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^{31}P and ^{1}H NMR studies of the transesterification polymerization of polyphosphonate oligomers

R. Dustan Myrex [a], Brandon Farmer [a], Gary M. Gray [a,*], Young-Jin Wright [b], Jennifer Dees [b], Prakash C. Bharara [b], Houston Byrd [b], Keith E. Branham [c]

[a] *Department of Chemistry, University of Alabama at Birmingham, 201 Chemistry Building, 901 14th Street, South Birmingham, AL 35294-1240, USA*
[b] *Department of Biology and Chemistry, University of Montevallo, Station 6480, Montevallo, AL 35115, USA*
[c] *Absorbable Polymer Technologies, Pelham, AL 35124, USA*

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Abstract

Polymeric phosphonate esters are an interesting class of organophosphorus polymers because both the polymer backbone and phosphorus substituents can be modified. These polymers have been prepared by ring-opening polymerizations of cyclic phosphites, stoichiometric polycondensations of dimethyl phosphonate with diols in conjunction with diazomethane treatment and by transesterification of polyphosphonate oligomers. Our initial attempts to prepare high molecular weight polymeric phosphonate esters by the transesterification methods were unsuccessful. Results indicate that the reactions of dimethyl phosphonate with diols to form polyphosphonate oligomers with only methyl phosphonate end groups are plagued by a serious side reaction that forms phosphonic acid end groups. These end groups do not participate in the transesterification reaction and limit the molecular weights of the polymers that can be obtained. The phosphonic acid end groups can be converted into reactive methyl phosphonate end groups by treatment with diazomethane, however diazomethane is explosive and the polymerization is slow. An alternative route for the production of high molecular weight polymers is the transesterification of the 1,12-bis(methyl phosphonato)dodecane, formed by the reaction of excess dimethyl phosphonate and 1,12-dodecanediol, with a Na_2CO_3 promoter. This allows polymers with molecular weights of up to 4.5×10^4 to be prepared, and no phosphonic acid end groups are observed in these polymers. Thermal analyses of the poly(1,12-dodecamethylene phosphonate) have shown that this polymer has reasonable thermal stability (onset of thermal decomposition at 273 °C). This polymer also undergoes a cold crystallization process at 15 °C similar to that which has been observed in some polyesters, polyamides and elastomers.

Keywords: Polymeric phosphonate esters; Transesterification; Diazomethane; Molecular weight; NMR

1. Introduction

In recent years, a variety of polymeric phosphonate and phosphate esters, which are related to the well-known polyesters as shown in Fig. 1, have been reported [1–18]. The polymeric phosphonate esters in which the R′ group is H [1–11] are particularly interesting because secondary phosphonates can be converted into a number of interesting functional groups. Oxidative chlorination of the polymers with Cl_2 followed by reaction with alcohols [3,7,9], amines [3,7] or amino acids [19] yields the corresponding polymeric phosphate esters and amides. Oxidation of the polymers with N_2O_4 yields polymeric phosphoric acids [4,7].

Three complimentary methods for the preparation of polymeric phosphonate esters in which the R′ group is H

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[*] Corresponding author.
E-mail address: gmgray@uab.edu (G.M. Gray).

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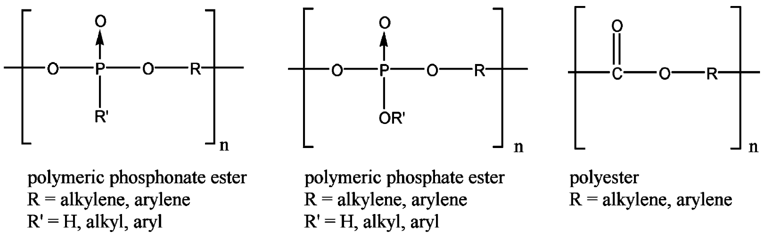

Fig. 1. Polymeric phosphonate esters, polymeric phosphate esters and polyesters.

have been reported. These are the ring-opening polymerization of cyclic phosphonate monomers, the polycondensation of dimethyl phosphonate with diols, and the transesterification of phosphonate oligomers. The latter two methods have received the most attention because of their potential to prepare polyphosphonates that are derived from a variety of diols.

Vogt [1] initially reported that the polycondensation procedure yielded polymers with number average molecular weights ($\overline{M}_n$) of approximately 10^3 due to an unidentified side reaction. We were able to identify this side reaction as the transfer of a methyl group from dimethyl phosphite or a methyl phosphite end group to an alcohol to form a methyl ether and an unreactive phosphonic acid end group (Fig. 2) [8,17,18]. We also demonstrated that the unreactive phosphonic acid end groups are converted to reactive methyl phosphite end groups by diazomethane, which allows polymers with number average molecular weights of approximately 10^4 to be prepared.

Although our modified polycondensation procedure yielded high molecular weight polymers, it was slow and

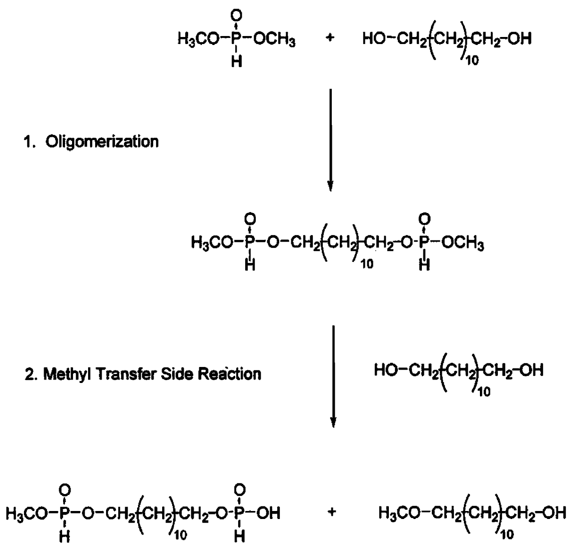

Fig. 2. Reaction scheme for the formation of the 1,12-dodecanediphosphonate monomer and the methyl transfer side reaction.

involved the use of explosive and toxic diazomethane. Thus, the transesterification route, reported by Penczek [4,5,9–11] to yield polymers with $\overline{M}_n$ values greater than 10^4 as measured by vapor phase or membrane osmometry and specific viscosity, appeared more practical. However, our initial attempts to prepare polymers via transesterification yielded only low molecular weight polymers similar to those obtained from the unmodified polycondensation route ($\overline{M}_w \sim 10^3$ by size exclusion chromatography (SEC) using a polystyrene calibration curve [8]). To better understand the factors that determine the molecular weights of polyphosphonates that are prepared using transesterification, we have carried out detailed $^{31}P\{^1H\}$ and ^1H NMR studies the transesterification reactions with and without a base promoter. The results of these studies, and their implications for the preparation of high molecular weight polymers are discussed in this paper. Also, some of the thermal properties of poly(1,12-dodecamethylene phosphonate), prepared by transesterification and determined by TGA and differential scanning calorimetry (DSC), are presented.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. Dichloromethane was dried by refluxing over calcium hydride for at least 12 h before distillation. The 1,12-dodecanediol and 1,4-cyclohexane dimethanol were purified by vacuum distillation and stored under nitrogen or in a vacuum atmospheres dry box with a nitrogen atmosphere until used. Dimethyl phosphonate was purified by a modification of the method of Penczek [4], stored under nitrogen and used within a few days of the final distillation. *N*-methyl-*N*-nitrosourea was prepared by the literature procedure [20], stabilized with acetic acid and stored at −20 °C until used.

2.2. Characterization methods

Multinuclear $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer. Chloroform-d_1 solutions of the polymers were prepared under nitrogen. The $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid (H_3PO_4) in a coaxial tube that also contained chloroform-d_1, and the ^1H NMR spectra were referenced to internal tetramethylsilane (TMS). A sweep width of 41,667 Hz was used, and 65,536 data points were taken in this window. From 16 to 32 scans were acquired. Pulse delays of 30 s for $^{31}P\{^1H\}$ spectra with inverse-gated decoupling were used to obtain quantitative integrations.

SEC of high molecular weight polymers was carried out on a system incorporating a Waters 510 pump, a Waters 410 differential refractive index detector and two Waters linear Ultrastyragel columns in series at 30 °C using a flow rate of 1 ml/min and THF as the solvent. High resolution SEC analysis of oligomers and low molecular weight polymers was carried out on a system incorporating a Waters M-6000A pump, a Waters 410 refractive index detector and 4 Waters Ultrastyragel columns (10^4, 10^3, 500 and 100) in series at ambient temperature using a flow rate of 1 ml/min and THF as the solvent. Injections of 20 μl of THF solutions containing 1–2% (w/v) of the polymers were used for both systems. Data were acquired using a Viscotec acquisition system and analyzed using Viscotec software. The weight-average ($\overline{M}_w$) number-average ($\overline{M}_n$) and z-average ($\overline{M}_z$) molecular weights and polydispersities ($\overline{M}_w/\overline{M}_n$) are estimates based on a polystyrene calibration curve.

Thermal analyses of polymer samples were performed on a Mettler-Toledo TA8000 thermal analysis system. DSC measurements were run on the DSC402 module. Each sample (5 mg) was heated to 130 °C for 10 min (under nitrogen gas) to remove any traces of solvent. Three scans from 25 to 200 °C using a heating rate of 10 °C/min were obtained for routine analyses. The midpoint of the glass transitions of each polymer was calculated using the Mettler software. The average of the second and third scans is reported. The effect of cooling rate on the cold crystallization of polymer samples was studied by heating the polymer to 80 °C and then cooling the polymers at various rates (5, 10, 20 and 30 °C/min). After each cooling cycle, the DSC measurements were run from −20 to 80 °C. Thermogravimetric analysis (TGA) measurements were run on the TG50(402) module. Samples ranging from 9.0 to 11.0 mg were heated from 25 to 400 °C using heating rates of 2, 5, 10, 15, 20 and 25 °C/min under a nitrogen atmosphere. The temperatures at 20% weight loss are reported as the decomposition onset temperatures and were used to construct an Arrhenius plot.

2.3. One-step transesterification of dimethyl phosphonate with 1,12-dodecanediol

The 1,12-dodecanediol was weighed into a Schlenk flask in a nitrogen-atmosphere glove box, and two equivalents of dimethyl phosphonate were added to the flask. The flask was then sealed with a septum, removed from the glove box and attached to a nitrogen purge system. Nitrogen was then slowly bubbled through the mixture, via a needle inserted through the septum, as the solution was heated at 80 °C. Samples were withdrawn at regular intervals, and ^{31}P and ^1H NMR spectra of these samples were taken. When these spectra showed that only methyl phosphonate end groups and internal phosphonate groups were present, vacuum was applied (0.02–0.5 mm Hg) and the temperature was increased to 120 °C. Transesterification was allowed to proceed until significant phosphonic acid end groups were observed in the ^{31}P and ^1H NMR spectra of aliquots that were withdrawn at regular intervals, generally after 8–15 days. At this point, the mixture was dissolved in dry dichloromethane under nitrogen, and a solution of diazomethane in dichloromethane was added to the solution until a yellow color persisted. This solution was purged with nitrogen until the yellow color disappeared and then for an additional hour. Finally, the dichloromethane was removed from the polymer solution on a rotary evaporator using a hot water bath (50 °C). The polymerization mixture was then returned to the vacuum/nitrogen manifold. Transesterification was allowed to continue at 120 °C under vacuum until few or no phosphonate groups were observed in the ^{31}P spectra and/or until the MW of the polymer stopped increasing.

2.4. Preparation of 1,12-bis(methyl phosphonato)dodecane

The reaction between dimethyl phosphonate and 1,12-dodecanediol was carried out in a 4:1 molar ratio. Typically 30.0 g (0.149 moles) of 1,12-dodecanediol was weighed out into a Schlenk flask in a glove box. A four molar excess of dimethyl phosphonate (62 ml) was added to the flask. The flask was sealed with a septum, removed from the glove box, and attached to a nitrogen purge system. Nitrogen was then slowly bubbled through the mixture, via a needle inserted through the septum, as the solution was heated at 80 °C. Samples were withdrawn under nitrogen at regular intervals, and ^{31}P and ^1H NMR spectra of these samples were taken. When the ^1H NMR spectra indicated that no free hydroxyl groups were present, as indicated by the disappearance of the ^1H NMR resonance for the methylene groups alpha to the oxygen, the excess dimethyl phosphonate was distilled from the reaction mixture under vacuum. Typically this reaction takes seven days.

2.5. Polymerization via transesterification of 1,12-dodecanediphosphonate monomer

The monomer, prepared as described in the previous paragraph, was placed under vacuum (0.1–0.5 mm Hg) and heated at 120 °C for 7–14 days. Samples were withdrawn at regular intervals and were analyzed by SEC and NMR spectroscopy.

2.6. Na_2CO_3 promoted transesterification of dimethyl phosphonate with 1,12-dodecanediol

The monomer was prepared as described above. Then sodium carbonate was added to the monomer (usually in a 1:10 molar ratio to the 1,12-dodecanediol). This mixture was placed under vacuum (0.1–0.5 mm Hg) and heated at 120 °C. Samples were withdrawn at regular intervals and were analyzed by SEC and NMR spectroscopy.

2.7. Na_2CO_3 promoted monomer formation and transesterification of dimethyl phosphonate with 1,12-dodecanediol

Typically 30.0 g (0.149 moles) of 1,12-dodecanediol was weighed out into a Schlenk flask in a glove box. Then a three molar excess of dimethyl phosphonate (41 ml) and 0.0465 g of sodium carbonate were added to the reaction flask. The flask was sealed with a septum, removed from the glove box and attached to a nitrogen purge system. Nitrogen was then slowly bubbled through the mixture via a needle inserted through the septum, as the solution was heated at 80 °C. Samples were withdrawn under nitrogen at regular intervals, and ^{31}P and ^{1}H NMR spectra of these samples were taken. When the ^{1}H NMR spectra indicated that both ends of the diol were substituted by methyl phosphonate, as indicated by the disappearance of the ^{1}H NMR resonance for the methylene groups alpha to the oxygen, the product was removed from the heat. SEC analysis indicated that after 19 h at 80 °C and ambient pressure, polymerization had begun. A high vacuum (0.1–0.5 mm Hg) was applied and heating began at 120 °C. Samples were withdrawn at regular intervals and were analyzed by SEC and NMR spectroscopy.

2.8. Preparation of diazomethane solutions

Diazomethane (CH_2N_2) was prepared using a modification of a literature procedure [21] from *N*-methyl-*N*-nitrosourea and aqueous NaOH in CH_2Cl_2 (*Note: Extreme care must be used in handling diazomethane as it is toxic and explosive*). A mixture of 100 ml of 40% (w/w) aqueous NaOH and 100 ml of CH_2Cl_2 in a 500 ml Erlenmeyer flask was immersed in an ice bath and stirred vigorously with a magnetic stirrer to form an emulsion. Then 1–3 g of *N*-methyl-*N*-nitrosourea were added slowly. When no solid remained in the flask, the yellow mixture was decanted into a separatory funnel. The lower layer (aqueous hydroxide) was removed, and the upper layer was dried over NaOH pellets in an ice bath for at least 2 h before use. Any solution that remained after the treatment of the polymer was quenched with glacial acetic acid.

3. Results and discussion

High molecular weight polyphosphonates have been prepared by both the stoichiometric polycondensation of dimethyl phosphonate with diols in conjunction with diazomethane treatment [17,18] and the transesterification method described by Penczek [4,6,9–11]. Penczek has reported that the use of a 20% molar excess of dimethyl phosphonate resulted in the formation of oligomers having only methyl phosphonate end groups with the degree of polymerization from 3 to 5 [9]. In our setup, a 20% molar excess of dimethyl phosphonate led to the formation of oligomers with both methyl phosphonate and diol end groups [8,17,18]. This difference was probably due to the purging procedures that were used to remove the methanol from the reaction mixture and that simultaneously remove some of the dimethyl phosphonate.

3.1. Multinuclear NMR spectroscopic and SEC studies of the transesterification polymerization of dimethyl phosphonate with 1,12-dodecanediol

We have carried out detailed NMR spectroscopic and SEC studies on the transesterification polymerization of dimethyl phosphonate with 1,12-dodecanediol to better understand the factors that affect the formation of high molecular weight polymers and to determine the nature and extent of any side reactions that occur during this polymerization.

In our apparatus, 2.0–2.5 moles of dimethyl phosphonate per mole of diol gave phosphonate oligomers with only methyl phosphonate end groups. The $^{31}P\{^{1}H\}$ (Fig. 3a) and ^{1}H (Fig. 4a) NMR spectra of samples taken after 186 h at 80 °C under nitrogen purge indicated that no dimethyl phosphonate or 1,12-dodecanediol-derived end groups were present. A high-resolution size exclusion chromatogram of a sample of this mixture (Fig. 5) showed that the degree of polymerization (*n*) for these oligomers ranged from 1 to greater than seven. The calculated molecular weights for the oligomer mixture were $\overline{M}_n = 1400$, $\overline{M}_w = 1700$, $\overline{M}_z = 2000$ and the value for $\overline{M}_w/\overline{M}_n$ was 1.22. Continued heating of this mixture at 80 °C, did not change either the ratio of internal phosphonate groups to methyl phosphonate end groups or the oligomer distribution indicating that transesterification did not take place at 80 °C. When this oligomer mixture was heated to 125 °C and placed under vacuum (0.1–0.5 mm Hg) for 298 h, both the ratio of internal phosphonate groups to methyl phosphonate end groups and the molecular weight of the mixture increased ($\overline{M}_n = 7000$, $\overline{M}_w = 15,000$, and $\overline{M}_z = 24,000$). This in-

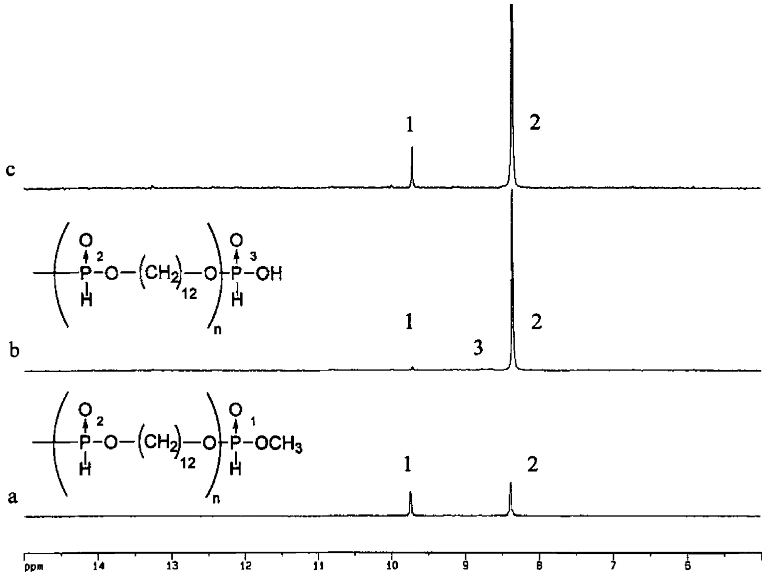

Fig. 3. $^{31}P\{^1H\}$ NMR spectra of the transesterification of 1,12 dodecanediol with dimethylphosphite: (a) $^{31}P\{^1H\}$ NMR spectrum of the transesterification polymerization mixture after 186 h 80 °C, (b) $^{31}P\{^1H\}$ NMR spectrum of the transesterification polymerization mixture after 298 h at 125 °C under high vacuum and (c) $^{31}P\{^1H\}$ NMR spectrum of the transesterification polymerization mixture after diazomethane treatment.

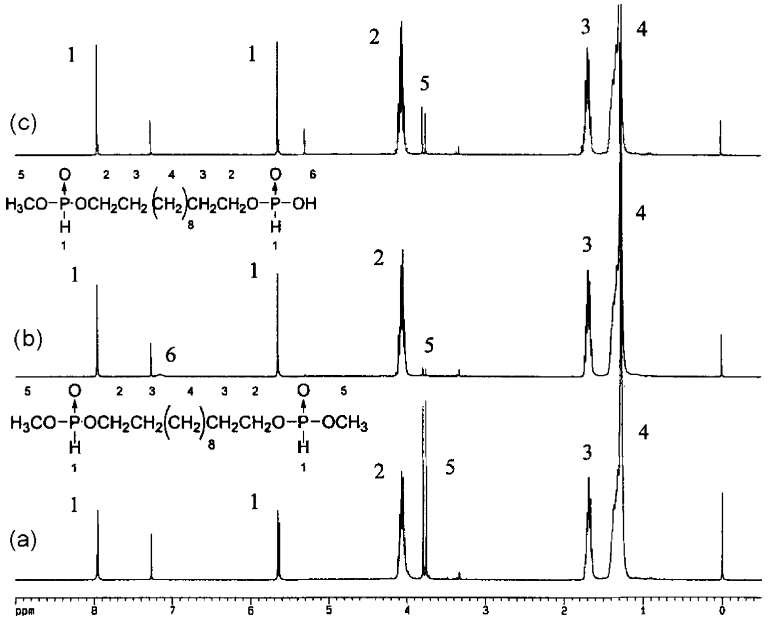

Fig. 4. ^1H NMR spectra of the transesterification of 1,12 dodecanediol with dimethylphosphite: (a) ^1H NMR spectrum of the transesterification polymerization mixture after 186 h 80 °C, (b) ^1H NMR spectrum of the transesterification polymerization mixture after 298 h at 125 °C under high vacuum and (c) ^1H NMR spectrum of the transesterification polymerization mixture after diazomethane treatment.

dicated that the transesterification reaction was occurring at a significant rate at this temperature. However, the broad resonances at 8.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Fig. 3b) and at 7.1 ppm in the ^1H NMR spectrum (Fig. 4b) also became more prominent as the polymerization continued. These resonances indicate the

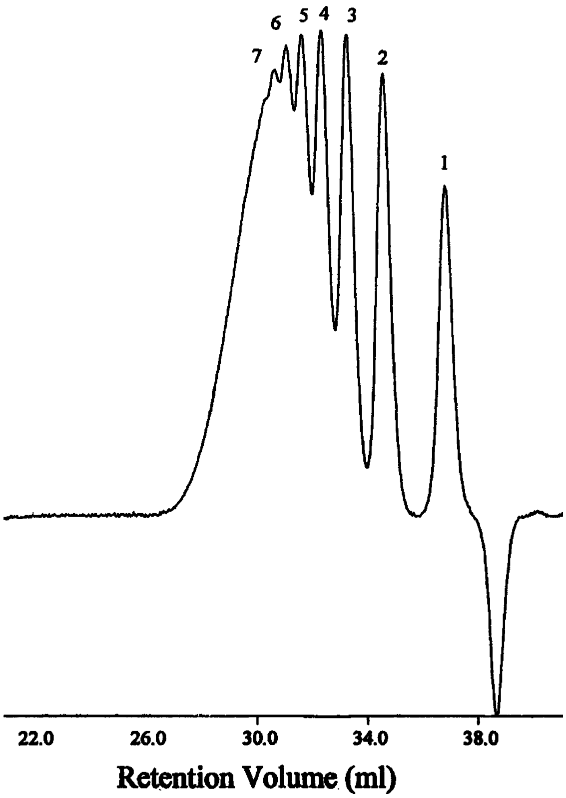

Fig. 5. SEC chromatogram of poly(dodecamethylene phosphonate) oligomers.

presence of phosphonic acid end groups [11,17,18]. Treating the polymerization mixture with diazomethane caused the broad resonances in both the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra (Figs. 3c and 4c) to disappear and the ratio of methyl phosphonate end groups to phosphonate internal groups to increase. The SEC of the reaction mixture after treatment with diazomethane gave $\overline{M}_n = 12,000$, $\overline{M}_w = 26,000$, $\overline{M}_z = 48,000$. The fact that this process took place with a slight increase in the molecular weight of the polymer clearly showed that the additional end groups were not formed by chain scission and that transesterification occurred as the mixture was heated to 125 °C before the SEC sample was taken. These results demonstrate that phosphonic acid end groups are cleanly converted to methyl phosphonate end groups by diazomethane.

When the reaction mixture was heated for an additional 264 h at 125 °C, the ratio of internal phosphonate groups to methyl phosphonate end groups and the molecular weight ($\overline{M}_n = 12,000$, $\overline{M}_w = 45,000$, and $\overline{M}_z = 121,000$) increased. It is important to note that the molecular weights of the polymers prepared using transesterification in conjunction with diazomethane treatment are significantly higher than those of polymers prepared either from transesterification without diazomethane treatment or from the stoichiometric polycondensation of dimethyl phosphonate with diols in conjunction with diazomethane treatment [17,18]. The polydispersity of 3.75 is higher than expected for a transesterification polymerization and may indicate that some, as yet unknown, reaction is occurring due to the diazomethane treatment. This conclusion is supported by the fact that higher than expected polydispersities are not observed for high molecular weight polymers prepared without diazomethane treatment as discussed below.

Table 1
Comparison of M_n data by SEC and $^{31}P\ \{^{1}H\}$ NMR for the transesterification of 1,12-bis(methyl phosphonato)dodecane

Time at 160 °C	^{31}P NMR integration		M_n	
	End	Internal	NMR	SEC
120 h	2.00	17.68	4740	6890
144 h	2.00	37.96	9774	10,300
168 h	2.00	52.08	13,275	13,600

SEC does not necessarily yield exact molecular weights for poly(1,12-dodecamethylene phosphonate) polymers because polystyrene is used to generate the SEC calibration curve. We have therefore compared the $\overline{M}_n$ data obtained from the SEC to exact $\overline{M}_n$ data calculated from the quantitative $^{31}P\{^{1}H\}$ NMR spectra of the polymers. These data are summarized in Table 1. There is a good agreement between the $\overline{M}_n$s calculated from SEC and $^{31}P\{^{1}H\}$ NMR spectra, and the agreement improves as the molecular weight of the polymer increases. The difference in $\overline{M}_n$s at low molecular weight is most likely due to the fact that the SEC software cuts off the lowest molecular weight data. This causes the calculated $\overline{M}_n$ to be higher than the actual $\overline{M}_n$ for low molecular weight polymers. Also, the SEC calculations assume a constant refractive index difference between the polymer and solvent. This assumption may not be valid at low molecular weights. As the molecular weight of the polymer increases, the amount of low molecular weight data decreases and the effect of this data on the molecular weight of the polymer decreases.

3.2. Preparation and transesterification of 1,12-dodecanediphosphonate

In both the polycondensation [17,18] and transesterification reactions of dimethyl phosphonate with diols, a side reaction occurs that produces phosphonic acid end-groups (Fig. 2). These end groups can be removed using diazomethane, but this reagent is both toxic and explosive thus requiring extreme caution. In an attempt to avoid this problem, we have investigated a two-step transesterification polymerization process. The first step involved the preparation of the 1,12-bis(methyl phosphonato)dodecane monomer by bubbling N_2 gas through a Schlenk flask at 80 °C that contained at least a 4:1 ratio of dimethyl phosphonate to 1,12-dodecanediol. The reaction was followed by ^{1}H NMR and was stopped when the ^{1}H NMR resonance of the free alcohol at 3.63 ppm disappeared (Fig. 6b). At this point, the excess dimethyl phosphonate was removed by vacuum distillation, and a $^{31}P\{^1H\}$ NMR spectrum was obtained on the reaction mixture (Fig. 6a). The ^{31}P data indicated that while the majority of the product was the monomer, a small amount of oligomer formation (~5%) had occurred. Most importantly, the ^{31}P data showed a barely detectable, broad resonance between 8 and 9 ppm due to phosphonic acid end-groups.

The second step in this reaction involved the transesterification of the monomer under a vacuum of 0.02–0.5 mm Hg at a temperature of 120 °C. At this temperature and pressure, any dimethyl phosphonate produced by the polymerization was removed from the reaction mixture. After 52 h, the broad peak in the $^{31}P\{^1H\}$ NMR spectrum (Fig. 7a) at 8.94 ppm became more apparent confirming the presence of phosphonic acid end-groups. Integrations of the $^{31}P\{^1H\}$ NMR spectra from later stages of the polymerization, shown in Table 2, indicated that the phosphonic acid ^{31}P NMR resonance is always 4–6% of the total ^{31}P NMR resonances. This result clearly indicated that the phosphonic acid end groups were not being formed during this stage of the polymerization and that they did not undergo transesterification. Thus, when the polymerization process was continued, a polymer was obtained in which all of the end groups were phosphonic acid end-groups. The degree of polymerization was determined therefore by the amount of phosphonic acid end groups that were formed during the preparation of the monomer.

3.3. Preparation and transesterification of 1,12-dodecanediphosphonate promoted by Na_2CO_3

Penczek has previously reported [10,11] that Na metal or sodium alkoxide catalyzes the reaction of 1,12-dodecanediol and dimethyl phosphonate without the observation of acid-end groups. These results suggest either that presence of the base inhibits acid formation or that the sodium phosphonate end groups are active in the transesterification. To determine if base would help in our system, Na_2CO_3 was added at the beginning of monomer formation. The addition of Na_2CO_3 reduced the time required to form the monomer by half, indicating that the Na_2CO_3 promotes the monomer formation. However, the $^{31}P\{^1H\}$ NMR spectrum at the completion of the monomer formation indicated that the Na_2CO_3 also promoted to formation of phosphonic acid end groups (Fig. 7b). It is clearly evident that Na_2CO_3 treatment aides in the polymerization, however, it also increases the rate of the methyl transfer side-reaction when alcohol is present (Fig. 2).

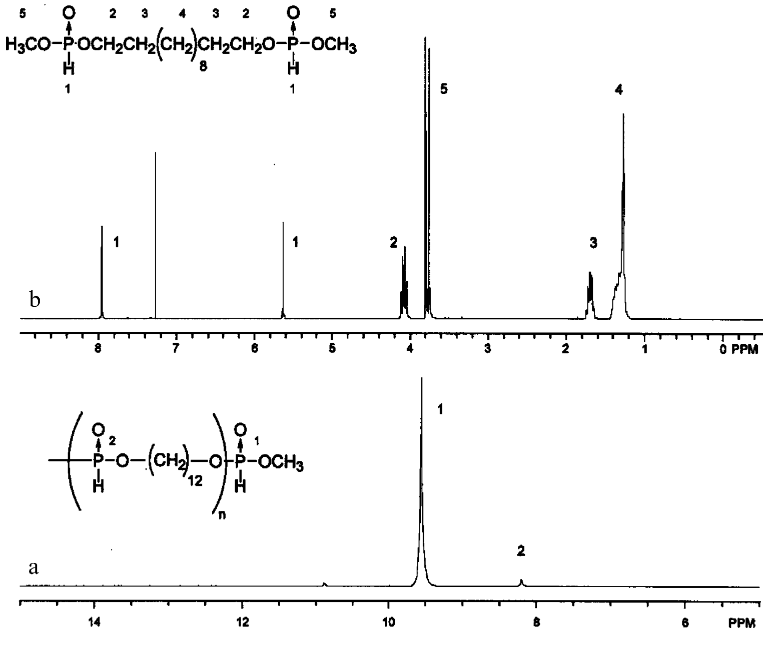

Fig. 6. NMR spectra of the formation of 1,12 bis(methyl phosphonato)dodecane monomer: (a) $^{31}P\{^1H\}$ NMR spectrum and (b) ^{1}H NMR spectrum.

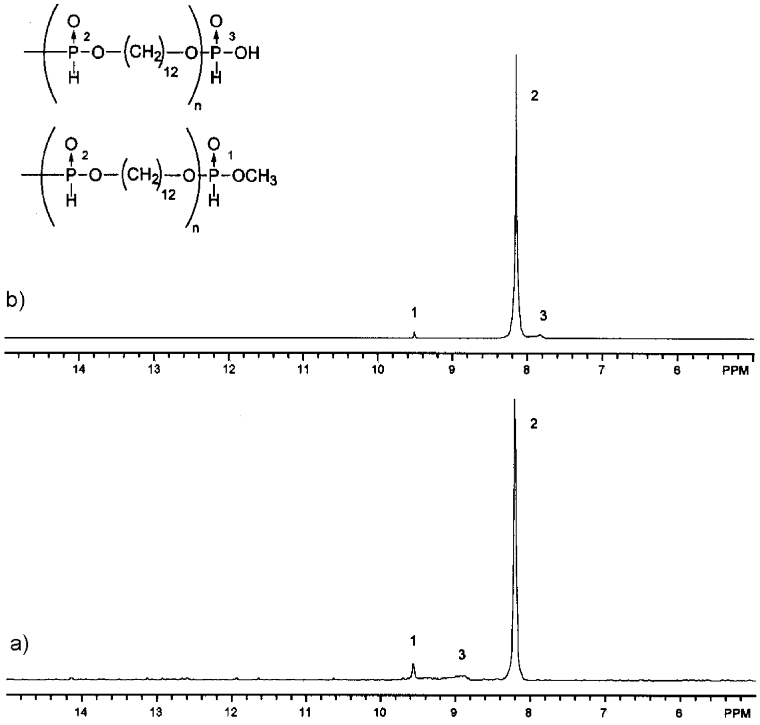

Fig. 7. (a) $^{31}P\{^{1}H\}$ NMR spectrum of the transesterification of the 1,12 bis(methyl phosphonato)dodecane monomer in the absence Na_2CO_3 and (b) $^{31}P\{^{1}H\}$ NMR spectrum of the transesterification of the 1,12 bis(methyl phosphonato)dodecane monomer with Na_2CO_3 added at the beginning of monomer formation.

Table 2
Comparison of the amount of methyl phosphonate and phosphonic acid end-groups to the degree of polymerization

Time (h)	Degree of polymerization[a]	Number of methyl phosphonate end-groups	Number of phosphonic acid end-groups	% of phosphonic acid end-groups
22	20.35	0.99	1.01	50.5
46	27.40	0.64	1.36	68.0
70	31.36	0.30	1.70	85.0
166	31.76	0.17	1.83	91.5
190	34.53	0.00	2.00	100
213	36.02	0.00	2.00	100
237	40.43	0.00	2.00	100

[a] The degree of polymerization is the number of repeating units of the polymer (*n*). This is calculated by intergrating the area of all three ^{31}P resonances and setting the combined areas of the end-groups equal to 2.

3.4. Transesterification of 1,12-bis(methyl phosphonato)dodecane with Na_2CO_3

The 1,12-bis(methyl phosphonato)dodecane monomer was prepared by the reaction of dimethyl phosphonate and 1,12-dodecane diol at 80 °C under a slow bubble of N_2 as previously described. This reaction was continued until no trace of 1,12-dodecanediol remained in the reaction mixture, as indicated by the disappearance of the ^{1}H NMR resonance due to the methylene group alpha to the hydroxyl. The monomer solution was then treated with Na_2CO_3 and immediately became viscous. The transesterification was then carried out at a vacuum of 0.02–0.5 mm Hg and a temperature of 120 °C. After 65 h, the polymerization was stopped due to the fact that the stir bar was frozen in the polymer mixture.

Analysis of this polymer by $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy indicated that no acid end groups were present (Fig. 8). The molecular weight analysis of the

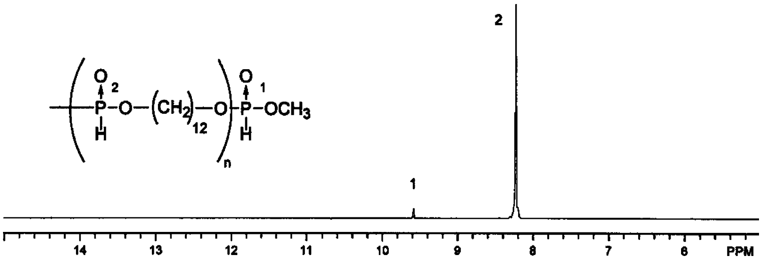

Fig. 8. $^{31}P\{^{1}H\}$ NMR spectrum of the transesterification of the 1,12 bis(methyl phosphonato)dodecane monomer with Na_2CO_3 added after monomer generation.

Table 3
Comparison of diazomethane treatment with the transesterification of 1,12-bis(methyl phosphonato)dodecane (1) and 1,4-bis-(methyl phosphonatomethyl)cyclohexane (2) in the presence of Na_2CO_3

Compound	Treatment	Time (h)	M_n	M_w	M_w/M_n
1	None	298	7000	15,000	2.14
1	CH_2N_2	264	12,000	45,000	3.75
1	K_2CO_3	45	13,100	25,200	1.90
1	Na_2CO_3	46	13,300	21,200	1.60
1	Na_2CO_3	64	18,400	38,000	2.07
1[a]	Na_2CO_3	65	12,794	21,845	1.70
1	Na_2CO_3	72	22,500	45,000	2.00
2	None	90	1900	3900	2.10
2	CH_2N_2	169	7400	14,100	1.91
2	Na_2CO_3	95	5100	8860	1.73

[a] Denotes magnetic instead of mechanical stirrer used.

polymer by SEC gave $\overline{M}_n = 12,794$, $\overline{M}_w = 21,845$ and $\overline{M}_z = 31,586$ with $\overline{M}_w/\overline{M}_n = 1.7$. These results are comparable to those obtained for the polymer prepared without using Na_2CO_3 after diazomethane treatment.

As shown in Table 3, polymers with $\overline{M}_w \cong 20,000$ and polydispersities of 1.7–2.0 can routinely be prepared within 72 h by transesterification of the 1,12-bis(methyl phosphonato)dodecane monomer in the presence of Na_2CO_3. The highest $\overline{M}_w$ that has been obtained to date is 45,000. Polymers have also been prepared by transesterification of 1,4-(methyl phosphonatomethyl)cyclohexane using a similar procedure although somewhat lower molecular weights are obtained.

3.5. Thermal properties of poly(dodecamethylene phosphonate)

To determine if thermal decomposition of the poly(dodecamethylene phosphonate) could be a source of acid end groups, the decomposition onset temperature and the activation energy of thermal decomposition for poly(dodecamethylene phosphonate) were determined using TGA. The molecular weights of the polymer used in these analyses were $\overline{M}_n = 7000$, $\overline{M}_w = 22,000$, and $\overline{M}_z = 66,000$ with $\overline{M}_w/\overline{M}_n = 3.0$. The decomposition onset temperature (temperature at 20% weight loss) determined using a heating rate of 20 °C/min was 307 °C. As continuously slower heating rates were used, the decomposition onset temperatures decreased to a minimum of 273 °C using a heating rate of 2.0 °C/min. Arrhenius parameters were calculated by constructing a plot of ln(heating rate) versus $1/T$ (K). The activation energy, E_a, for thermal decomposition was calculated to be 190 kJ/mol K and the preexpontial factor, A, was 2.9×10^{18} $M^{-1}\,s^{-1}$. The decomposition onset temperature and E_a of the polymer indicate that it has reasonable thermal stability and should not decompose under the conditions used in the polymerization reaction.

The glass transition temperature and melting point of the poly(dodecamethylene phosphonate) have been determined by DSC. The DSC studies indicated that melt-quenched samples of poly(dodecamethylene phosphonate) underwent crystallization upon heating between the glass transition temperature (T_g) and the normal melting temperature (T_m). This process, called "cold crystallization" [22], is known to occur in some polyesters, polyamides and elastomers [23–28]. The thermogram for a sample of poly(dodecamethylene phosphonate) that was melt-quenched at 30 °C/min is shown in Fig. 9. This data shows an intense melting transition at about 40 °C, a broad and less intense glass

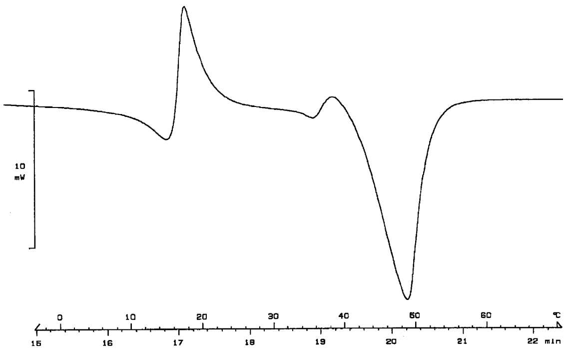

Fig. 9. Thermogram for a sample of poly(dodecamethylene phosphonate) that was melt-quenched at 30 °C/min.

transition at about 10 °C and an exotherm due to cold crystallization at about 15 °C. These values were reproducible at several cooling rates. As the rate of cooling was decreased, the size of the cold crystallization exotherm decreased, as expected. If the sample was cooled slowly enough to allow recrystallization upon cooling, then no cold crystallization was observed.

To our knowledge, there are no data on the thermal properties of polyphosphonates reported in the literature for comparison. However, Penczek has reported T_gs and T_ms for several polyphosphates including poly(dodecamethylene phosphate) [9]. The value reported for the onset of the glass transition was −10 °C and the value for T_m was 43 °C. A value of 40 °C was reported for T_m for poly(dodecamethylene phosphonate) by Kokkinia [12], but this polymer had a very low MW. The higher T_m of the polyphosphate compared to that of the polyphosphonate is likely due to the hydrogen bonding between phosphate groups in the polyphosphate.

4. Conclusions

The preparation of phosphonate monomers or oligomers by the reaction of dimethyl phosphonate with diols generates small amounts of phosphonic acid end groups even when the reactions are carried out under mild reaction conditions. The phosphonic acid end groups prevent the formation of high molecular weight polyphosphonates by transesterification reactions. The phosphonic acid end groups can be converted to methyl phosphonate end groups by treatment of the oligomers with diazomethane. However, this is a less than ideal method because the diazomethane is explosive and the transesterification reaction is slow. A simpler alternative is to carry out the transesterification of the monomer in the presence of Na_2CO_3. If care is taken to ensure that no alcohol end groups are present before the addition of the Na_2CO_3, this method reproducibly and rapidly yields high molecular weight ($\overline{M}_w$ up to 4.5×10^4) polyphosphonates. This method eliminates the use of highly reactive components, such as diazomethane, sodium, and sodium methoxide, that were used in previously reported methods for the preparation of these polymers.

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