activated monomer radical, and polymer, respectively.

As mentioned, additional signals other than signals **1** and **2** are also present in the mass spectra. The mass of the peak labeled **3** corresponds to an oligo(DISP) chain in which one of the isopropyl groups is eliminated. The peak observed at *m*/*z* 941.30 corresponds to a sodiated adduct formed from a oligo(DISP) chain with three monomer units, in which one monomer has lost one isopropyl group. The *m*/*z* 941.39 in the mass spectrum of oligo(DISP) collected using a Q-TOF instrument, which provides spectra of a higher accuracy than the ion trap detector, confirms the elimination of a propene unit from oligo(DISP). (It may be likely that the elimination of the propene unit occurs during the acquisition of the mass spectrum, but from the given data, we cannot rule out the possibility of it occurring before.) The peak observed at *m*/*z* 919.20 (which has been labeled **4** in Figure 1) represents the protonated form of the oligo(DISP), which has lost one isopropyl group by elimination. To clarify the chemical structure giving rise to the peak labeled **5** in Figure 1, the acquisition of mass spectra from the oligo(DISP) sample were repeated using dopant cations other than Na^+, namely K^+ and Li^+. The mass spectra obtained with the various dopant cations are given in Figure 3. A comparison of the spectra revealed that the separation between the peak labeled **5** in Figure 1 and any other peak varies when different dopant cations are used. The position of the signals equivalent to peak **5** in each spectra are denoted as * in Figure 3. The following relation is found between the *m*/*z* of the peak labeled as **5** and **1**:

$$m/z(\mathbf{5}) = m/z(\mathbf{1}) - m/z(\text{proton}) + m/z(\text{cation})$$

These data suggest that a proton in the main reaction product **P** is replaced with a dopant cation. The mass spectra in Figure 3 show the incorporation of Na as well as K and Li into the main reaction product **P** when K^+ and Li^+ are used as dopant cations. At this stage of the study, the exact position of the metal

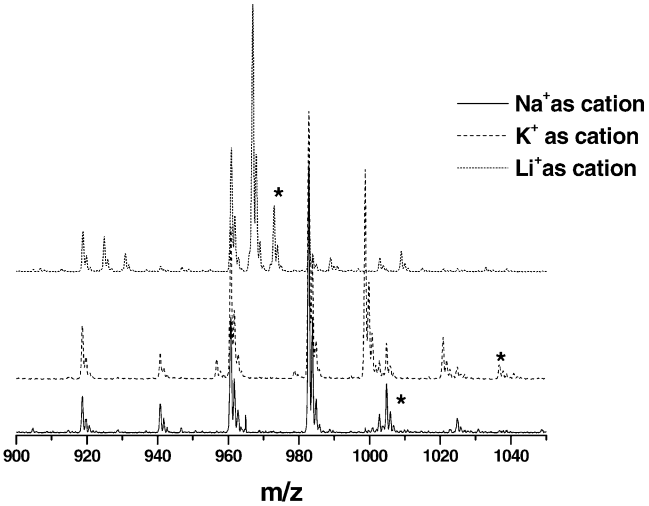
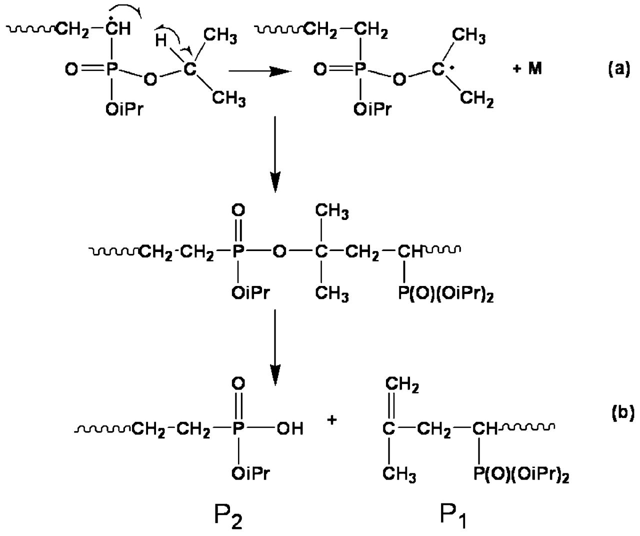


Figure 3. Electrospray ionization-mass spectra obtained on a Thermo Finnigan LCQ Deca ion trap mass spectrometer using various dopant cations (0.1 mM sodium acetate/methanol; 0.03 mM potassium iodide/methanol; 0.03 mM lithium iodide/methanol) from a sample of oligo(diisopropyl vinyl phosphonate) synthesized in the presence of 0.06 mol % 2,2′-azobis(2-methylpropionitrile) as initiator in bulk, shown over *m*/*z* ranges corresponding to a single diisopropyl vinyl phosphonate repeat unit.

Scheme 2. Possible Chain Scission Reaction of Oligo(diisopropyl vinyl phosphonate) Repeat Unit



being incorporated into the polymer is unknown. The reason for the higher number of signals observed in spectra collected when K^+ and Li^+ are used as dopant cations is due to the presence of sodium adducts in these spectra, in addition to potassium or lithium adducts, respectively.

Last, the signal located at *m*/*z* 1025.27 (labeled **6** in Figure 1) originates from sodiated adducts formed from oligo(DISP) $\mathbf{P}_1$ trimer chains, in which a propene unit has been incorporated as a result of chain scission. Such structures have already been reported for oligo(vinyl phosphonate)s in the literature.[4,14] In other words, propagating radicals formed from activated monomer units attacking other monomer units abstract a proton from the methine carbon in the backbone intramolecularly (Scheme 2a), leading to the relocation of the radical to the pendant group. Thus, a new propagating radical is formed (Schemes 2a,b). Chain scission at the alkoxy group contained in the main chain thus leads to two polymer chains $\mathbf{P}_1$and $\mathbf{P}_2$, as shown in Scheme 2b. Product $\mathbf{P}_2$ will give rise to the same signals observed from oligo(DISP) chains in which one of the isopropyl groups has been eliminated. The corresponding signals are labeled **3** in Figure 1.

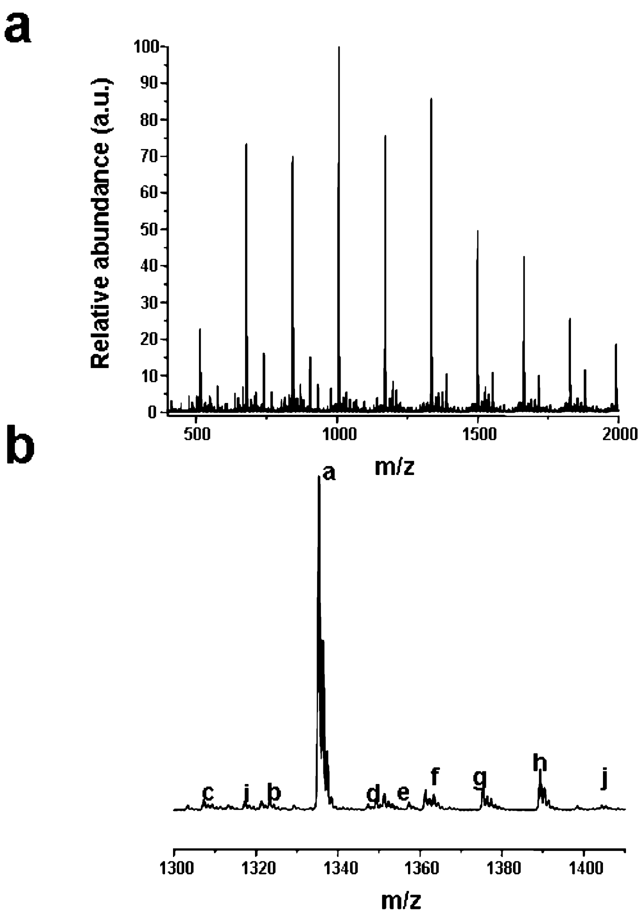


Figure 4. ESI mass spectrum obtained on a Thermo Finnigan LCQ Deca ion trap mass spectrometer from a sample of oligo(diethyl vinyl phosphonate) synthesized in the presence of 0.06 mol % 2,2′-azobis-(2-methylpropionitrile) as initiator in bulk (a) shown over a full *m*/*z* scan range and (b) shown over a *m*/*z* range corresponding to a single diisopropyl vinyl phosphonate repeat unit.

Characterization of Oligo(DMVP) and Oligo(DEVP). In order to explore the influences of different ester groups on the polymerization behavior of vinyl phosphonates, oligo(vinyl phosphonate)s with ethyl and methyl group were prepared by free radical polymerization and analyzed using ESI-MS.

An ESI ion trap spectrum of oligo(DEVP) is depicted in Figure 4, and theoretical as well as experimental *m*/*z* values used in the assignments of the mass spectrum of oligo(DISP) are given in Table 2. The mass spectrum of oligo(DEVP) is dominated by signals arising from an oligomer chain **P** (see Scheme 1). For instance, the peak observed at *m*/*z* 1335.38 corresponds to a sodiated adduct formed from a oligo(DEVP) **P** 6-mer. This peak is labeled **a** in Figure 4b. The signals labeled as **d** and **i** in Figure 4b correspond to the potassium and proton adducts of **P**. The replacement of protons in oligo(DEVP) with sodium and potassium atoms is indicated by the presence of signals observed at *m*/*z* 1357.35 (labeled **e**) and *m*/*z* 1389.53 (labeled **h**), which correspond to the respective sodium and potassium adducts. The ESI ion trap mass spectrum obtained from oligo(DEVP) also reveals that ethyl groups within the oligomer chains are eliminated. The signals labeled **c** (*m*/*z* 1307.20) and **b** (*m*/*z* 1323.40) are due to sodium and potassium adducts formed from chains of oligo(DEVP) in which one ester group is converted to an acid group (−OH). At this stage, the precise origin of signal **f** and **g** is unknown. However, MS/MS experiments conducted upon the signal labeled **g** showed no

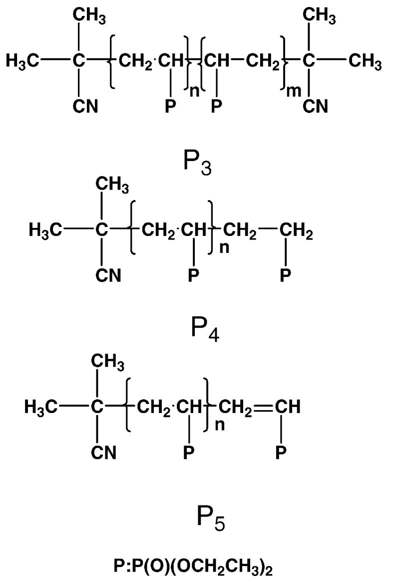
Table 2. Peak Assignments for the Mass Spectrum Obtained from Oligo(diethyl vinyl phosphonate) Shown in Figure 4 Obtained Using a Quadrupole Ion Trap Detector

peak	ion assignment	$m/z_{\text{theoretical}}$	$m/z_{\text{experimental}}$	error (m/z)
a	[**P** + Na]$^+$	1335.47	1335.38	0.11
b	[(**P**-1 ester group) + K]$^+$	1323.41	1323.40	0.01
c	[(**P**-1 ester group) + Na]$^+$	1307.44	1307.20	0.24
c	[$\mathbf{P_3}$ + Na]$^+$	1307.51	1307.20	0.31
d	[**P** + K]$^+$	1351.44	1351.46	0.02
e	[(**P**-1H + Na) + Na]$^+$	1357.45	1357.33	0.12
h	[(**P**-1H + K) + K]$^+$	1389.42	1389.53	0.11
i	[**P** + H]$^+$	1313.48	1313.26	0.22
j	[$\mathbf{P_4}$ + Na]$^+$	1404.33	1404.53	0.20

evidence for the presence of polymer chains capped with AIBN fragments. Only the elimination of water and ethylene were observed upon fragmentations of the ions contributing toward signal **g**, and no fragment ions associated with products containing AIBN derived cyanoisopropyl end groups were observed. This suggests that this peak is be related to a species arising from the chain transfer initiation mechanism.

In addition to the reaction products arising from the chain transfer initiation mechanism, the ESI ion trap mass spectrum of oligo(DEVP) also indicates the presence of chains with AIBN fragments as end groups (Scheme 3). In addition to the aforementioned product assignment, the peak labeled **c** can also be assigned to a polymer chain with initiator fragments at both ends, as shown in Scheme 3. The formation of $\mathbf{P_3}$ is possible under the condition that radicals formed from the decomposition of AIBN initiate the polymerization of DEVP, and termination takes place via combination. The *m*/*z* expected from a singly charged sodium adduct formed from a 7-mer of such an oligomeric chain is 1307.51. Peak assignments for $\mathbf{P_3}$ or oligo(DEVP) chains which have lost one ester group are both within the error range of the ESI ion trap instrument. In an attempt to obtain more accurate *m*/*z* data for peak **c**, a mass spectrum for oligo(DEVP) was collected using a Q-TOF instrument; however, no signals corresponding to peak **c** were observed in these spectra. Additionally, the ESI ion trap mass spectrum of oligo(DEVP) indicates the presence of oligo(DEVP) chains with an initiator fragment as one end group $\mathbf{P_4}$. The signal (*m*/*z* 1404.33) assigned to $\mathbf{P_4}$ is labeled **j** in the spectrum. $\mathbf{P_4}$ may be formed via the free radical polymerization of DEVP when AIBN acts as initiator and termination occurs by disproportionation. Termination of the polymerization by disproprotionation would give rise to two products, i.e., $\mathbf{P_4}$ and $\mathbf{P_5}$; however, signals corresponding to adducts formed from $\mathbf{P_5}$ are absent in the mass spectrum obtained from oligo(DEVP). These observations suggest that termination leading to the formation of $\mathbf{P_4}$ occurs by chain transfer to monomer. Although oligo(DEVP) chains with initiator fragments as end groups were observed in the mass spectrum, the relative intensities of these products were very low compared to the intensities of the oligomer chains formed as a result of chain transfer initiation mechanism. Thus, the suggested chain transfer mechanism is the predominant initiation pathway.

Scheme 3. Reaction Products Expected from the Polymerization of Diethyl Vinyl Phosphonate 2,2′-Azobis(2-methylpropionitrile)-Derived Radicals Acting as Initiating Species



Q-TOF mass spectra obtained from oligo(DMVP) revealed a polymer chain analogous to **P** as the main reaction product of free radical polymerization of DMVP. For instance, the *m*/*z* of the most abundant peak in the distribution, 567.05, corresponds to a sodiated adduct formed from an oligo(DMVP) 2-mer carrying a monomer unit at both ends (expected *m*/*z*: 567.11). In addition to sodium adducts, signals corresponding to protonated adducts formed from oligo(DMVP) chains are also observed in the spectrum. It is worth noting that the expected signals arising from oligomer chains with AIBN fragments as end groups are very close to the *m*/*z* observed for the most abundant signals in the Q-TOF spectra. For example, the expected *m*/*z* for such an AIBN fragment-capped oligo(DMVP) 2-mer cationized with sodium is 567.18. Assigning the signals for the oligo(DMVP) with such a product would lead to an error of 0.13 *m/z*, which is unacceptably high for a Q-TOF mass analyzer. Therefore, the main signal in each distribution was assigned to an oligomeric chain formed as a result of transfer reactions during the polymerization of DMVP. Table 3 shows the theoretical and experimental *m*/*z* values used in the interpretation of the mass spectrum obtained from oligo(DMVP).

Implications of the End-Group Characterizations. Analyses of the mass spectra obtained from oligo(vinyl phosphonate)s with different ester groups reveals that chain transfer reactions dominate in the polymerization of vinyl phosphonates. Chain transfer reactions are important in free radical polymerizations because they limit the maximum attainable molecular weight. The mass spectra of all of the oligo(vinyl phosphonate)s reported

Table 3. Comparison of Theoretical *m*/*z* Values for the Oligo(dimethyl vinyl phosphonate) Chain Formed via the Chain Transfer Initiation Mechanism with Experimental *m*/*z* Values Obtained Using an Ultima Hybrid Quadrupole Time-of-Flight Mass Spectrometer (*n* Represents the Degree of Polymerization)

n	$m/z_{\text{theoretical}}$	$m/z_{\text{experimental}}$	error (m/z)
2	567.11	567.05	0.06
3	703.13	703.10	0.03
4	839.16	839.12	0.04
5	975.19	975.16	0.03
6	1111.22	1111.18	0.04
7	1247.25	1247.21	0.04
8	1383.28	1383.24	0.04

in this study indicate that the major reaction products do not possess any initiator fragments as end groups, thus suggesting that an activated monomer (i.e., a monomeric radical) acts as the initiating species in the polymerizations. The formation of the activated monomer (i.e., monomeric radical) occurs via a transfer reaction from the initiator to monomer, which involves a hydrogen atom transfer (Scheme 1a). The active radical may be located either on the methine carbon in the vinyl moiety or on one of the carbon atoms in the pendant group. It is already reported in the literature that mechanisms for transfer to monomer involving the loss of a vinylic hydrogen seem unlikely due to the very strong C−H bonds.[15] Therefore, it is expected that the nature of the activated monomer varies with the structure of the ester group in each vinyl phosphonate. For example, transfer to DISP will most likely result in the formation of a tertiary carbon radical, whereas primary and secondary radicals are expected to form upon transfer to DMVP and DEVP, respectively. Tertiary carbon-centered radicals are known to be more stable than primary and secondary ones. Additionally, the chain transfer constants to isopropyl esters are higher than those for methyl and ethyl esters.[13] In other words, the stability of the monomer radicals and the efficiency of the formation of the activated monomer will vary depending on the ester moiety present in each vinyl phosphonate. At this stage of the study the precise nature of the activated monomer remains open, but it is apparent that the activated monomer attacks the vinyl phosphonates leading to chain growth in all cases. The peak assignments for the most abundant signals in all of the mass spectra recorded in this study indicate that termination occurs by chain transfer.

Chain Lengths and Conversions. Although identical experimental conditions were employed during the synthesis of the oligo(vinyl phosphonate)s with various ester moieties, differences in conversion were observed for each of these different vinyl phosphonates. For example, almost the same conversion of 35% and 41% was determined for the polymerization of DISP in the presence of AIBN and CVA. However, the conversions in the polymerizations of DEVP and DMVP were found to be only 17% and 27%, respectively, when AIBN was used as initiator. For all of the above experiments, an identical reaction time of 12.5 h was used. Since the activated monomer unit acts as an initiator in all of the polymerizations, the concentration of the monomeric radicals in the reaction medium will depend on the efficiency of the chain transfer to monomer. The relative concentration of the monomeric radicals is expected to be the highest in the polymerization of DISP due to the higher chain transfer constant of isopropyl esters when compared to methyl and ethyl esters.[13] In other words, the number of the polymer chains initiated is higher in the polymerization of DISP than in the case of other vinyl phosphonates, which leads to a higher conversion, as observed in the polymerization of DISP. This scenario is consistent with the observation that initiator derived radicals cannot be identified as oligomer end groups, and therefore, they do not initiate the polymerization directly.

The average degree of polymerization of oligo(vinyl phosphonate)s prepared via free radical polymerization in the presence of AIBN were estimated on the basis of mass spectra. For both oligo(DISP) and oligo(DEVP), an average degree of polymerization of 6 was calculated from the respective ESI ion trap spectra recorded for each of these oligomers. ESI spectra recorded from oligo(DMVP) indicated the average degree of polymerization as 9. At this stage of study, we hesitate to compare the oligo(vinyl phosphonate)s with various ester groups in terms of their molecular weight. However, we can conclude that vinyl phosphonates give rise to oligomers via free radical oligomerization with AIBN as initiator. In other words, the maximum attainable molecular weight is limited by the chain transfer reactions. The ratio of the propagation rate constant over the transfer rate constant seems to depend on the nature of the alkyl residue in the phosphonate—not too surprising, when one considers the generally accepted wisdom that rate constants for transfer to solvents depend on the molecular structure of the solvents used in free radical polymerizations.[13]

Conclusions

Only oligomers of vinyl phosphonates with various ester groups can be successfully synthesized via free radical oligomerization at 60 °C in bulk. High-resolution ESI mass spectra for oligo(DISP), oligo(DEVP), and oligo(DMVP) were obtained, and all of the product signals observed in these spectra were assigned with the exception of two minor signals observed in the products of polymerization of DEVP. Detailed analyses of the mass spectra revealed that the polymerization of vinyl phosphonates proceeds via chain transfer from initiator to monomer, forming an activated monomer which acts as the initiating species in the polymerization. The chain growth is dominated by transfer reactions. Intramolecular hydrogen transfer from side group located hydrogens to the backbone free radical results in an isomerization reaction, which in consequence creates a P−O−C− bond in the main chain. The bond is thermally labile and leads to a specific chain scission reaction which is detected in ESI-MS. Alternatively, chain transfer to side groups of already formed oligomers (intermolecular hydrogen transfer) may lead to the formation of branches. However, there is no evidence for such branching at present.

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