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Polycondensations of dimethyl phosphonate with diols: SEC and ^{1}P and ^{13}C NMR spectroscopic studies

K.E. Branham[a], J.W. Mays[b], G.M. Gray[b,*], P.C. Bharara[c], H. Byrd[c], R. Bittinger[c], B. Farmer[c]

[a]Absorbable Polymer Technologies, Pelham, AL 35124, USA
[b]Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, USA
[c]Department of Chemistry, University of Montevallo, Montevallo, AL, 35115, USA

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Abstract

Polymeric phosphonate esters have a variety of potential applications. These polymers can be prepared by the polycondensations of dimethyl phosphonate with certain diols. However, this method does not consistently yield high molecular weight polymers. NMR spectroscopy and size exclusion chromatography studies demonstrate that low molecular weights result from methyl group transfer from a methyl phosphonate end group to an alcohol. The inactive phosphonic acid end groups formed by this reaction can be converted into reactive methyl phosphonate end groups by treatment with diazomethane. This allows the preparation of polymers with number average molecular weights greater than 10^4 Da. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymeric phosphonate esters; Polycondensation; Diazomethane

1. Introduction

In recent years, a variety of polymeric phosphonate and phosphate esters, related to the well-known polyesters as shown in Fig. 1, have been reported [1–15]. The polymeric phosphonate esters with $R' = H$ [1–9] are particularly interesting because of the ease with which the phosphorus can be functionalized. Oxidative chlorination of the polymers with chlorine followed by reaction with alcohols [3,7,9], amines [3,7] or amino acids [16] yields 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 with $R' = H$ have been reported. These are the ring-opening polymerization of cyclic phosphonate monomers, the polycondensation of dimethyl phosphonate with diols [1–3] and the transesterification of short oligomers formed by the reaction of excess dimethyl phosphonate and diols [4,5,9,10]. The last two methods are quite similar and differ only in whether polycondensation or transesterification occurs in the latter stages of the polymerization. Vogt and Balasubramanian [1] have reported that the polycondensation route is plagued by side reactions that prevent the formation of polymers with number average molecular weights ($\bar{M}_n$) much greater than 10^3. We have confirmed these results in a preliminary study [8]. In contrast, Penczek and others [4,5,9,10] have reported that the transesterification route yields polymers with $\bar{M}_n$s greater than 10^4.

Because the mechanisms of polycondensation and transesterification are so similar, it was surprising that the procedures yield polymers with such different molecular weights. We have carried out detailed NMR spectroscopic and size exclusion chromatographic (SEC) studies of the polymerizations of dimethyl phosphonate with both 1,12-dodecanediol and 1,4-cyclohexane dimethanol. Based on these studies, we have developed a modification of the polycondensation procedure that allows high molecular weight polymers to be prepared. Both the results from the NMR/SEC studies and the modified polycondensation procedure are presented in this paper.

2. Experimental

Materials. All solvents, reactants and products were handled under an atmosphere of dry nitrogen at all times. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. Dichloromethane was dried by distillation from calcium hydride after refluxing for at least 12 h. The 1,4-cyclohexane dimethanol and 1,12-dodecanediol were

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* Corresponding author. Tel.: +1-205-934-4747; fax: +1-205 -934-2543.

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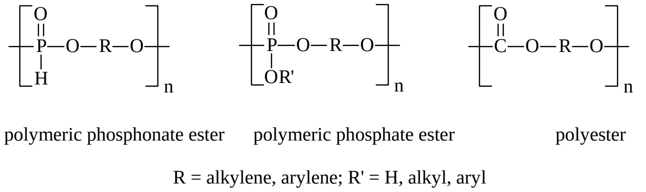

Fig. 1. Polymeric phosphonate esters, phosphate esters and polyesters.

purified by vacuum distillation. Dimethyl phosphonate was purified by a modification of the method of Pretula and Penczek [4] and used within a few days of the final distillation. *N*-methyl-*N*-nitrosourea was prepared by a literature procedure [17], stabilized with acetic acid and stored at −20°C until use. Dimethyl phenylphosphonate was prepared from dichlorophenylphosphine by a modification of the procedure used to prepare similar dialkyl phosphonates [18].

Characterization methods. Multinuclear ($^{31}P\{^1H\}$ and $^{13}C\{^1H\}$) NMR spectra were recorded on a GE NT-300 wide-bore, multinuclear NMR spectrometer. Chloroform-*d* solutions of the polymers were prepared under nitrogen and were 0.1 M in polymer repeat units. 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*, and the $^{13}C\{^1H\}$ NMR spectra were referenced to internal tetramethylsilane (TMS). SEC 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. Injections of 20 ml of THF solutions containing 1–2% (w/v) of the polymers were used. The weight-average ($\bar{M}_w$) number-average ($\bar{M}_n$) and *z*-average ($\bar{M}_z$) molecular weights and polydispersities ($\bar{M}_w/\bar{M}_n$) are estimates based on a polystyrene calibration curve and were calculated using Viscotek software. Gas chromatographic–mass spectroscopic spectra (GC/MS) were recorded on a Hewlett Packard 5985 GC/MS System equipped with a HP Ultra 2 column (25 m, crosslinked 5% phenylmethylsiloxane, film thickness 0.11 m).

Polycondensations of dimethyl phosphonate with diols. The diol was weighed into a Schlenk flask in a dry box, and then a 1.2 to 1.3 molar excess of dimethyl phosphonate was added to the flask. The flask was sealed with a septum, removed from the glove box and attached to a vacuum/nitrogen double manifold. Nitrogen was slowly bubbled through the solution, via a needle inserted through the septum, as the solution was heated at 80°C. Samples were withdrawn at regular intervals, and ^{31}P NMR spectra of these samples were taken. When the ^{31}P NMR spectrum showed that no dimethyl phosphonate was present, vacuum was applied (0.02–0.5 mm Hg) and heating at 80°C was continued. Samples were withdrawn at 48 h intervals and were analyzed by SEC and NMR spectroscopy. When the ^{31}P and ^{13}C NMR spectra indicated that only diol end groups were present, a small amount of dimethyl phosphonate was added to maintain approximately equal amounts of diol and phosphonate end groups and allow a greater extent of conversion. Polycondensation was allowed to proceed until a significant concentration of phosphonic acid end groups was observed in the ^{31}P NMR spectrum (8–15 days after the polymerization was initiated). At this point, the polymerization mixture was dissolved in dry dichloromethane under nitrogen, and a dichloromethane solution of diazomethane was slowly added to the solution until a yellow color persisted. Nitrogen was bubbled though the solution until the yellow color disappeared and then for an additional hour. Finally, the dichloromethane was removed from the polymer on a rotary evaporator using at hot water bath (50°C). The polymerization mixture was then heated at 80°C under vacuum. Heating was discontinued when few or no methyl phosphonate or diol end groups were observed in the ^{31}P or ^{13}C NMR spectra and the MW of the polymer, determined by SEC, stopped increasing.

Attempted polycondensation of dimethyl phenylphosphonate with 1,4-cyclohexane dimethanol. This reaction was run in a reaction vessel incorporating an air condenser with a sidearm and flask for collecting evolved liquid. The reactants, 9.05 g (0.0627 mol) of 1,4-cyclohexane dimethanol and 11.67 g (0.0627 mol) of dimethyl phenylphosphonate, were transferred into the reaction vessel in the dry box. The reactor was then connected to the vacuum/nitrogen manifold, and the reaction mixture was heated at 80°C in an oil bath under a nitrogen atmosphere. Samples were withdrawn at 24 h intervals and were analyzed by NMR spectroscopy. After 90 h, the ^{31}P and ^{13}C NMR spectra of the reaction mixture were unchanged. In an attempt to catalyze the reaction, approximately 50 mg of metallic sodium was added, and the temperature was raised to 110°C. After 90 h at 110°C, resonances for dimethyl phenylphosphonate and what appeared to be methyl phenylphosphonate end groups and internal phenylphosphonate groups were present in the ^{31}P NMR spectrum. After 169 h at 110°C, a number of additional resonances had appeared in the ^{31}P NMR spectrum suggesting that decomposition was occurring. After 600 h at 110°C, the reaction was placed under vacuum, and a colorless liquid to distilled into the collection flask. The GC/MS and ^{13}C NMR spectra of this liquid indicated that it was the dimethyl ether of 1,4-cyclohexane dimethanol. ^{13}C NMR (chloroform-d): 78.61 (*trans*-CH_2O, s); 76.12 (*cis*-CH_2O, s); 58.65 (CH_3, s), 38.08 (*trans*-CH, s); 35.24 (*cis*-CH, s); 29.28 (*trans*-CH_2 (ring), s); 25.63 (*cis*-CH_2 (ring), s). GC/MS: 172 (M^+); 140 ($M–CH_3OH^+$); 108 ($M–2CH_3OH^+$); 95 ($M–CH_3OH–CH_3OCH_2^+$); 45 ($CH_3OCH_2^+$).

Preparation of diazomethane solutions. Diazomethane (CH_2N_2) was prepared using a modification of a literature procedure [19] from *N*-methyl-*N*-nitrosourea and aqueous potassium hydroxide in dichloromethane (*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 potassium hydroxide solution and 100 ml of dichloromethane

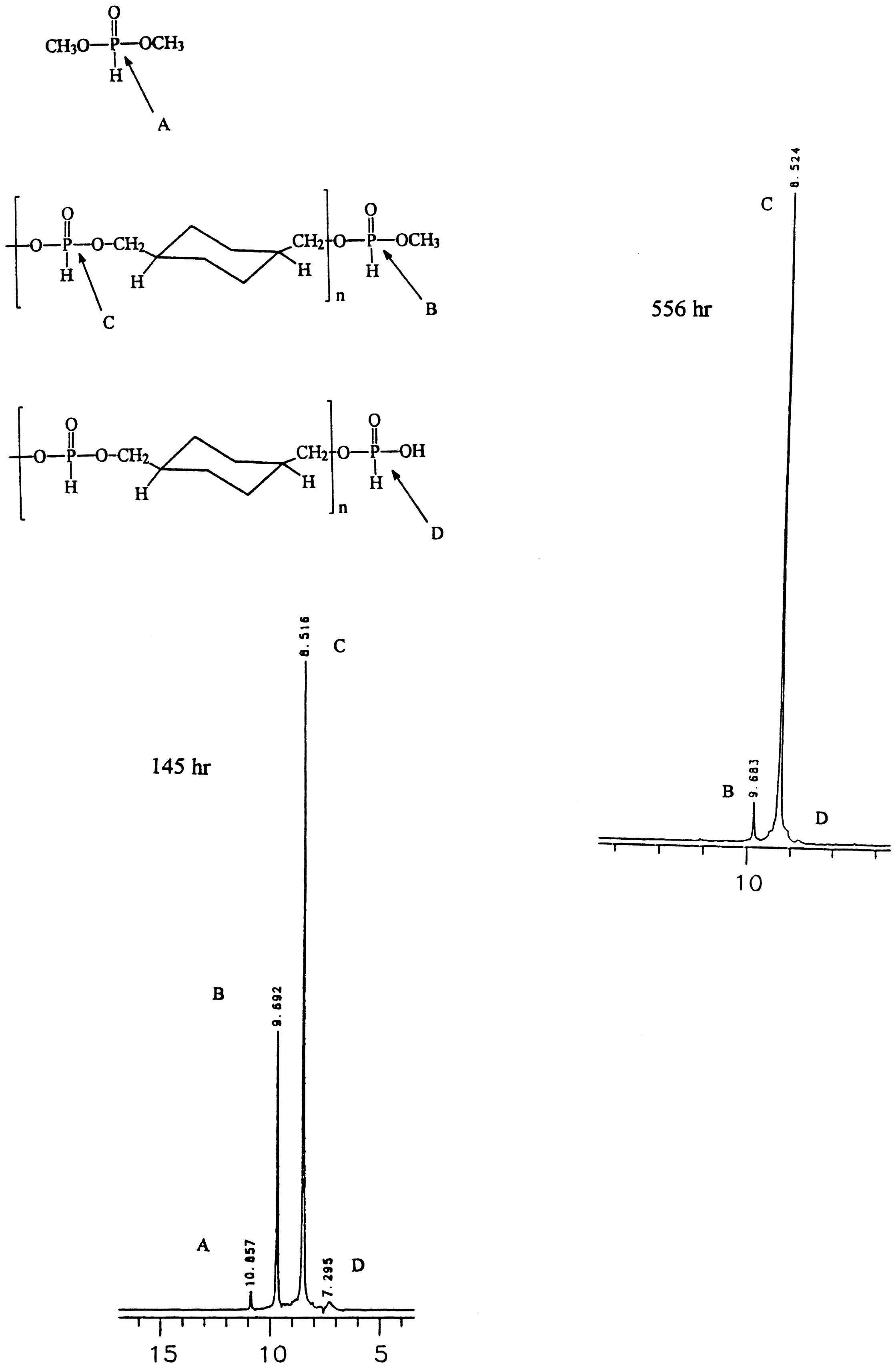

Fig. 2. ^{31}P NMR spectra of the product of the polycondensation of dimethyl phosphine and 1,4-cyclohexane diol after 145 and 556 h at 80°C.

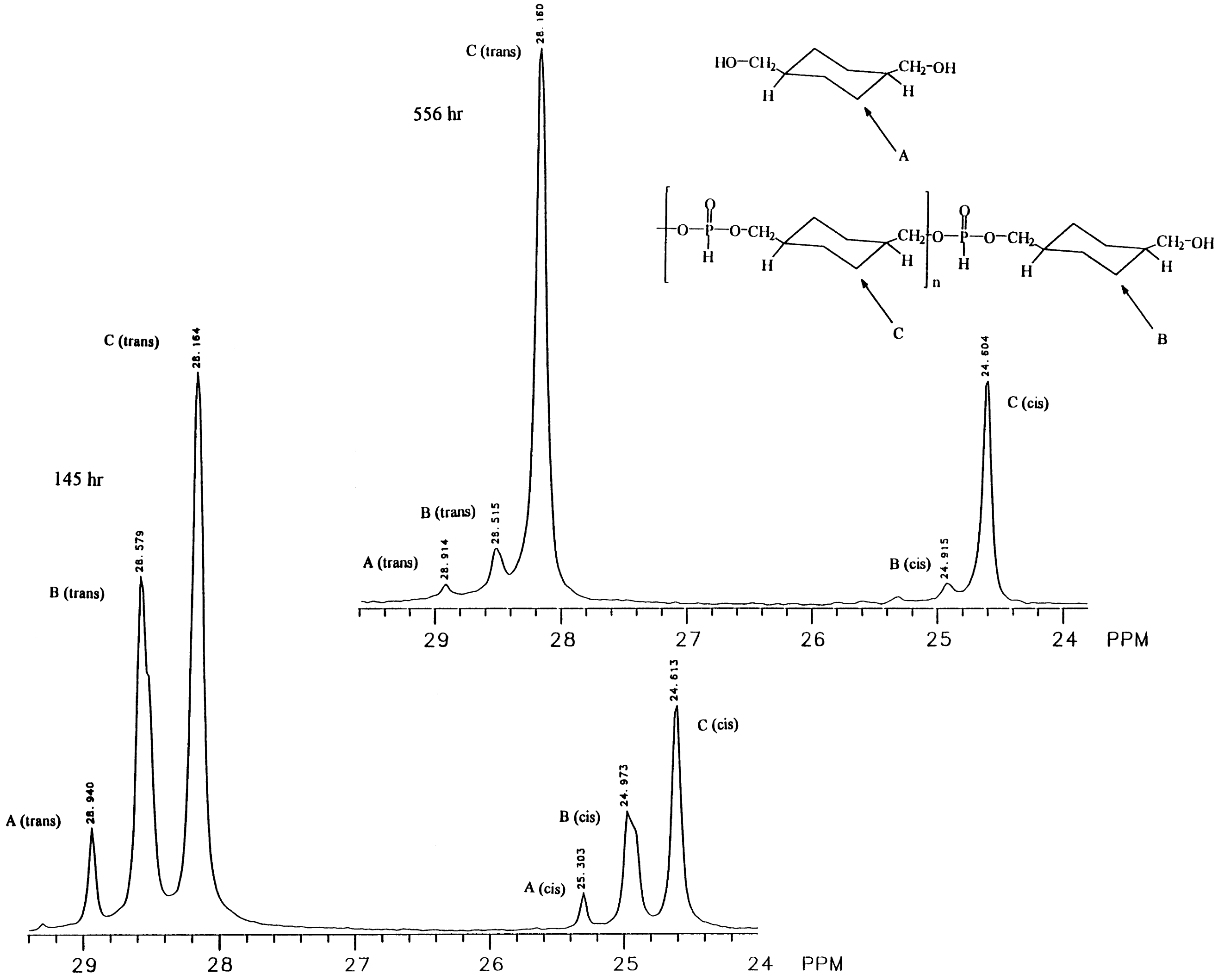

Fig. 3. ^{13}C NMR spectra (ring methylene region) of the product of the polycondensation of dimethyl phosphine and 1,4-cyclohexane diol after 145 and 556 h at 80°C.

in a 500 ml Erlenmeyer flask was placed in an ice bath and stirred vigorously with a magnetic stir bar 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 fitted with a Teflon stopcock, and the lower layer (dichloromethane/diazomethane) was drained into a 500 ml Erlenmeyer flask containing potassium hydroxide pellets. This solution was allowed to stand 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

To carry out the polycondensation of dimethyl phosphonate and a diol, it is necessary to maintain a 1:1 ratio of the reactants through out the course of the polymerization. It is not possible to use an exact 1:1 ratio of dimethyl phosphonate with either 1,12-dodecanediol or 1,4-cyclohexane dimethanol because in the initial stages of the reaction some dimethyl phosphonate is lost during the removal of methanol. Thus, we found it necessary to use a 20% excess of the dimethyl phosphonate to reach an approximate 1:1 ratio of methyl phosphonate and alcohol end groups in the intermediate stages of the polymerization. It should be noted that Penczek and Pretula [9] also used 20% excesses of dimethyl phosphonate in their transesterification reactions. Apparently the loss of dimethyl phosphonate in their apparatus was significantly less than in ours, and their initial polycondensation reactions yielded methyl phosphonate capped oligomers. Thus, the later stages of their polymerization reactions proceeded via transesterification (loss of dimethyl phosphonate) rather than polycondensation (loss of methanol).

The polycondensations of dimethyl phosphonate with either 1,12-dodecanediol or 1,4-cyclohexane dimethanol

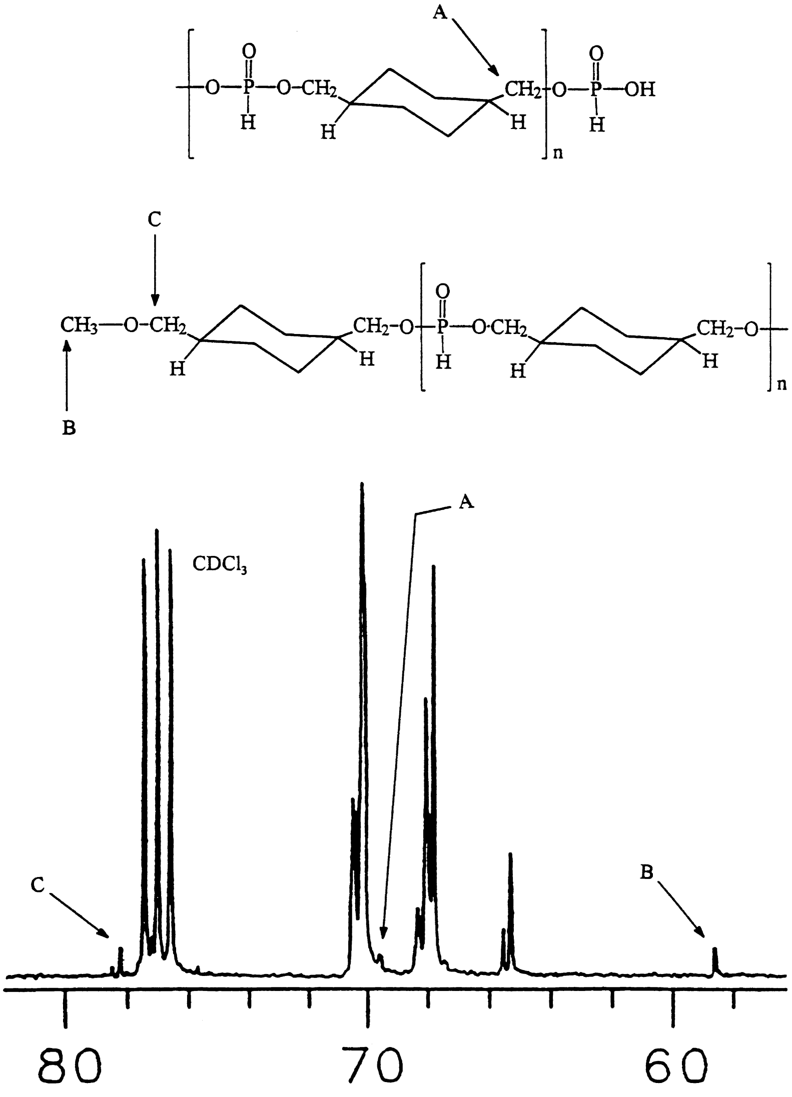

Fig. 4. ^{13}C NMR spectrum (58–82 ppm region) of the product of the polycondensation of dimethyl phosphine and 1,4-cyclohexane diol after 145 h at 80°C.

were carried out in two stages that are similar to the first two stages of the transesterification reactions described by Penczek. In the first stage, the reaction mixture was heated at 80°C as nitrogen was slowly bubbled through the reaction mixture. Heating was continued until no free dimethyl phosphonate was observed in the reaction mixture. Then, the reaction mixture was placed under vacuum and heating was continued at 80°C. The reaction was followed by NMR spectroscopy and SEC.

3.1. SEC and multinuclear NMR spectroscopic studies of the polycondensation of dimethyl phosphonate with 1,4-cyclohexane dimethanol

To better understand the factors that affect the polycondensations of dimethyl phosphonate and diols and to identify any side reactions, we carried out a detailed SEC and NMR spectroscopic study of the polycondensation of dimethyl phosphonate with 1,4-cyclohexane dimethanol. The number and type of dimethyl phosphonate-derived end groups were determined from the ^{31}P NMR resonances that were observed. The number and type of diol-derived end groups were determined from the ^{13}C NMR resonances of the ring methylenes. The other carbons in 1,4-cyclohexane dimethanol also gave resonances that could be assigned to diol-derived end and internal groups, but these regions were more complicated.

Our NMR studies indicated that the polycondensation of dimethyl phosphonate and 1,4-cyclohexane dimethanol proceeded in the expected stepwise manner. After 145 h at 80°C, the monomers had reacted to form short oligomer chains. These chains were capped by both dimethyl phosphonate- and diol-derived end groups as indicated by the intense resonances for these end groups in the ^{31}P (Fig. 2) and ^{13}C (Fig. 3) NMR spectra. Only small amounts of monomers remained in the reaction mixture at this point. After 281 h at 80°C, only diol-derived end groups were observed, and a small amount of dimethyl phosphonate was added to generate additional methyl phosphonate end groups. The reaction mixture was then heated at 80°C for 12 h under a nitrogen atmosphere before being placed under a vacuum. After 556 h at 80°C (267 h after the addition of the dimethyl phosphonate), only small amounts of end groups were observed in the ^{31}P (Fig. 2) and ^{13}C (Fig. 3) NMR spectra. Molecular weight measurements (SEC) indicated that this polymer had a relatively low molecular weight ($\bar{M}_n = 1900$, $\bar{M}_w = 3900$, $\bar{M}_z = 6300$). Further heating of this polymer under vacuum caused the molecular weight to decrease, and the rate of decrease in molecular weight increased as the heating was continued.

Side reactions have previously been reported for polycondensations of dialkyl phosphonates and diols, however, there is disagreement in the literature as to their nature. Vogt and Balasubramanian [1] have suggested that these reactions involve alkylation of the diols by the dialkyl phosphonate to yield phosphonic acids and ethers. In contrast, Pretula and Penczek [6] have suggested that the phosphonic acids are formed: "at least in part from the reaction with water, either present or formed in the reaction mixture (formed, e.g. from the high temperature dehydration of the alcohol)". Our NMR studies indicate that, at 80°C, the mechanism proposed by Vogt and Balasubramanian appears to be operating. The small resonance in the ^{31}P NMR spectrum at 7.30 ppm (D in Fig. 2) is consistent with the presence of a phosphonic acid end group in the polymer. This assignment is supported by the presence of the ^{13}C NMR resonance at 69.7 ppm (A in Fig. 4), which can be assigned to a methylene adjacent to a phosphonic acid end group. The small ^{13}C resonances at 78.3 and 58.7 ppm (C and B, respectively, in Fig. 4) are consistent with the presence of methylene and methyl carbons of a methyl ether of 1,4-cyclohexane dimethanol (see discussion in the subsequent section) or to an end group derived from this compound. No carbon resonances for vinyl groups are observed indicating that the dehydration of the diol does not occur at 80°C in this reaction mixture.[1]

3.2. Attempted polycondensation of dimethyl phenylphosphonate with 1,4-cyclohexane dimethanol

Significant insight into the nature of the side reaction that occurs during the polycondensations of dimethyl phosphonate and diols was provided by the results from our attempted polycondensation of dimethyl phenylphosphonate and 1,4-cyclohexane dimethanol. Heating a mixture of these materials at 80°C under a nitrogen atmosphere gave little polycondensation. In an attempt to increase the rate of the reaction, a small amount of metallic sodium was added, and the temperature was increased to 110°C. A ^{31}P NMR spectrum taken 70 h after the Na was added suggested that some polycondensation was occurring because ^{31}P NMR resonances for dimethyl phenylphosphonate (22.04 ppm), methyl phenylphosphonate end groups (19.77 ppm) and phenylphosphonate internal groups (18.53 ppm) were all observed. However, the polymer was not stable and decomposed on further heating as indicated by the presence of a number of new resonances in the ^{31}P NMR spectrum. When the reaction mixture was placed under vacuum, a clear liquid distilled from the reaction mixture. It was identified as the dimethyl ether of 1,4-cyclohexane dimethanol on the basis of its ^{13}C NMR and mass spectra. The formation of this material further supports the methyl transfer mechanism proposed by Vogt and Balasubramanian [1].

3.3. Preparation of high molecular weight polyphosphonates

The above results suggested that the high molecular weight polyphosphonates are not formed via polycondensation due to the methyl transfer reaction. If this were the case, methylation of the phosphonic acid end groups should regenerate the methyl phosphonate end groups and allow high polyphosphonates to be prepared. However, for this process to succeed, the byproduct from the methylating agent must be readily removed from the polymerization mixture. In addition, the methylating agent must not cause degradation of the polymer chain. These conditions preclude the use of methylating agents such as dimethyl sulfate, which produces nonvolative sulfuric acid, or methyl iodide, which can cleave phosphorus esters. In contrast, diazomethane does not generate any nonvolative byproducts and cleanly converts the phosphonic acid end groups into reactive methyl phosphonate end groups. Because the methyl transfer side reaction should be especially prevalent early in the polycondensations when high concentrations of methyl phosphonate and alcohol groups are present, the diazomethane treatment was carried out on the mixtures of oligomers that were obtained after several days of reaction.

In a typical reaction, a mixture of oligomeric polyphosphonates was prepared by the stoichiometric polycondensation of dimethyl phosphonate with 1,4-cyclohexane dimethanol at 80°C for 360 hr. A ^{31}P NMR spectrum of the reaction mixture, Fig. 5, contains resonances due to methylphosphonate end groups (B), internal phosphonate groups (C) and phosphonic acid end groups (D). The ratio of the internal phosphonate groups to methyl phosphonate end groups, obtained from integration of the ^{31}P NMR spectrum, was 7.3 to 1. An SEC of the oligomer mixture gives $\bar{M}_n = 1600$, $\bar{M}_w = 3200$, $\bar{M}_z = 5000$. After treatment with diazomethane, the ^{31}P NMR spectrum of the oligomer mixture, shown in Fig. 5, does not contain any resonances for phosphonic acid groups. The ratio of internal

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[1] The molecular weight of a mixture of oligomers with methyl phosphonate end groups remains unchanged when the mixture is heated at 80°C for several days. This indicates that polymerization via the loss of dimethyl phosphonate (transesterification) does not occur to an appreciable extent at this temperature.

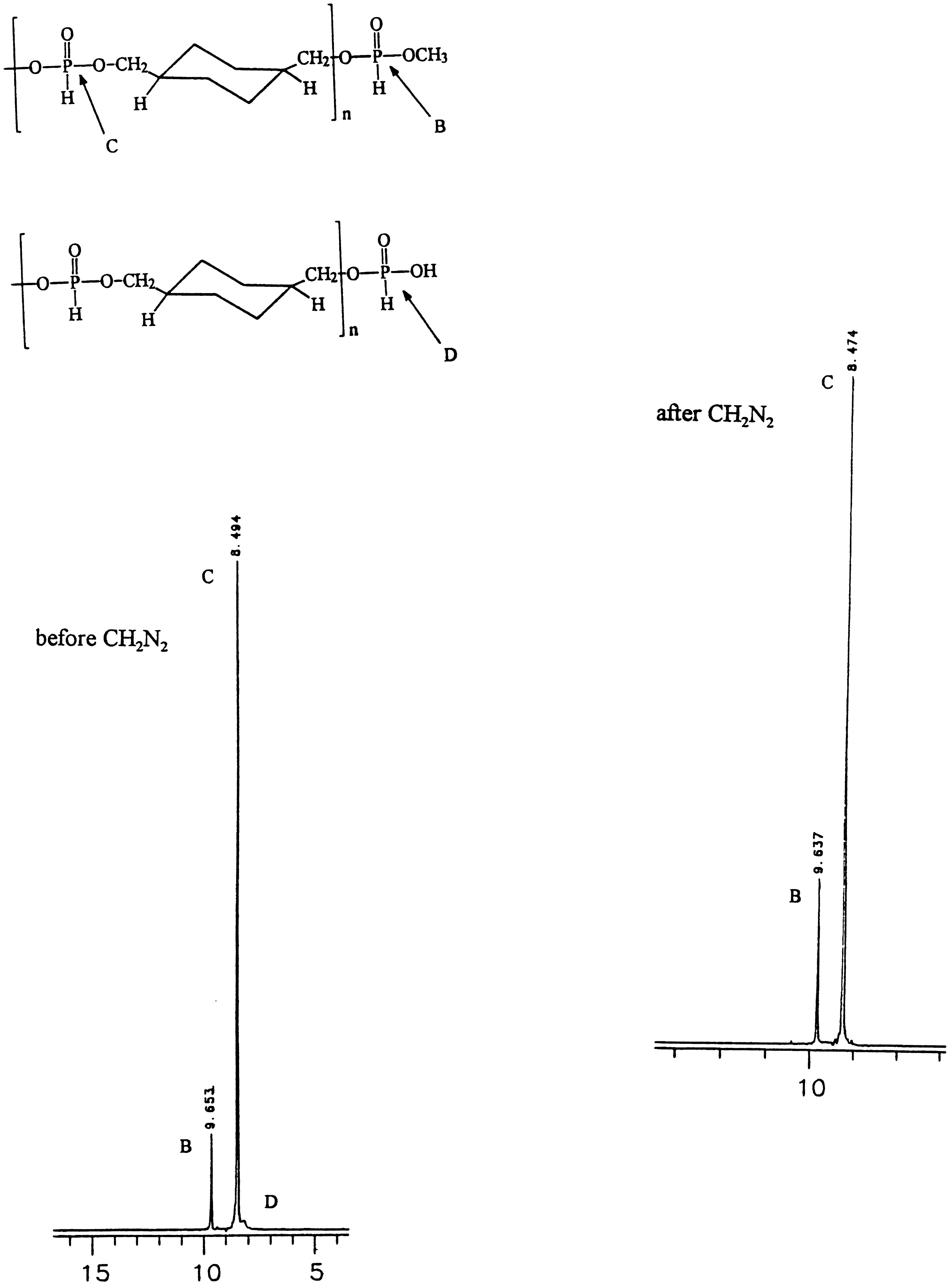

Fig. 5. ^{31}P NMR spectra of the product of the polycondensation of dimethyl phosphine and 1,4-cyclohexane diol before and after treatment with diazomethane.

Table 1
Effect of diazomethane treatment on the molecular weights of polyphosphonates prepared by the polycondensations of dimethyl phosphonate and diols

Diol	CH_2N_2 treatment	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1,12-Dodecanediol	No	1700	2600	1.51
1,4-Cyclohexane dimethanol	No	1900	3900	2.10
1,12-dodecanediol	Yes	10 800	21 800	2.03
1,4-Cyclohexane dimethanol	Yes	7400	14 100	1.91

phosphonate groups to methyl phosphonate end groups is 4.3 to 1, indicating that the diazomethane treatment has produced additional methyl phosphonate end groups. The SEC of the oligomer mixture after treatment with diazomethane gives $\bar{M}_n = 2200$, $\bar{M}_w = 4600$, $\bar{M}_z = 7000$. The fact that this process takes place without a concurrent decrease in molecular weight clearly shows that the additional end groups are not formed by chain scission. The slight increase in the molecular weight of the polymer is most likely due to polycondensation occurring due to heating as the solvent was removed.

Table 1 shows the effect of diazomethane treatment on the maximum molecular weights of polyphosphonates prepared from the polycondensations of dimethyl phosphonate with both 1,12-dodecanediol and 1,4-cyclohexane dimethanol. If diazomethane treatment is not used then polymers having $\bar{M}_n$s of approximately 10^3 are formed. However, with diazomethane treatment, polymers having $\bar{M}_n$s of approximately 10^4 are obtained. The latter molecular weights are of the same order of magnitude but somewhat smaller than those reported by Penczek and coworkers for the polymers prepared by transesterification [5,6,9,10].

It is more difficult to compare our results to those reported by Vogt and Balasubramanian [1] for polymers prepared by polycondensation. The $\bar{M}_n$s that he reported for polymers that were prepared by polycondensation without diazomethane treatment were determined both by viscosity and by end group analysis and are in poor agreement. It seems likely that the use of viscosity overestimates the $\bar{M}_n$s of the polymers because the acid end groups in polymers result in high viscosities even when $\bar{M}_n$ is relative low ($\backsim 10^3$). The end group analysis used by Vogt and Balasubramanian is not likely to be accurate, because it was based on pH measurements and involves a number of questionable assumptions. Because both methods employed by Vogt and Balsubramanian overestimates the $\bar{M}_n$s of the polymers, the true $\bar{M}_n$s of the polymers are likely to be significantly lower than those reported in his paper and thus consistent with our results for polymers produced via polycondensation without diazomethane treatment.

Table 2
Comparison of $\bar{M}_n$ data determined by SEC and from the integrations of $^{31}P\{^1H\}$ NMR spectra for the polycondenstation of dimethyl phosphonate and 1,12-dodecanediol

Time (h) at 160°C	^{31}P NMR integration		$\bar{M}_n$	
	End	Internal	NMR	SEC
120	1.00	8.84	4740	6890
144	1.00	18.98	9774	10 300
168	1.00	26.04	13 275	13 600

SEC does not necessarily yield exact molecular weights for polyphosphonates because polystyrene is used to generate the SEC calibration curve. We have therefore compared the $\bar{M}_n$ data obtained from the SEC to exact $\bar{M}_n$ data calculated from the quantitative $^{31}P\{^1H\}$ NMR spectra of the polymers. These data are summarized in Table 2. There is a good agreement between the $\bar{M}_n$s calculated from SEC and $^{31}P\{^1H\}$ NMR spectra, and the agreement improves as the molecular weight of the polymer increases. The difference in $\bar{M}_n$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 $\bar{M}_n$ to be higher than the actual $\bar{M}_n$ for low molecular weight polymers. Also, the SEC calculations assume a constant refractive index difference between the polymer and solvent, which may not be valid at low molecular weights. This affect would also decrease as the molecular weight of the polymer increases.

It is interesting to note that methyl ether end groups derived from the diols are not observed in the final polymers. One possible explanation for this is all methyl ethers are formed by reaction of the methyl phosphonate end groups with molecular diols and thus are never incorporated into the polymers. These ethers, which are more volatile than are the diols, would then be removed under the high vacuum polymerization conditions. This is supported by the observation that free diol is generally in excess during the course of the polymerization, due to the higher volatility of dimethyl phosphonate relative to the diol, requiring addition of dimethyl phosphonate to maintain the 1:1 stoichiometry. A second possible explanation is that the methyl ether end groups are formed but are lost as the polycondensation proceeds. This could occur by exchange of a diol for an ether and would be driven by the higher volatility of the ethers. Our results cannot distinguish between these two possibilities.

4. Conclusions

The polycondensation of dimethyl phosphonate and diols allows a variety of polymeric phosphonate esters to be prepared in a single step from commercially available starting materials. A serious side reaction in these polymerization is the transfer of a methyl group from a methyl phosphonate end group to an alcohol to form a methyl ether and a phosphonic acid end group. This prevents the formation of high molecular weight polymers. However, the phosphonic acid end groups, which are formed by this side reaction, can be converted into reactive methyl phosphonate end groups by treatment with diazomethane. This allows polymers with molecular weights similar to those prepared by transesterification to be obtained.

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References

[1] Vogt W, Balasubramanian S. Makromol Chem 1973;163:111.
[2] Pretula J, Kaluzynski K, Penczek S. J Polym Sci: Polym Chem Ed 1984;22:1251.
[3] Pretula J, Kaluzynski K, Penczek S. Macromolecules 1986;19:1797.
[4] Pretula J, Penczek S. Makromol Chem, Rapid Commun 1988;9:731.
[5] Baran J, Klosinski P, Penczek S. Makromol Chem 1989;190:1903.
[6] Pretula J, Penczek S. Makromol Chem 1990;191:671.
[7] Penczek S, Baran J, Biela T, Lapienis G, Nyk A, Klosinski P, Pretula B. Br Polym J 1990;23:213.
[8] Gray GM, Branham KE, Ho L-H, Mays JW, Bharara PC, Hadjipetrou A, Beal JB. In: Harrod J, Laine R, editors. Inorganic and organometallic oligomers and polymers, Dordrecht, Netherlands: Kluwer Academic, 1991. p. 249.
[9] Penczek S, Pretula J. Macromolecules 1993;26:2228.
[10] Pretula J, Kaluzynski K, Szymanski R, Penczek S. Macromolecules 1997;30:8172.
[11] Kokkinia A, Paleos C, Dias P. Polym Prepr 1989;30(2):448.
[12] Kokkinia A, Keramaris K, Margaritis K, Malliaris L, Paleos C. J Polym Sci: Part A: Polym Chem 1995;33:455.
[13] Banerjee S, Palit S, Maiti S. J Polym Sci: Part A: Polym Chem 1994;32:219.
[14] Nishikubo T, Kameyama A, Minegishi S. Macromolecules 1994;27:2641.
[15] Imai Y, Kamata H, Kakimoto M. J Polym Sci: Polym Chem Ed 1984;22:1259.
[16] Kaluzynski K, Penczek S. Macromol Chem Phys 1994;195:3855.
[17] Arndt F. In: Blatt AH, editor. Organic synthesis colloqium, 2. New York: Wiley, 1943. p. 461.
[18] Gray GM, Whitten JE, Box JW. Inorganica Chim Acta 1986;116:21.
[19] Arndt F. In: Blatt AH, editor. Organic synthesis colloqium, 2. New York: Wiley, 1943. p. 165.