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G. C. Corfield^a; H. H. Monks^a

^a Department of Chemistry and Biology, Sheffield Polytechnic, Sheffield, England

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Determination of Ring Size in Cyclopolymers from Divinyl Phosphonates

G. C. CORFIELD and H. H. MONKS

Department of Chemistry and Biology
Sheffield Polytechnic
Sheffield S1 1WB, England

ABSTRACT

Divinyl phenylphosphonate and divinyl methylphosphonate have been synthesized using modifications of the method of Gefter and Kabachnik. In contrast to the results reported by these authors, it has been possible to obtain soluble, fusible, linear polymers (cyclopolymers) from both monomers by polymerization in dilute solution.

By ^{31}P NMR spectroscopy it is possible to distinguish and quantitatively determine phosphorus atoms in five- and six-membered ring environments. Using a series of phosphonates as model compounds, this technique has shown that poly(divinyl phenylphosphonate) contains both five- and six-membered ring repeating units in amounts which depend upon the method of polymerization, whereas poly(divinyl methylphosphonate) produced under a variety of conditions contains only six-membered rings. This work has established that ^{31}P NMR can be used to determine the ring size in cyclopolymers from divinyl phosphonates by direct analysis of the polymers.

INTRODUCTION

Divinyl phosphonates (I) are examples of 1, 6-dienes; if cyclopolymerization of these monomers could be achieved, polymers with five- (II) and/or six-membered ring repeating units (III) would be expected. Other phosphorus-containing 1, 6-dienes have been reported to yield cyclopolymers [1-3]. Butler and Berlin [1] described the polymerization of diallylphenylphosphine oxide and dimethallylphenylphosphine oxide and suggested that the cyclopolymers produced contained only six-membered rings. They noted the possibility that five-membered rings could be formed but rejected this theory on the grounds that such a structure would necessitate formation of a primary radical rather than a secondary (or tertiary) radical. They also stated, at that time (1960), that a five-membered ring had never been reported in cyclic polymerizations involving symmetrical 1, 6-diene systems with terminal methylene groups.

More recent investigations of the cyclopolymerization reaction [4] have shown that five-membered rings are formed in addition to six-membered rings. Determination of the distribution of five- and six-membered ring units in cyclopolymers from 1, 6-dienes has been effected by spectroscopic or chemical methods. In such cases the analysis is carried out directly on the cyclopolymer. Other workers have used the indirect method of relating the products of telomerization reactions of 1, 6-dienes with various chain-transfer agents to the cyclopolymerization reaction. However, a systematic study of the effect of temperature, solvent, initiator, molecular weight, and structure of the monomer on the ring size distribution in cyclopolymerization reactions or cyclotelomerization reactions of 1, 6-dienes has yet to be investigated. Also, the relationship, if any exists, between cyclotelomerization and cyclopolymerization reactions needs to be studied. For such work to be carried out, it is necessary to find a method which will enable the ring size to be determined in both cyclotelomers and cyclopolymers directly. This paper describes the use of ^{31}P NMR as a means of estimating the amount of five- and/or six-membered rings in poly(divinyl phosphonates).

Few cases are reported where high molecular weight polymers have been obtained from phosphorus-containing monomers. Thus high molecular weight polymers were not expected (nor were they obtained) from polymerizations of divinyl phenylphosphonate and divinyl methylphosphonate. However, the polymers obtained were soluble, fusible solids and had no residual unsaturation, in contrast to previous reports of their properties. Gefter and Kabachnik [5] reported poly(divinyl phenylphosphonate) as a black, insoluble, noncombustible solid, and poly(divinyl methylphosphonate) as a light yellow, insoluble, noncombustible solid. Previous to this, Upson [6] reported poly(divinyl

phenylphosphonate) as a viscous liquid or a soft tacky solid. Both papers were published before the discovery of the cyclopolymerization reaction and hence the possibility of linear polymers was not expected, nor was it investigated. The insoluble polymers (presumably cross-linked) were obtained by polymerizations in bulk; Gefter and Kabachnik [5] heated divinyl phenylphosphonate for 150 hr at 50°C with benzoyl peroxide as initiator.

This work has shown that soluble polymers (proposed as cyclopolymers) can be obtained by polymerization of divinyl phosphonates in dilute solution, especially if polymerization is carried out at low temperature and the initiator is decomposed photolytically.

³¹P NMR is directly applicable to recognition of phosphorus atoms in different chemical environments (ring size) and is able to give a quantitative measure of the relative amounts of nuclei in these different environments. The cyclopolymers obtained from divinyl phosphonates were studied in this way with a view to determining the relative amounts of six- and/or five-membered ring content.

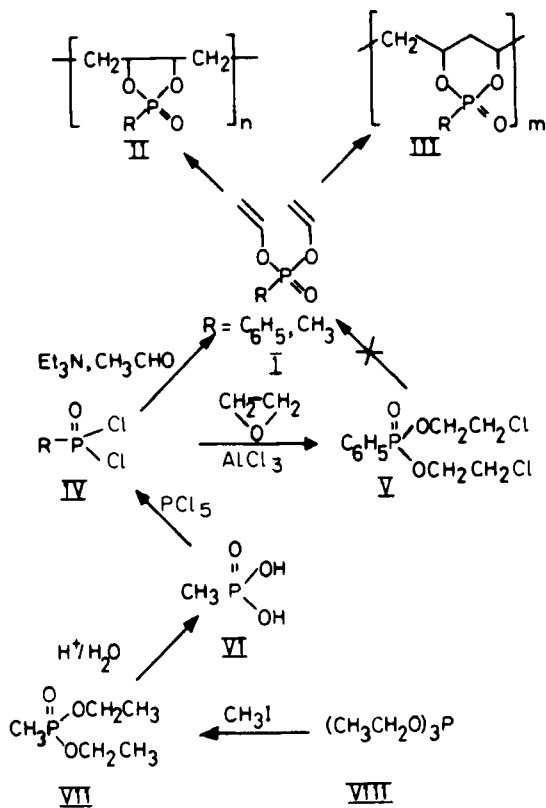
MONOMER SYNTHESIS AND CYCLOPOLYMERIZATION

Divinyl phenylphosphonate (I, R = C₆H₅) was prepared by the method of Gefter and Kabachnik [5] (IV - I). Low yields were reported by these authors and only very brief experimental details were given. An alternative route to divinyl phenylphosphonate, which involved dehydrochlorination of bis(2-chloroethyl) phenylphosphonate [6] (V, R = C₆H₅), was attempted many times without success. These findings agree with those of other workers [7, 8] who consider the results published by Upson [6] to be erroneous.

Divinyl methylphosphonate (I, R = CH₃) was prepared by the method outlined by Gefter and Kabachnik [5] and given in greater detail in a later publication by Gefter [8] (VIII - I).

The polymerization of divinyl phenylphosphonate was achieved using benzoyl peroxide or azobisisobutyronitrile as initiator, the results and conditions being summarized in Table 1. The polymers were isolated from the polymerization reaction as white amorphous powders by dropwise addition into vigorously stirred diethyl ether or light petroleum. All the polymers shown in Table 1 (with the exception of the sample from polymerization in bulk) had softening points in the range 130 to 160°C.

All the polymers of divinyl phenylphosphonate were soluble in N,N-dimethylformamide and dimethylsulfoxide, with the exception of the sample from polymerization in bulk, which was presumed to be cross-linked in view of its insolubility and infusibility. After repeated



reprecipitation of the soluble polymers, IR and NMR spectra were obtained. The IR spectra showed no evidence of any residual vinyl unsaturation and bands at 1280 cm^{-1} ($\text{P}=\text{O}$); 755 , 722 , and 692 cm^{-1} (P -phenyl). The NMR spectra of poly(divinyl phenylphosphonate) showed three sets of broad peaks at 2.2 - 2.7 and 7.8 - 8.8τ , which is very different from the spectrum of the monomer. The spectra showed no evidence of residual vinyl unsaturation, and the new peaks are attributed to protons in saturated systems. A sample of poly(divinyl phenylphosphonate) had a reduced specific viscosity of 0.042 in solutions of N,N -dimethylformamide. This suggests that the polymers are of low molecular weight.

To explain the formation of soluble, fusible, and hence linear polymers from divinyl phenylphosphonate, containing no residual unsaturation, it is proposed that they are produced via a chain-growth

TABLE 1. Polymerization of Divinyl Phenylphosphonate

Wt of monomer (g)	Solvent (% w/w)	Initiator	mole %	Time (hr)	Temperature (°C)	Conversion ^a (%)
1.0	-	BP ^c	2.0	60	70	90 ^b
5.0	n-Hexane (15)	ABIN ^d + hν	2.0	20	20	30
2.0	DMFe (50)	ABIN ^d + hν	2.0	16	20	26
3.0	DMFe (40)	ABIN ^d + hν	2.0	5	20	39
5.0	n-Hexane (15)	ABIN ^d	2.0	48	55	32
2.0	DMFe (40)	ABIN ^d	2.0	20	70	50
2.0	THF ^f (50)	ABIN ^d + hν	2.0	15	20	27

^aEstimated gravimetrically.

^bInsoluble polymer (presumably cross-linked).

^cBenzoyl peroxide.

^dAzobisisobutyronitrile.

^eN,N-Dimethylformamide.

^fTetrahydrofuran.

mechanism involving alternating intramolecular and intermolecular steps. This mechanism is known as cyclopolymerization.

Divinyl methylphosphonate was polymerized in solution using azobisisobutyronitrile as initiator. The results and conditions are summarized in Table 2. The polymers were isolated from the polymerization reaction by dropwise addition into vigorously stirred ether or light petroleum. All the polymers in Table 2 had softening points in the range 105 to 120°C.

All the polymers given in Table 2 were soluble in *N,N*-dimethylformamide and had IR and NMR spectra which indicated the absence of residual unsaturation. The NMR spectra again showed a considerable difference between the spectrum of the polymer and that of the monomer. The polymers had peaks in the ranges 4.4-5.1, 7.0-7.5, and 8.2-8.7 τ . A reduced specific viscosity of 0.08 (*N,N*-dimethylformamide) was measured for one sample of the polymer.

The cyclopolymerization mechanism must again be used to explain the formation of soluble, fusible, and hence linear polymers from divinyl methylphosphonate. Thus both divinyl methylphosphonate and divinyl phenylphosphonate can yield cyclopolymers under suitable conditions.

ANALYSIS OF RING SIZE

As model compounds for the assignment of ^{31}P chemical shifts in the polymers, a number of cyclic phosphonate esters were synthesized by either 1) addition of an acid chloride to a solution of a diol in the presence of pyridine, or 2) the method of Toy [9] which consisted of heating a diol with an acid chloride under vacuum. Table 3 shows the conditions employed and the physical constants of the esters obtained. The cyclic esters are named using the nomenclature proposed by Mann [10].

The ^{31}P NMR spectrum of certain samples of poly(divinyl phenylphosphonate) showed two regions of absorption for 20% solutions of the polymer in *N,N*-dimethylformamide. The chemical shifts of the regions of absorption are shown in Table 4 along with the conditions used in the polymerizations.

If the two chemical shift values of the soluble polymer are due to phosphorus atoms in different chemical environments, then compounds with similar structural units (five- and six-membered rings) should show similar chemical shifts. This assumes that cyclopolymerization has occurred in the soluble polymers obtained. Evidence which suggests that this is the case is given earlier. Table 5 shows the structure and ^{31}P chemical shifts of some cyclic five- and six-membered phenylphosphonates along with certain acyclic phenylphosphonates.

TABLE 2. Polymerization of Divinyl Methylphosphonate

Wt of monomer (g)	Solvent (% w/w)	Initiator	mole %	Time (hr)	Temperature (°C)	Conversion ^a (%)
1.48	DMF ^b (45)	ABIN ^c	2.0	10	70	20
1.48	THF ^d (50)	ABIN ^c + h ν	2.0	17	20	30
1.48	DMF ^b (50)	ABIN ^c	2.0	14	70	27
1.48	THF ^d (50)	ABIN ^c	2.0	20	70	15

^aEstimated gravimetrically.

^bN,N-Dimethylformamide.

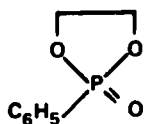
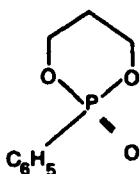
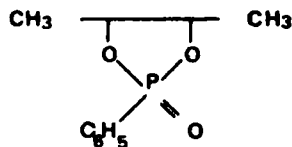
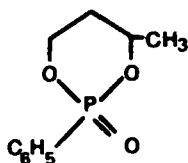
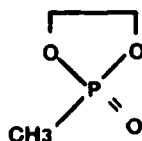
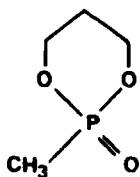
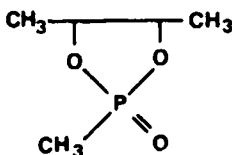
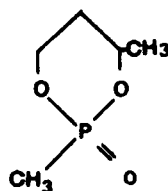
^cAzobisisobutyronitrile.

^dTetrahydrofuran.

TABLE 3. Synthesis of Phosphonate Esters

Acid chloride	Alcohol	Method	Structure Ref.	bp (°C)/Torr (mp, °C)	Phosphonate	Literature bp (°C)/Torr (mp, °C)
Phenylphosphonic dichloride	1,2-Ethanediol	a	IX	169-171/0.7	2-Phenyl-1,3,2-dioxaphospholane-2-oxide	210-215/6-7 [9] 182-185/0.3 [11]
	1,3-Propanediol	a	X	148-149/0.2 (33)	2-Phenyl-1,3,2-dioxaphosphorinane-2-oxide	212-214/7.5 [9] 170-174/0.1 [11]
	2,3-Butanediol	a	XI	130-131/0.02	4,5-Dimethyl-1,3,2-dioxaphosphorinane-2-oxide	210-215/15 [9]
Methylphosphonic dichloride	1,3-Butanediol	a	XII	158-160/0.3 (64)	4-Methyl-1,3,2-dioxaphosphorinane-2-oxide	267 [12]
	Ethanol	a	XIII	126-128/1.0	Diethyl phenylphosphonate	109-111/5 (40-41) [13]
	1,2-Ethanediol	b	XIV	130-132/2.0	2-Methyl-1,3,2-dioxaphospholane-2-oxide	(98-99) [14]
	1,3-Propanediol	b	XV	122-124/0.4 (98-100)	2-Methyl-1,3,2-dioxaphosphorinane-2-oxide	

2, 3-Butanediol	b	XVI	126-128/4.0 (42-44)	2, 4, 5-Trimethyl-1, 3, 2-dioxaphosphorinane-2-oxide	86-90/0.5 (42-44) [14]
1, 3-Butanediol	b	XVII	70-71/0.2 (40-41)	2, 4-Dimethyl-1, 3, 2-dioxaphosphorinane-2-oxide	71/0.25 (40) [15]

IXXXIXIIXIIIXIVXVXVIXVII

All the ^{31}P NMR spectra of poly(divinyl phenylphosphonate) given in Table 4 showed peaks with chemical shifts near -28 ppm which by comparison with chemical shift values of five-membered cyclic phosphonates given in Table 5 suggests that the polymers contained phosphorus atoms in environments very similar to phosphorus atoms in five-membered rings. On this basis it is proposed that divinyl phenylphosphonate does polymerize to give products with five-membered rings (II). Three spectra also showed peaks with chemical shifts near -14 ppm; this value is similar to the six-membered cyclic phosphonates, especially 4-methyl-2-phenyl-1,3,2-dioxaphosphorinane-2-one which is very similar structurally to the six-membered ring repeating unit proposed for cyclopolymerization of divinyl phenylphosphonate (III).

Apparently, therefore, divinyl phenylphosphonate can cyclopolymerize to give products containing predominantly five-membered rings or

TABLE 4. ^{31}P Chemical Shifts of Samples of Poly(divinyl Phenylphosphonate)

Polymerization conditions	Chemical shift (δ ppm)
40% Solution in DMF ^a using 2 mole % ABIN ^b as initiator for 20h at 70°C	-28.0
50% Solution in THF ^c using 2 mole % ABIN ^b + $h\nu$ as initiator for 15 hr at 20°C	-28.2, -13.0
50% Solution in DMF ^a using 2 mole % ABIN ^b + $h\nu$ as initiator for 16 hr at 20°C	-28.5, -13.8
40% Solution in DMF ^a using 2 mole % ABIN ^b + $h\nu$ as initiator for 5 hr at 20°C	-28.0, -12.8

^aN,N-Dimethylformamide.^bAzobisisobutyronitrile.^cTetrahydrofuran.TABLE 5. ^{31}P Chemical Shifts of Phenylphosphonates

Compound	Structure	^{31}P chemical shift (δ ppm)
2-Phenyl-1,3,3-dioxaphospholane-2-oxide	IX	-31.0
2-Phenyl-1,3,2-dioxaphosphorinane-2-oxide	X	-11.2
4,5-Dimethyl-1,3,2-dioxaphospholane-2-oxide	XI	-28.0
4-Methyl-1,3,2-dioxaphosphorinane-2-oxide	XII	-13.0
Divinyl phenylphosphonate	I, R = C ₆ H ₅	-11.4
Diethyl phenylphosphonate	XIII	-16.9
Bis(2-chloroethyl) phenylphosphonate	V	-17.2

a mixture of five- and six-membered rings dependent on the polymerization conditions.

Before using the ^{31}P NMR spectra of poly(divinyl phenylphosphonate) in a quantitative manner to calculate the amount of five- and six-membered rings in the polymer, the method was tried using known mixtures of cyclic phosphonates. The results (Experimental section) show that, in general, the precision limits for calculating the amount of five- and six-membered rings are $\pm 2\%$. In some ^{31}P NMR spectra this limit is raised to $\pm 5\%$ because of noise. Table 6 gives the calculated amount of five- and six-membered rings in poly(divinyl phenylphosphonate).

The ^{31}P spectra of samples of poly(divinyl methylphosphonate) were similarly obtained. However, these spectra showed only one region of absorption at approximately -24 ppm (Table 7). By comparison with the chemical shifts of some cyclic and acyclic methylphosphonates (Table 8), a six-membered ring (III) is proposed as the repeating unit in the cyclopolymers from divinyl methylphosphonate.

This work has shown that the ring size in cyclopolymers of divinyl phosphonates is dependent on the solvent, method of initiation, and the structure of the monomer. In the case of divinyl phenylphosphonate the five- and six-membered ring content in the polymer is markedly altered when the solvent or initiation technique is changed. Divinyl methylphosphonate does not give variations in ring size content when conditions are altered. However, this work has indicated that these factors are important and should enable a more

TABLE 6. Calculated Amount of Five- and Six-Membered Rings in Samples of Poly(divinyl Phenylphosphonate)

Polymerization conditions		Five-membered rings (%)	Six-membered rings (%)
Solvent	Initiator		
DMF ^a	ABIN ^c	100	-
THF ^b	ABIN ^d	46	54
DMF ^a	ABIN ^d	63	37
DMF ^a	ABIN ^d	32	68

^a N,N-Dimethylformamide.

^b Tetrahydrofuran.

^c Azobisisobutyronitrile, thermally at 70°C .

^d Azobisisobutyronitrile, photochemically at 20°C .

TABLE 7. ^{31}P Chemical Shifts for Samples of Poly(divinyl methylphosphonate)

Polymerization conditions	chemical shift (δ ppm)
50% Solution in DMF ^a using 2 mole % ABIN ^b as initiator for 14 hr at 70°C	-24.2
50% Solution in THF ^c using 2 mole % ABIN ^b + $h\nu$ as initiator for 17 hr at 20°C	-25.0

^aN,N-Dimethylformamide.^bAzobisisobutyronitrile.^cTetrahydrofuran.TABLE 8. ^{31}P Chemical Shifts of Methylphosphonates

Compound	Structure	^{31}P chemical shift (δ ppm)
2-Methyl-1,3,2-dioxaphospholane- 2-oxide	XIV	-42.6
2-Methyl-1,3,2-dioxaphosphorinane- 2-oxide	XV	-23.2
2,4,5-Trimethyl-1,3,2-dioxaphos- pholane-2-oxide	XVI	-39.2
2,4-Dimethyl-1,3,2-dioxaphosphor- inane-2-oxide	XVII	-26.4
Divinyl methylphosphonate	I, R = CH ₃	-22.8
Diethyl methylphosphonate	VII	-26.0

systematic study to be completed in view of the ease of assignment of ^{31}P chemical shifts to five- and/or six-membered rings.

EXPERIMENTAL

^{31}P Nuclear magnetic resonance spectra were determined at normal temperatures for chloroform or N,N-dimethylformamide solutions

(unless otherwise stated) containing 85% phosphoric acid ($\delta = 0.0$ ppm) in a sealed capillary as an internal standard, using a JEOL C-60 HL high resolution 24 MHz instrument.

Divinyl Phenylphosphonate (I, R = C₆H₅)

Freshly distilled phenylphosphonic dichloride, bp 86 to 88°C at 0.5 Torr (138.0 g, 0.70 mole), was added dropwise over 2 hr to a stirred solution of acetaldehyde (230.0 g, 5.2 mole) and triethylamine (196.0 g, 1.94 mole) which was previously cooled to -15°C and swept with dry nitrogen. The solution was maintained at -15°C for 5 hr during which time the precipitate and solution slowly darkened in color. The solution was allowed to warm to room temperature, stirred for a further 15 hr, and then light petroleum, bp 40 to 60°C (200 ml), was added with stirring. The precipitate (triethylamine hydrochloride, mp 253° from alcohol) was removed by filtration and the volatile fractions removed under reduced pressure. Distillation of the residue gave divinyl phenylphosphonate, bp 116 to 118°C at 1.5 Torr, which was redistilled through a Nester-Faust spinning band column with an 18 in. stainless steel band and partial take-off head (60.0 g, 41%), bp 107 to 108°C at 0.5 Torr as a colorless liquid n_D^{25} 1.5149.

Analysis. Found: C, 57.4; H, 5.25; P, 14.8%; M⁺, 210; Calculated for C₁₀H₁₁PO₃: C, 57.15; P, 14.75%; M, 210; ν_{\max} 3060(C-H phenyl and vinyl), 1642(C=C vinyl), 1593, 1443(C=C phenyl), 1280(P=O), 1020(P-O-CH=CH₂), 980-960(CH=C), 792(P-O-C assym.), 755, 722, 692 cm⁻¹(C-H phenyl); τ (CCl₄), 1.9-2.6(5H, m, P-phenyl), 3.1-3.6(2H, q, P-O-CH=CH₂), 4.9-5.5(4H, t, P-O-CH=CH₂); δ ³¹P(CHCl₃), -11.4 ppm.

Poly(divinyl Phenylphosphonate)

Conditions and results are given in Table 1. A typical example of a free radical initiated polymerization was carried out as follows. Divinyl phenylphosphonate (2.10 g, 0.01 mole) was dissolved in freshly distilled N,N-dimethylformamide (2.10 g, bp 44 to 45° at 20 Torr), added to a Pyrex tube containing azobisisobutyronitrile (30 mg, 2 × 10⁻⁴ mole, 2.0 mole %) and the tube purged with dry nitrogen and sealed with a rubber serum cap. The mixture was irradiated with a medium pressure mercury discharge lamp for 16 hr, then

slowly poured into vigorously stirred diethyl ether (200 ml), the precipitate collected by filtration, washed repeatedly with diethyl ether, and dried under reduced pressure 55°C at 0.5 Torr. The solid was ground to a fine powder, Soxhlet extracted with hexane, and dried under reduced pressure at 55°C at 0.5 Torr giving poly(divinyl phenylphosphonate) (0.45 g, 21%) softening point 155 to 160°C.

Analysis. Found: C, 56.5; H, 5.55%. Calculated for $(C_{10}H_{11}PO_3)_n$: C, 57.15; H, 5.25%; ν_{\max} 3100-2900(br)(C-H), 1600-1550, 1450(C=C phenyl), 1300-1250(br)(P=O), 1040-990(br)(P-O-C), 755-690 cm^{-1} (C-H phenyl); τ $((CD_3)_2SO)$, 2.2-2.7(br), 4.8-5.8(br), 7.7-8.8(br); δ ^{31}P (N,N-dimethylformamide), -14.2, -29.0 ppm. The sample had a reduced specific viscosity (η_{sp}/c) of 0.042 (N,N-dimethylformamide).

Bis(2-chloroethyl) Phenylphosphonate (V)

Ethylene oxide (13.2 g, 0.3 mole) was added through a wide bore gas inlet tube over 2 hr to a stirred solution of phenylphosphonic dichloride (19.5 g, 0.1 mole) and anhydrous aluminium chloride (1.95 g) at room temperature. Distillation of the reaction mixture gave bis(2-chloroethyl) phenylphosphonate (19.8 g, 70%), bp 192 to 194°C at 2.0 Torr as a colorless viscous liquid n_D^{25} 1.5236;

ν_{\max} 3060(C-H phenyl), 2980, 2900(C-H aliphatic), 1593, 1445(C=C), 1255(P=O), 1140, 1030(P-O-CH₂-CH₂), 760, 700 cm^{-1} (C-H phenyl); τ (CCl_4) , 2.0-2.6(5H, m, P-phenyl), 4.6-4.9(4H, m, P-O-CH₂-) 6.3-6.5(4H, t, O-CH₂-CH₂); δ ^{31}P (CHCl₃), -17.2 ppm.

Diethyl Methylphosphonate (VII)

Triethyl phosphite (110.0 g, 0.66 mole) and iodomethane (100.0 g, 0.705 mole) were refluxed for 2 hr on a steam bath using an efficient condenser and an anhydrous calcium chloride guard tube. Iodoethane (96 g) was distilled from the reaction mixture and the residue distilled giving diethyl methylphosphonate (95.0 g, 95%), bp 59 to 60°C at 1.0 Torr as a colorless liquid n_D^{25} 1.4128.

Analysis. Found: C, 39.45; H, 8.6%. Calculated for $C_5H_{13}PO_3$: C, 39.45; H, 8.55%; ν_{\max} 2970, 2910(C-H aliphatic), 1308(P-CH₃), 1230(P=O), 1160, 1025 cm^{-1} (P-O-C₂H₅); τ $(CDCl_3)$, 5.6-6.2(4H, m, P-O-CH₂), 8.4-8.8(9H, q, CH₃ protons); δ ^{31}P (CHCl₃), -26.0 ppm.

Methylphosphonic Acid (VI)

Diethyl methylphosphonate (140.0 g, 0.985 mole) was refluxed for 8 hr with hydrochloric acid (600 ml) and water (600 ml). Water, hydrochloric acid, and ethanol were removed by distillation giving methylphosphonic acid (80.0 g, 83%) as a colorless viscous liquid crystallized on standing, mp 103 to 105°C (white plates from hexane/ethyl acetate).

Methylphosphonic Dichloride (IV, R = CH₃)

Phosphorus pentachloride (180.0 g, 0.865 mole) was added to methylphosphonic acid (36.0 g, 0.375 mole) in a flask equipped with an efficient reflux condenser and an anhydrous calcium chloride guard tube. A vigorous exothermic reaction started on gentle heating and the contents of the flask soon became liquid. The solution was refluxed for a further 12 hr and distilled through a 30-cm Vigreux column. Phosphoryl chloride was removed as the first fraction followed by methylphosphonic dichloride (48.0 g, 77%), bp 160 to 162°C as a colorless liquid n_D^{25} 1.4595, which crystallized on standing, mp 32 to 34°C.

Analysis. Found: Cl, 53.15%. Calculated for CH₃POCl₂: Cl, 53.35; ν_{\max} 2980, 2900(C-H aliphatic), 1303(P-CH₃), 1268 cm⁻¹ (P=O).

Divinyl Methylphosphonate (I, R = CH₃)

Methylphosphonic dichloride (26.6 g, 0.20 mole) in anhydrous benzene (40 ml) was added dropwise over 2 hr to a stirred solution of acetaldehyde (64.0 g, 1.45 mole) and triethylamine (55.5 g, 0.55 mole) which had been previously cooled to -15°C and swept with dry nitrogen. The solution was maintained at -15°C for 4 hr with continuous stirring during which time the precipitate and solution slowly darkened in color. The solution was allowed to warm to room temperature, stirred for a further 12 hr, and then light petroleum, bp 40 to 60°C (200 ml), was added with stirring. The precipitate (triethylamine hydrochloride, mp 253°C from alcohol) was removed by filtration and the volatile fractions removed under reduced pressure. Distillation of the residue gave divinyl methylphosphonate, bp 68 to 70°C at 6.0 Torr, which was redistilled through a Nester-Faust spinning band column equipped with an 18 in stainless

TABLE 9

5-Membered ring phosphonate ^a (g)	6-Membered ring phosphonate ^b (g)	Acyclic phosphonate (g)	Calculated ratio 5:6: acyclic (% w/w)	³¹ P NMR peak position (ppm)	Ratio found 5:6:acyclic peak areas
0.35	0.65	-	1:1.97	-31.0(5) -11.2(6)	1:2.01
0.50	0.50	-	1:1	-31.0(5) -11.2(6)	1:1.02
0.75	0.25	-	3:1	-31.0(5) -11.2(6)	2.94:1
0.50	0.50	0.50 ^c	1:1:1	-31.0(5) -11.2(6 + acyclic)	1:1.89
0.33	0.33	0.33 ^d	1:1:1	-31.0(5) -16.9 (acyclic) -11.2(6)	1:1.11:1.12

^a2-Phenyl-1,3,2-dioxaphospholane-2-oxide.^b2-Phenyl-1,3,2-dioxaphosphorinane-2-oxide.^cDivinyl phenylphosphonate.^dDiethyl phenylphosphonate.

steel band and partial take-off head (9.3 g, 32%), bp 52 to 53°C at 1.0 Torr, as a colorless liquid n_D^{25} 1.4369.

Analysis. Found: C, 40.34; H, 6.45; P, 21.25%; M^+ , 148. Calculated for $C_5H_9PO_3$: C, 40.5; H, 6.1; P, 20.95%; M , 148; ν_{\max} 3010 (C-H vinyl), 2920 (C-H methyl), 1643 (C=C), 1308 (P-CH₃), 1270 (P=O), 1020 (P-O-CH=CH₂), 910 (CH=C), 818 cm⁻¹ (P-O-C assym); τ (CCl₄), 3.1-3.6 (2H, m, P-O-CH=CH₂), 5.0-5.6 (4H, q, P-O-CH=CH₂), 8.3-8.6 (3H, d, CH₃-P=O); δ ³¹P (CHCl₃), -22.8 ppm.

Poly(divinyl Methylphosphonate)

Conditions and results are given in Table 2. A typical example of a free radical initiated polymerization was carried out as follows. Divinyl methylphosphonate (1.48 g, 0.01 mole) was dissolved in freshly distilled tetrahydrofuran (1.5 g), added to a Pyrex tube containing azobisisobutyronitrile (30 mg, 2×10^{-4} mole, 2 mole %) and the tube purged with dry nitrogen and sealed with a rubber serum cap. The mixture was irradiated with a medium pressure mercury discharge lamp for 20 hr, then slowly poured into vigorously stirred ether (200 ml), the precipitate collected by filtration, washed repeatedly with ether, and dried under reduced pressure at 55°C at 0.5 Torr. The solid was ground to a fine powder, Soxhlet extracted with hexane, and dried under reduced pressure giving poly(divinyl methylphosphonate) (0.41 g, 30%) softening point 105 to 110°C.

Analysis. Found: C, 40.1; H, 6.9%. Calculated for $(C_5H_9PO_3)_n$: C, 40.5; H, 6.1%; ν_{\max} 2990-2900 (br) (C-H), 1310 (P-CH₃), 1270-1220 (br) (P=O), 1040-980 (br) (P-O-C), 825-800 cm⁻¹ (br) (P-O-C assym); τ ((CD₃)₂SO), 4.4-5.1 (br), 7.0-7.5 (br), 8.2-8.7 (br); δ ³¹P (N,N-dimethylformamide), -24.6 ppm. The sample had a reduced specific viscosity (η_{sp}/c) of 0.08 (N,N-dimethylformamide).

Calibration of the NMR Method for Analysis of the Ring Size in Phosphonate Polymers

Varying amounts of 2-phenyl-1,3,2-dioxaphospholane-2-oxide, 2-phenyl-1,3,2-dioxaphosphorinane-2-oxide, and acyclic phosphonates were dissolved in chloroform (2.0 ml) and ³¹P NMR spectrum of the mixture obtained. The results are summarized in Table 9.

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REFERENCES

- [1] K. D. Berlin and G. B. Butler, J. Amer. Chem. Soc., **82**, 2712 (1960).
- [2] K. D. Berlin and G. B. Butler, J. Org. Chem., **25**, 2006 (1960).
- [3] G. B. Butler, D. L. Skinner, W. C. Bond Jr., and C. L. Rogers, J. Macromol. Sci. Chem., **A4(6)**, 1437 (1970).
- [4] G. C. Corfield, Chem. Soc. Rev., **1(4)**, 523 (1972)
- [5] E. L. Gefter and M. I. Kabachnik, Dokl. Akad. Nauk SSSR, **114**, 541 (1957).
- [6] R. W. Upson, U.S. Patent 2, 557, 805; J. Amer. Chem. Soc., **75**, 1763 (1953).
- [7] J. F. Allen, S. K. Reed, O. H. Johnson, and N. J. Brusvold, Ibid., **78**, 3715 (1956).
- [8] E. L. Gefter, Organophosphorus Monomers and Polymers, Associated Technical Services, Glen Ridge, New Jersey, 1962, p. 26.
- [9] A. D. F. Toy, U.S. Patent 2, 382, 622.
- [10] F. G. Mann, Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth, Wiley-Interscience, New York, 1970, pp. 274, 295.
- [11] R. S. Edunson and J. O. L. Wrigley, Tetrahedron, **35**, 732 (1965).
- [12] I. M. Heilbron and H. M. Bunbury, Dictionary of Organic Compounds, Eyre and Spottiswoode, London, 1965, p. 271.
- [13] K. A. Petrov, R. A. Baksova, and L. V. Khorkhoyanu, Zh. Obshch. Khim., **35**, 732 (1965).
- [14] A. F. McKay, R. O. Braun, and G. R. Vavasour, J. Amer. Chem. Soc., **74**, 5549 (1952).
- [15] A. F. McKay, R. A. B. Bannard, R. O. Braun, and R. L. Benness, Ibid., **76**, 3546 (1954).

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