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Cyclopolymerization of Diallyldiphenylphosphonium Salts. Polymeric Phosphonium Salts, Phosphine Oxides, and Phosphorus Ylides

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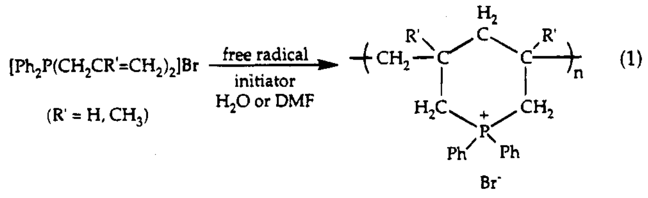
ABSTRACT: The free-radical cyclopolymerization of $[Ph_2P(CH_2CH{=}CH_2)_2]^+Br^-$, initiated by 4,4′-azobis(4-cyanovaleric acid) (azo-CNV) and by ^{60}Co γ-radiation, and of $[Ph_2P(CH_2CH{=}CH_2)_2]^+PF_6^-$, initiated by azo-CNV, has been investigated. ^{31}P NMR studies indicated that the major structural components of the polymers are five- and six-membered cyclic phosphonium units but that some linear components can be present as well. Basic aqueous hydrolysis converted these phosphonium salt cyclopolymers to the respective polymeric phosphine oxides. GPC molecular weight studies of the latter were carried out. The phosphonium salt cyclopolymers were converted to polymeric cyclic phosphorus ylides by deprotonation with $NaCH_2S(O)CH_3$ in DMSO. Reactions of the polymeric ylides with benzaldehyde and allyl bromide were carried out. The GPC molecular weight determinations of the product of the reaction of the polymeric ylide with benzaldehyde provided indirect evidence for the presence or absence of linear units in the polymeric phosphonium salt.

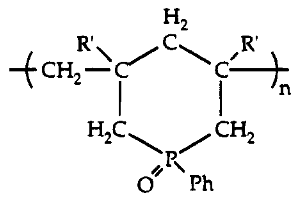
Introduction

Some years after his pioneering work on the cyclopolymerization of diallyldimethylammonium halides,[1] Butler reported the formation of polyphosphonium salts via cyclopolymerization of a number of diallylphosphonium halides (eq 1).[2] In these early studies only IR spectra, elemental analyses, and viscosity data were used in the characterization of the polymeric products. These were soluble in ethanol and dimethylformamide (DMF). According to their IR spectra, they contained little or no C=C unsaturation. All polymers were isolated as hydrates (one H_2O per P^+ unit). Base hydrolysis of the polymers gave the polymeric phosphine oxide, **2**. The six-membered ring structure shown for the polymers **1** and **2** was based on the assumption that the regiochemistry of polymerization was driven by thermodynamic factors, i.e., that formation of the more stable secondary radicals, **3**, would be favored in the initiation and propagation steps.



1

(initiator: AIBN, t-BuOOH, Bz_2O_2)



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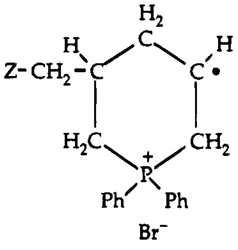
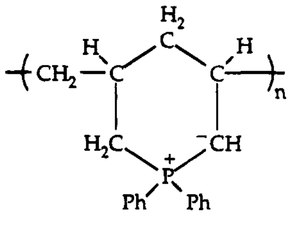


3

A polymer of type **1** should react with a base such as an organoalkali reagent or an alkali metal hydride in nonaqueous solution to generate a reactive polymeric Wittig reagent, **4**, and it was this possibility which prompted our studies which are the subject of this report.



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Results and Discussion

1. Cyclopolymerization of $[Ph_2P(CH_2CH{=}CH_2)_2]$Br. Diallyldiphenylphosphonium bromide (DAPP-Br) was polymerized by heating its aqueous or ethanolic solution under an inert atmosphere at 75–80 °C in the presence of 4,4′-azobis(4-cyanovaleric acid) (azo-CNV), a free-radical initiator, for 20 h. In ethanol the reaction mixture remained homogeneous throughout the polymerization. In water the initiator initially was insoluble but dissolved on heating at the concentrations used. The polymer was not soluble in water and precipitated very

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quickly, giving a heterogeneous reaction mixture. In hot water the polymer is swollen. In neither case was a rapid temperature rise due to autoacceleration observed during the polymerization, as had been observed in the cyclopolymerization of diallyldimethylammonium chloride.[3] Upon completion of the reaction the water was removed at reduced pressure with mild warming, leaving a mixture of the product polymer and a small amount of unconverted monomer. Invariably, when the monomer was recovered after a polymerization experiment, it was not pure DAPP-Br but rather a mixture of DAPP-Br and isomerized salts that contained the 1-propenyl substituent, i.e., $[Ph_2P(CH_2CH{=}CH_2)(CH{=}CHCH_3)]Br$, **5**, and $[Ph_2P(CH{=}CHCH_3)_2]Br$, **6**, as could be determined readily by ^1H NMR spectroscopy. Neither of these phosphonium salts was capable of undergoing free-radical-initiated cyclopolymerization.

Such isomerization of allyl- to 1-propenylphosphonium halides is well known. It can be catalyzed by bases[4] and has been claimed to be thermally induced.[5,6] Acetone served well in the extraction of unconverted phosphonium salts and did not extract the polymer. The polymer was isolated in the form of an off-white solid in 50–75% yield.

The polymerization of DAPP-Br should be carried out using high initial concentrations of monomer (40–60 wt %, based on solvent) and high initiator concentration (2.5–6 mol %, based on DAPP-Br). When relatively low initial monomer and initiator concentrations are used, little or no polymer is produced and partial monomer isomerization to 1-propenylphosphonium salts is the only observed reaction. The required use of a high initiator concentration is in sharp contrast to the typical procedure applicable in the polymerization of monovinyl monomers and more reactive diallyl systems, such as $[(CH_3)_2N(CH_2CH{=}CH_2)_2]Cl$. The polymerization behavior of DAPP-Br more closely parallels that of monoallyl systems, where degradative chain transfer is a controlling factor[7,8] and leads to polymers with only low to moderate degrees of polymerization. This observation is in agreement with the fact that DAPP-Br is easily isomerized to **5** and **6**, very likely by radical sources, as in the present study, as well as by bases. The lability of the α-allylic hydrogen atoms of DAPP-Br suggests that this monomer itself is a moderately effective degradative chain transfer agent.

The DAPP-Br-derived cyclopolymer is extremely hygroscopic. Determination of its water content by Karl Fischer titration showed it to be a hydrate, containing 0.5 H_2O per P^+ unit. This composition was shown for many different samples of polymer prepared in water. Even long heating (~1 week) in excess of 100 °C at 0.1 Torr failed to dry the bulk polymer beyond the half-hydrate stage. X-ray diffraction showed the polymer to be amorphous.

The DAPP-Br-derived cyclopolymer is quite stable thermally. Differential scanning calorimetry (DSC) under nitrogen and thermogravimetric analysis (TGA) under argon confirmed abrupt decomposition at ca. 315 °C which is accompanied by the distinctive odor of phosphines. A glass transition temperature could not be detected by DSC. The polymer exhibits nonlinear, downward-sloping reduced viscosity vs concentration behavior in 1:1 v/v H_2O/EtOH,[9] which is characteristic for polyelectrolytes (Figure 1).

The possible radical attack on DAPP-Br and the further reaction of the new radical thus formed are shown in Scheme 1. Five-, six-, and seven-membered rings may be formed, and, if inter- rather than intramolecular attack occurs, a dangling $CH_2P^+Ph_2(CH_2CH{=}CH_2)$ group and branching may result. Attack of another radical at the C=C bond of such a dangling group will introduce phosphorus into the main chain of the polymer. This will have important consequences in reactions of the polymer.[10]

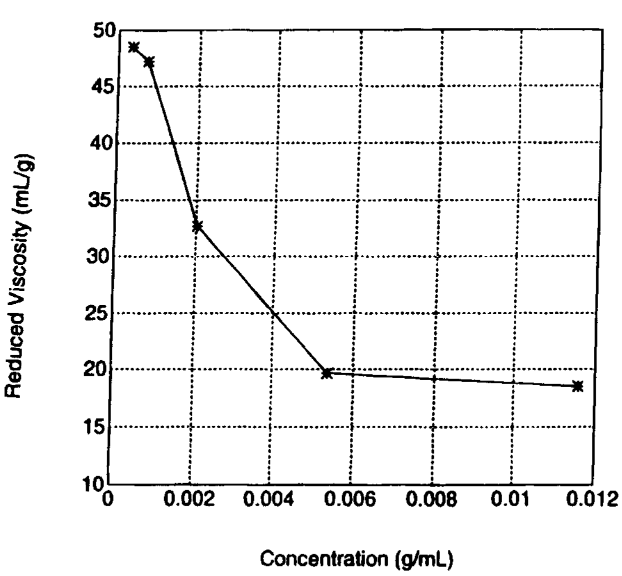


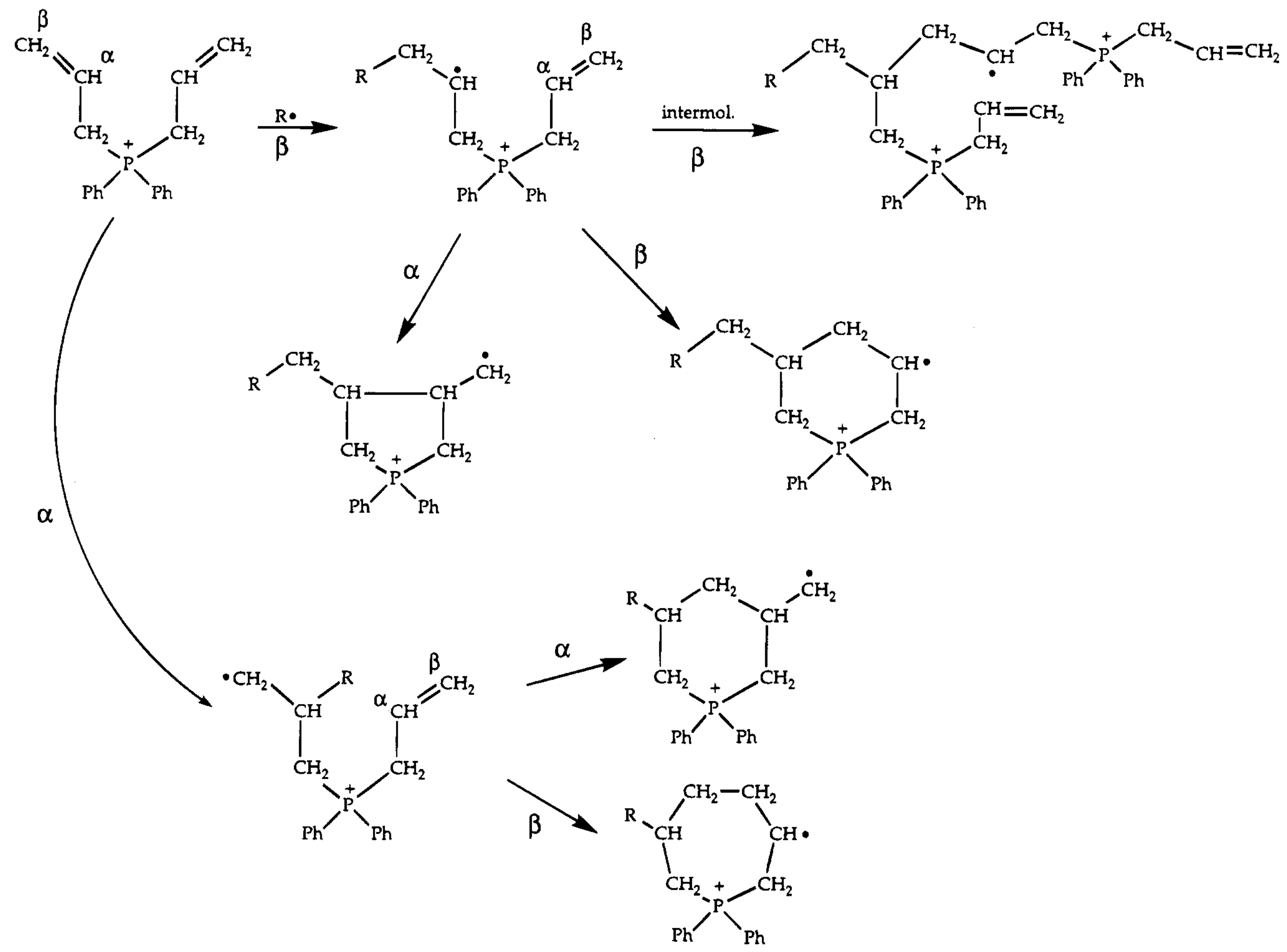
Figure 1. Reduced viscosity vs concentration behavior of the DAPP-Br-derived cyclopolymer (in 1:1 v/v H_2O/EtOH at 25 °C).

As noted above, the determination of the constitution of the DAPP-Br-derived cyclopolymer prepared by Butler and his co-workers was not secure. Without doubt, it was a cyclopolymer, but it was not certain whether it contained five- and/or six-membered cyclic organophosphonium units and whether it contained any linear units. An answer to this question should be possible by application of ^{31}P NMR spectroscopy since it is well documented that for cyclic organophosphorus compounds (phosphines, phosphine oxides, phosphonate esters, phosphonium salts, etc.) the ^{31}P NMR chemical shift is a function of ring size, with the ^{31}P NMR signals of five-, six-, and seven-membered phosphorus-containing rings being quite separated from one another.[11] In fact, ^{31}P NMR spectroscopy has been applied successfully in the determination of the constitution of cyclopolymers derived from divinyl phosphonates.[12]

The $^{31}P\{^1H\}$ NMR spectrum of the DAPP-Br-derived cyclopolymer is shown in Figure 2. There are essentially two different phosphorus environments, one giving a signal centered at about 43 ppm, the other a signal centered at about 19 ppm. In order to assign these resonances to appropriate organophosphorus building blocks of the polymer, the $^{31}P\{^1H\}$ NMR chemical shifts of appropriate model compounds (**7**–**12**) were recorded. Their ^{31}P NMR signals are given in Chart 1. The cyclic units of the DAPP-Br-derived cyclopolymer have alkyl substitution on the 3,5 positions (six-membered ring) and 3,4 positions (five-membered ring), and this will have an effect on the ^{31}P NMR chemical shifts of these units. Such effects should be rather minor if the ^{14}N NMR chemical shifts of related cyclic ammonium halides, **13**–**15**, are considered (Chart 2).[13] The chemical shift changes on going from the unsubstituted piperidinium halide, **13**, to the 3,5-dimethyl-substituted piperidinium salts, **14** and **15**, are minor.

Comparison of the ^{31}P NMR chemical shifts in Chart 1 with those of the DAPP-Br-derived cyclopolymer leads us to the conclusion that the polymer contains both five-

Scheme 1



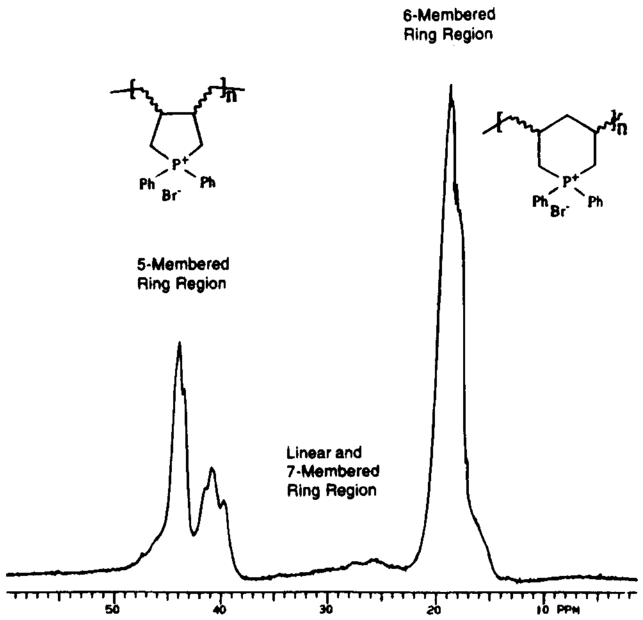
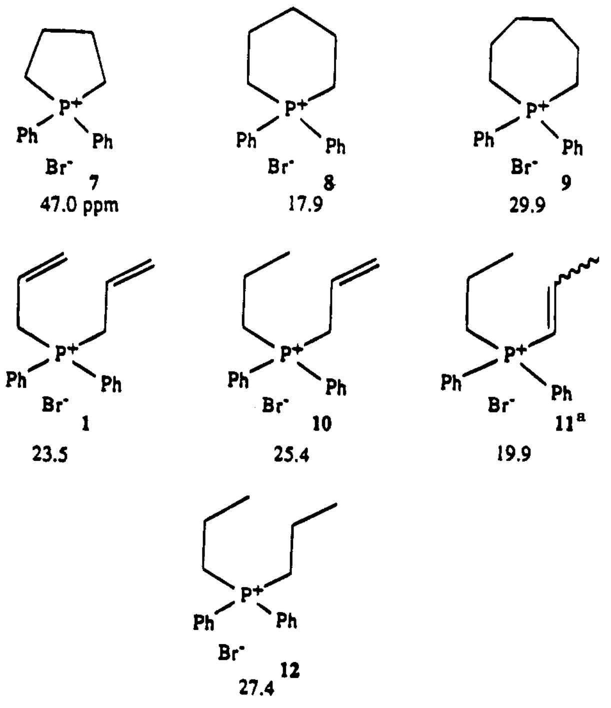


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of the DAPP-Br-derived cyclopolymer (azo-CVN) in DMSO-d_6.

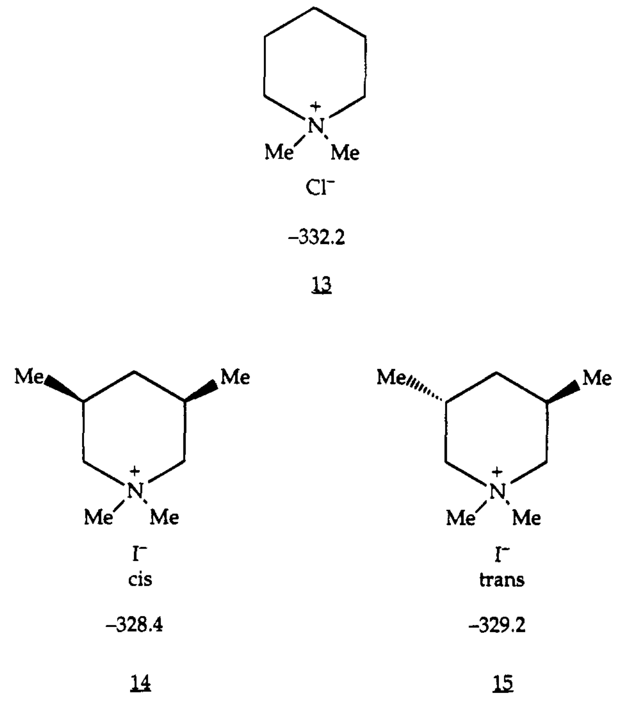
membered and six-membered rings (signals centered at ca. 43 and 19 ppm, respectively). Peak multiplicity of the five-membered ring region shows that the stereochemistry of this unit consists of approximately equal amounts of 3,4-*cis* and 3,4-*trans* connectivity to other rings. Stereochemical details for the six-membered ring units of the polymer remain unresolved. Signals can be integrated using the procedure of Kasler and Tierney[14] using $Cr(acac)_3$ and sufficient delay between pulses. Such experiments showed the polymer to con-

Chart 1. ^{31}P NMR Chemical Shifts of Phosphonium Bromide Model Compounds in DMSO-d_6[a]



[a] *cis*/*trans* could not be resolved.

Chart 2. ^{14}N Chemical Shifts of Cyclic Quaternary Ammonium Halides in D_2O



tain six- and five-membered rings in 2:1 ratio. This ratio remained unchanged as experimental conditions for the polymerization of DAPP-Br were varied. The $^{31}P\{^1H\}$ NMR spectrum of the cyclopolymer in Figure 2 also shows broad, diffuse resonances in the 23–35 ppm range. These might be due to noncyclic segments and/or seven-membered ring units. These resonances amount to only about 2% of the total ^{31}P NMR signal intensity for the polymer whose spectrum is shown in Figure 2.

^{60}Co γ-radiation also was used to initiate the polymerization of DAPP-Br in water or absolute ethanol.[15] In ethanol the solution remained homogeneous throughout the irradiation. In water, however, the polymer precipitated as it was formed. A dose of ca. 10 Mrad was required for 100% conversion of monomer to polymer. In contrast to the polymerizations initiated by azo-CNV at 75–80 °C, in these polymerizations no allyl-to-1-propenyl isomerization was observed, very likely because they were carried out at room temperature. Yields of purified polymer were 80–90%. The $^{31}P\{^1H\}$ NMR spectrum of the polymer is shown in Figure 3. It is very similar to the $^{31}P\{^1H\}$ NMR spectrum of the polymer obtained with azo-CNV initiation except that the resonances in the acyclic and seven-membered ring phosphonium salt region are of greater intensity. This most likely is due to the difference in reaction temperature. It has been noted that higher reaction temperatures favor cyclopolymerization,[16,17] probably due to entropic effects, while lower reaction temperatures to a greater degree favor linear propagation.

2. Cyclopolymerization of $[Ph_2P(CH_2CH{=}CH_2)_2]PF_6$. The fact that the cyclopolymers of DAPP-Br could only be isolated in the form of hydrates made them unattractive as starting materials for Wittig ylide chemistry. For that reason, the cyclopolymerization of $[Ph_2P(CH_2CH{=}CH_2)_2]PF_6$ (DAPP-PF_6) was investigated. The monomer was prepared by adding aqueous KPF_6 to a solution of DAPP-Br in water. Unlike the bromide, the phosphonium hexafluorophosphate is not hygroscopic. At room temperature it is soluble in DMSO, methylene chloride, THF, acetone, and 1:1 v/v H_2O/THF and insoluble in water. Like the bromide, it was found to isomerize to the 1-propenylphosphonium salt when its solutions were heated in base-washed glassware.

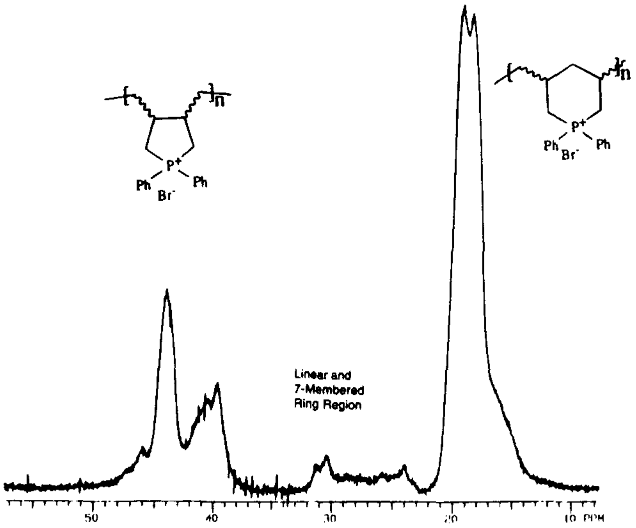


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the DAPP-Br-derived cyclopolymer (γ-ray) in DMSO-d_6.

DAPP-PF_6 was polymerized by heating a ca. 59 wt % solution in DMSO at 75–80 °C in the presence of azo-CNV (4–8 wt % based on monomer) for 20 h. The polymer thus produced was precipitated by addition of THF, redissolved in acetone, and reprecipitated with diethyl ether. Unlike the phosphonium bromide cyclopolymer, the DAPP-PF_6-derived cyclopolymer was not isolated as a hydrate. Polymer yields ranged between 55 and 65%.

The $^{31}P\{^1H\}$ NMR spectrum of the DAPP-PF_6-derived polymer is shown in Figure 4. In addition to the PF_6^- resonance at −143 ppm, there are two other groups of signals centered at 42 and 18 ppm, which may be compared with signal groups at 43 and 19 ppm in the $^{31}P\{^1H\}$ NMR spectrum of DAPP-Br, discussed above. To confirm the assignments as resonances due to six- and five-membered ring units, respectively, the model phosphonium hexafluorophosphates **16**–**19** shown in Chart 3 were prepared. It is clear that the major components of the polymer are the six- and five-membered ring units. Peak multiplicity of each of the regions confirms that the dialkyl substitution on both the five- and six-membered ring units involves a mixture of *cis* and *trans* isomers. Integration as in the case of the ^{31}P NMR spectrum of the DAPP-Br-derived polymer showed that these units were present in 2:1 ratio, respectively. Here also there was a broad, diffuse region of resonances in the range 22–30 ppm which may be attributed to acyclic and/or seven-membered ring units.

3. Conversion of the $[Ph_2P(CH_2CH{=}CH_2)_2]^+$ Salt-Derived Cyclopolymers to the Poly(phosphine oxides). Since the phosphonium salt cyclopolymers prepared in this study are polyelectrolytes, direct molecular weight measurements are difficult to effect because of their nonideal solution behavior[9] and other problems inherent in determining the molecular weights of polyelectrolytes.[18–20] In order to obtain information, albeit indirect, concerning the molecular weights of the phosphonium salt cyclopolymers prepared in this study, it was necessary to convert them to nonelectrolytes

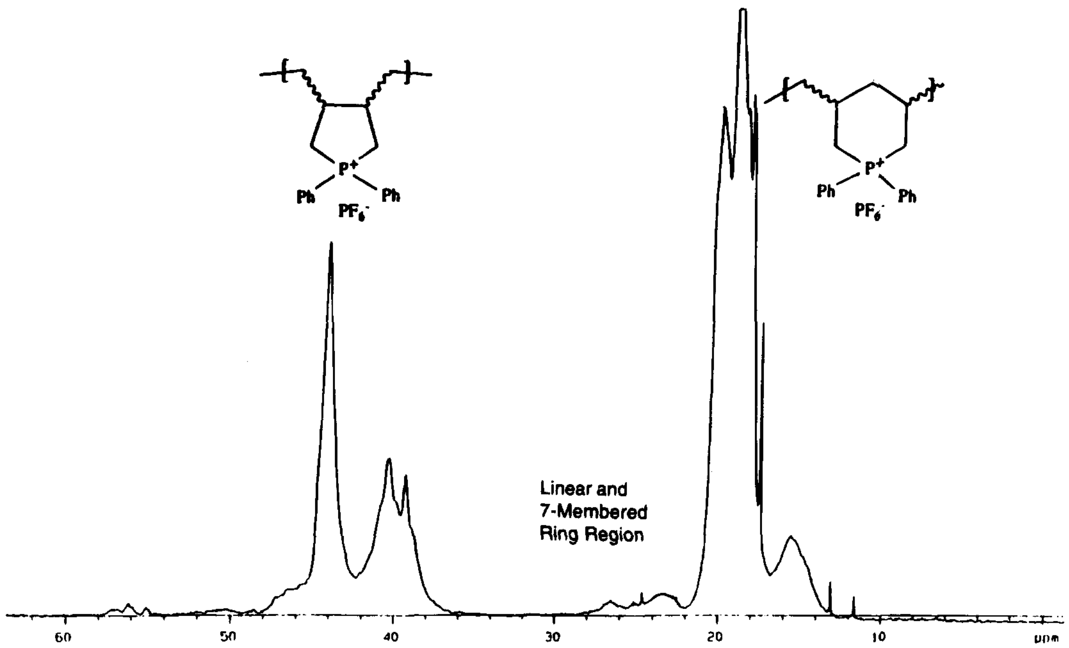
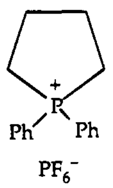


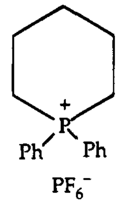
Figure 4. $^{31}P\{^1H\}$ NMR spectrum of the DAPP-Br-derived cyclopolymer in DMSO-d_6 (expansion).

Chart 3. ^{31}P NMR Chemical Shifts of Phosphonium Hexafluorophosphate Model Compounds in DMSO-d_6



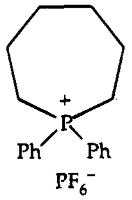
46.9

16



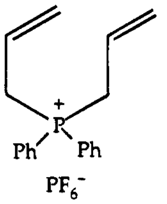
17.7

17



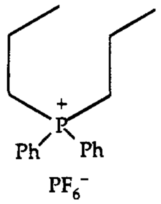
29.9

18



23.3

DAPP-PF_6



27.2

19

using chemistry that would not decrease or increase the chain length.

Among the known reactions of phenylphosphonium salts is their basic hydrolysis which yields phosphine oxides (eq 2).[21] Since this reaction involves exclusive loss

$$[Ph_3PR]Br + H_2O \xrightarrow{OH^-} Ph_2RP{=}O + C_6H_6 \quad (2)$$

of a phenyl group and since it proceeds quantitatively, it is applicable to the purpose discussed above. A relative one-to-one relationship should exist between the molecular weights of the phosphonium salt and the phosphine oxide cyclopolymers.

The phosphonium salt polymers were converted to the respective phosphine oxide polymers by reaction with KOH in 85:15 (v/v) methanol/water at 60 °C for 96 h. After removal of most of the methanol at reduced pressure, water was added to precipitate the phosphine oxide polymer. These polymers are very hygroscopic solids and were isolated as hydrates (0.5 H_2O per P=O) which could not be further dehydrated. In contrast to the phosphonium salt cyclopolymers, they were found to exhibit the linear, upward-sloping reduced viscosity vs concentration behavior characteristic of a nonelectrolyte.[9]

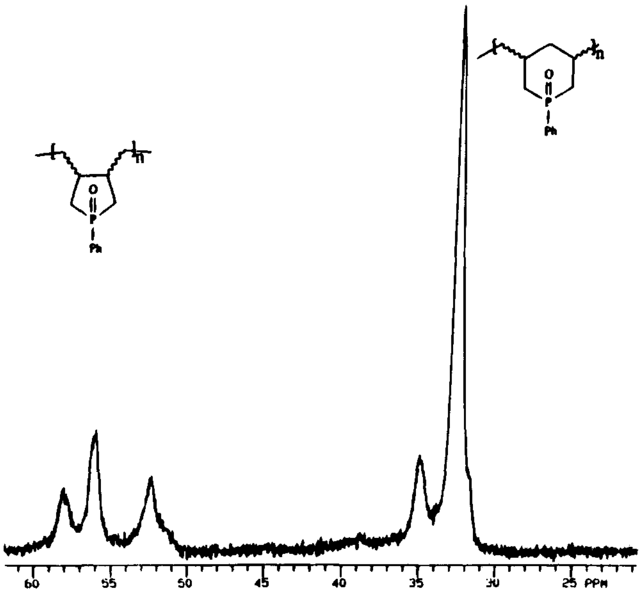


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of the phosphine oxide cyclopolymer in DMSO-d_6.

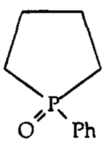
The $^{31}P\{^1H\}$ NMR spectrum of the phosphine oxide cyclopolymer obtained by basic hydrolysis of the phosphonium bromide cyclopolymer prepared by initiation of DAPP-Br polymerization with azo-CNV is shown in Figure 5. It is characterized by two sets of resonances, one centered at ca. 55 ppm, due to the five-membered ring phosphine oxide units, the other centered at ca. 35 ppm, due to the six-membered ring phosphine oxide units. Peak multiplicity, as in the case of the phosphonium salt polymers, confirmed stereoirregularity. The five-membered ring region of the ^{31}P NMR spectrum shows three resonances probably due to the presence of the 3,4-*cis,cis* oxide, 3,4-*cis,trans* oxide, and 3,4-*trans*

Table 1. Molecular Weights of the DAPP-Br- and DAPP-PF_6-Derived (Relative to Polystyrene) Phosphine Oxide and Wittig Reaction Product Cyclopolymers (in 10:1 (v/v) $CHCl_3$/DMSO)

			mol wt ($\times 10^3$)	
preparative conditions for the phosphonium cyclopolymer	anion	% yield	phosphine oxide cyclopolymer	Wittig reaction product polymer
200 mg of azo-CNV 5.00 g of monomer 5.00 mL of H_2O 20 h, 80 °C	Br^-	66	$M_n = 8.4, 8.2^a$ $M_w = 41.5, 38.1$ $D = 4.9, 4.7$	$M_n = 4.7^b$ $M_w = 10.6$ $D = 2.3$
200 mg of azo-CNV 5.00 g of monomer 15.0 mL of H_2O 20 h, 80 °C	Br^-	53	$M_n = 6.6$ $M_w = 20.2$ $D = 3.1$	
200 mg of azo-CNV 5.00 g of monomer 15.0 mL of H_2O 48 h, 80 °C	Br^-	52	$M_n = 5.8$ $M_w = 16.7$ $D = 2.9$	
200 mg of azo-CNV 5.00 g of monomer 5.00 mL of EtOH 20 h, 80 °C	Br^-	59	$M_n = 3.4, 3.6^a$ $M_w = 7.6, 7.4$ $D = 2.3, 2.1$	$M_n = 3.8$ $M_w = 6.5$ $D = 1.7$
200 mg of azo-CNV 5.00 g of monomer 15.0 mL of EtOH 20 h, 80 °C	Br^-	43	$M_n = 1.9$ $M_w = 4.1$ $D = 2.2$	
200 mg of azo-CNV 5.00 g of monomer 5.0 mL of DMSO 20 h, 80 °C	PF_6^-	55–65	$M_n = 10.5$ $M_w = 20.0$ $D = 1.9$	

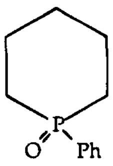
[a] Duplicate determinations on the same sample. [b] Drop in molecular weight believed due to polymer chain cleavage.

repeat units. The six-membered ring region shows only two resonances; evidently it is not possible to resolve the signals due to all the possible diastereomers.[22] Integration of the signal intensities of the two regions in the ^{31}P NMR spectrum of the phosphine oxide polymer indicated a 2:1 ratio of six- to five-membered rings in the phosphine oxide polymer, so, as expected, there was no change in composition of the cyclic components on going from the phosphonium salt polymer to the phosphine oxide polymer. Assignment of the two regions in the ^{31}P NMR spectrum of the phosphine oxide polymer to the six- and five-membered ring units is based on comparison with the ^{31}P NMR chemical shifts of model compounds **20** and **21** (in DMSO-d_6).



δ_P 58.7

20



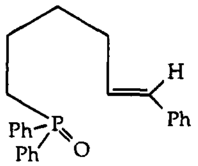
δ_P 32.2

21

Molecular weights of the phosphine oxide polymers were determined by gel permeation chromatography (GPC) using a 10:1 (v/v) $CHCl_3$/DMSO solvent mixture. The molecular weights were not high. All M_n values were below 12 000 (Table 1). This is consistent with the fact that DAPP-Br is a relatively facile degradative chain transfer agent, as has been noted earlier in this discussion.

Assuming a 1:1 relationship between the molecular weight of the phosphine oxide polymer and the phosphonium salt polymer from which it was derived, the observed M_n and M_w values allow several conclusions. The phosphonium salt polymers prepared in aqueous solution have higher molecular weights than those prepared in ethanol but M_n values comparable to those prepared in DMSO. Obviously, the chain termination processes are affected by the solvent used. For a given set of conditions, polymerization in aqueous solution gives a broader distribution of molecular weights. This may be due to the fact that the DAPP-Br-derived polymer, when prepared in water, precipitates from solution during polymerization and the process, therefore, is a "precipitation polymerization", while the polymer prepared in ethanol and DMSO remains in solution. Precipitation polymerization[23,24] is known to sometimes alter chain termination processes and degree of branching and the corresponding parameters of molecular weight, polydispersity, and polymer morphology, when compared with a strictly homogeneous polymerization. Conversion in aqueous solution is significantly greater than in ethanol for a given condition. The data in Table 1 show that dilution has a large effect on the molecular weight of the DAPP-Br-derived cyclopolymer, its polydispersity, and the conversion of the polymerization process: all tend to be higher at higher concentration.

4. Wittig Reactions of the $[Ph_2P(CH_2CH{=}CH_2)_2]^+$ Salt-Derived Cyclopolymers. As noted in the Introduction, we were interested in the polymeric phosphorus ylides prepared by deprotonation of the $DAPP^+$ salt-derived cyclopolymers and, in particular, in their Wittig-type reactivity. The poly(phosphorus ylide) could be prepared by reaction of the phosphonium bromide cyclopolymer with $NaCH_2S(O)CH_3$ in DMSO.[25] Upon addition of the polymer solution to the base the reaction mixture turned red-orange and the polymeric phosphorus ylide precipitated. Upon addition of benzaldehyde the mixture became homogeneous. After a 72 h reaction time at 80 °C, the product polymer was precipitated by addition of water. Further workup gave an off-white, hygroscopic solid in 80% yield. The expected reaction is shown in Scheme 2.[26] The $Ph_2P(O)$ functions introduced into the product polymer will be essentially the same whether they are derived from the Wittig reaction of the five- or six-membered cyclic phosphonium unit, so their ^{31}P NMR chemical shifts should be nearly identical. As expected, the $^{31}P\{^1H\}$ NMR spectrum of the product polymer showed only one major resonance at about 30.5 ppm (Figure 6). The ^{31}P NMR spectrum of a model compound, **22**, prepared by Wittig reaction of **8** with benzaldehyde, showed a single peak at 31.3 ppm in DMSO-d_6.

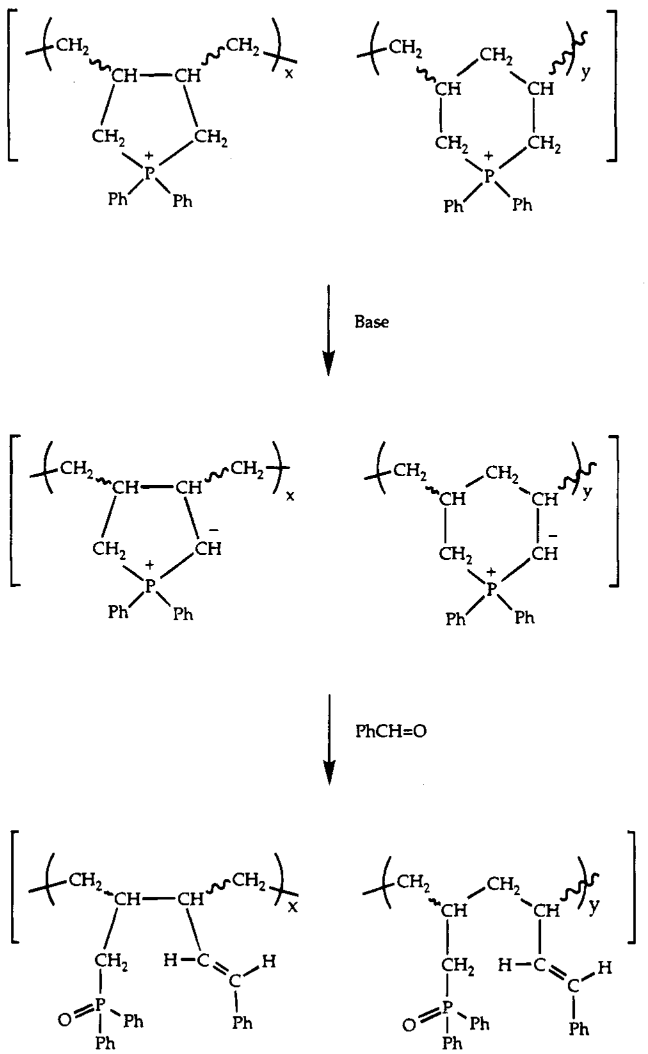


δ_P 31.3

22

Inspection of Figure 6 shows minor peaks at ca. 32, 35, 52, and 56 ppm. These are in the range of the resonances observed in the ^{31}P NMR spectrum of the polymeric phosphine oxide prepared by base hydrolysis of the DAPP-Br-derived cyclopolymer. Since the DAPP-Br-derived cyclopolymer contained 0.5 mol of H_2O per P^+, such hydrolysis may be an expected side reaction. (In fact, an extra ca. 0.5 molar equiv of $NaCH_2S(O)CH_3$

Scheme 2



was used in the reaction to deal with this water). The Wittig reactions of the phosphorus ylides derived from the model cyclic phosphonium salt and the polymeric phosphonium salt with benzaldehyde were stereospecific, giving the *trans* olefin in both cases. The same procedure was used to generate the phosphorus ylide from the DAPP-PF_6-derived cyclopolymer and in its Wittig reaction with benzaldehyde. The physical properties of the product polymer were identical to those of the DAPP-Br-derived Wittig product. Its ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were identical except that the resonances due to the cyclic phosphine oxide units introduced by hydrolysis were much less intense (as expected, since the DAPP-PF_6-derived cyclopolymer is not a hydrate). The molecular weights of the polymeric Wittig reaction products prepared from the DAPP-Br-derived cyclopolymers were measured by GPC (Table 1). Of interest is a comparison of these values with the molecular weights of the poly(phosphine oxides) prepared by basic hydrolysis of the same DAPP-Br-derived cyclopolymers. For the phosphonium salt polymer prepared in aqueous solution, M_n of the polymeric Wittig reaction product is smaller by roughly a factor of 2, M_w by a factor of about 4, and the polydispersity by a factor of 2. A similar effect was not observed in the case of the polymeric Wittig reaction product prepared using the DAPP-Br-derived cyclopolymer that had been prepared in ethanol solution. The observed decrease in molecular weight in the former case is indirect evidence of chain scission during the Wittig reaction, and this must occur because some linear phosphonium salt units are in the main chain of the polymer. This in turn is evidence of branching as shown in Scheme 3. Wittig reaction of such a phosphonium salt unit would result in chain cleavage; hence the observed decrease in molecular weight. From the observed molecular weights of the Wittig reaction products it would appear that there is much less branching during the cyclopolymerization in ethanol than in water solution.

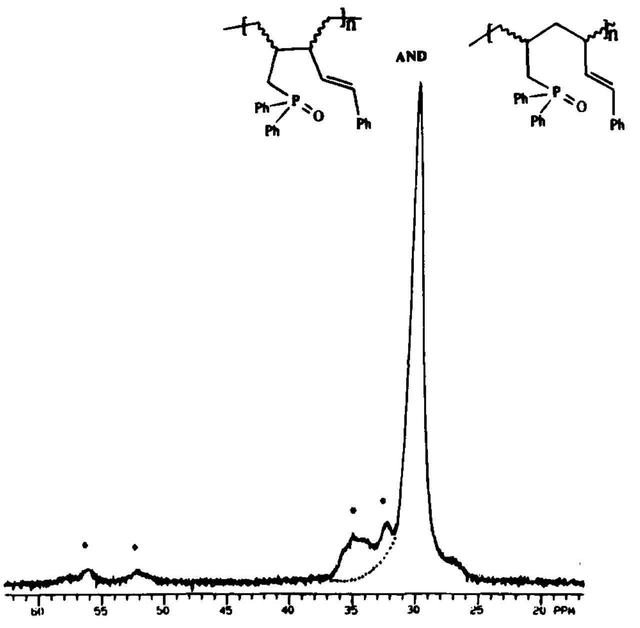
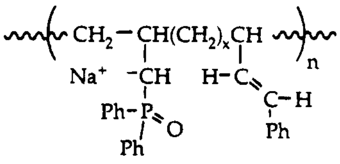


Figure 6. $^{31}P\{^1H\}$ NMR spectrum of the Wittig reaction-derived polymer in DMSO-d_6 (asterisks indicate resonances due to hydrolytically formed cyclic phosphine oxide units).

The polymeric Wittig reaction product in Scheme 2 contains olefinic side chains and $CH_2P(O)Ph_2$ substituents whose C–H bonds are relatively acidic. Treatment of this polymer with $NaCH_2S(O)CH_3$ in DMSO gave a blood-red solution of the carbanionic polymer **23**, shown schematically below. This metalated polymer



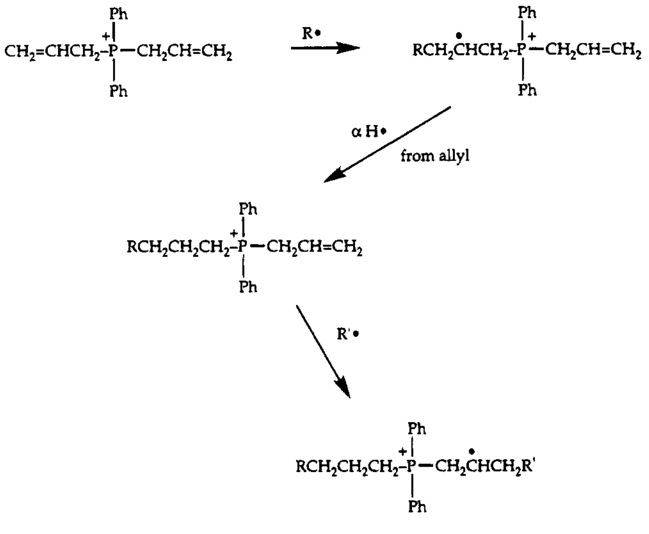
$$\left(CH_2-\underset{\underset{Ph-P(=O)Ph}{Na^+\ {}^-CH}}{CH}(CH_2)_x\underset{\underset{\underset{Ph}{C-H}}{H-C}}{CH}\right)_n$$

23

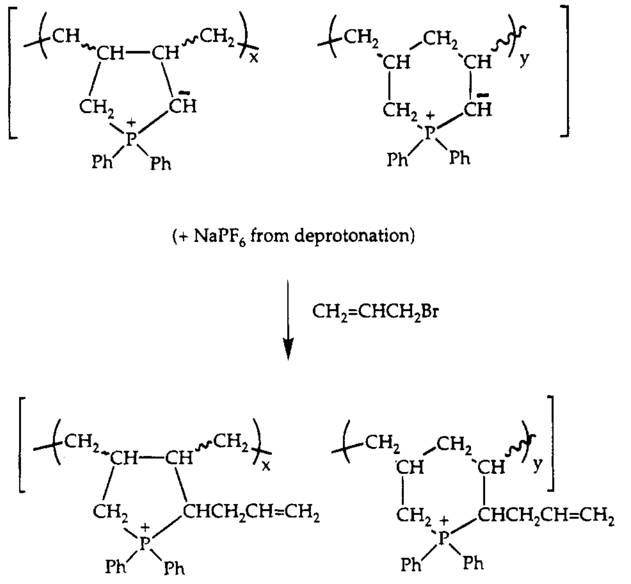
should show an extensive derivative chemistry, leading to polymers with diverse functional phosphine oxide side chains. For the purposes of this study, a reaction of the metalated polymer with *p*-anisaldehyde was carried out. The product polymer, a slightly yellow solid, contained the expected *p*-$CH_3OC_6H_4$ groups (CH_3O protons in the ^1H NMR spectrum). Its $^{31}P\{^1H\}$ NMR spectrum, however, showed two resonances which did not differ greatly in chemical shift. One of these is due to protonated **23**, so it would appear that the derivativization of the $CH_2P(O)Ph_2$ groups was approximately 50% complete.

One reaction also was carried out in which the cyclic units of the polymeric phosphorus ylide were retained (Scheme 4). The polymeric allylation product was isolated as a yellow-orange solid in 70% yield. Analysis showed it to contain about 1 wt % of Br^- in addition to PF_6^-. Proton NMR spectroscopy confirmed that significant allylation had taken place, as evidenced by

Scheme 3


(R•, R'• = polymer chain end radicals)

Scheme 4



allylic proton resonances. The ^{31}P NMR spectrum of this allylated product is more complicated than that of the DAPP-PF$_6$ cyclopolymer since the allylated phosphonium cyclopolymer is a complicated mixture of diastereomeric cyclic phosphonium units.

It is clear from the results of this investigation that a rich functional organophosphorus polymer chemistry is made possible by the cyclopolymerization of diallyldiphenylphosphonium salts. The polymeric phosphorus ylide presents many opportunities more than those described here. Its Wittig reactions introduce olefinic side chains which can undergo diverse reactions at the C=C bonds. The pendant Ph$_2$P(O)CH$_2$ groups, as indicated, can through their metalation be used to introduce a variety of new functions. In similar fashion, the cyclopolymeric phosphine oxides obtained by basic hydrolysis of the DAPP$^+$ salt-derived cyclopolymer also can be metalated and further functionalized.

Experimental Section

General Comments. All NMR spectra were recorded using a Bruker WM 250, Varian XL 300, or Varian XR 500 NMR spectrometer at room temperature. ^{1}H NMR chemical shifts are reported relative to the solvent (residual, DMSO-d_6 at 2.49 ppm) or internal tetramethylsilane (0.00 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent (DMSO-d_6 at 39.5 and CDCl$_3$ at 77.0 ppm, respectively), and ^{31}P NMR chemical shifts are reported relative to 85% H$_3$PO$_4$ (external, 0.00 ppm). ^{1}H NMR spectra were recorded at 50 mg of compound/g of solvent and ^{31}P and ^{13}C spectra at 100–250 mg of compound/g of solvent. All coupling constants are reported as magnitude only. Typical line broadening used for the ^{31}P{^{1}H} NMR spectra of the polymers was 10 Hz, and typical line broadening used for ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of the model compounds was 1–2 Hz.

Mass spectra were recorded using a Finnigan MAT System 8200 mass spectrometer with a direct insertion probe in either EI or FAB (Xe, in 3-nitrobenzyl alcohol (3NBA), or glycerol) modes. All spectra were recorded under low resolution in the positive-ion mode by ramping the probe temperature from 25 to ca. 250 °C.

DSC scans were performed on a Perkin-Elmer PC Series DSC7 (under N$_2$), and TGA scans on a Perkin-Elmer TGS-2 (under argon). Elemental analyses were performed by either Scandinavian Microanalytical Laboratories or Galbraith Laboratories. Karl Fischer titrations were performed by Galbraith Laboratories.

Where necessary, syntheses were performed under an argon atmosphere. Polymerizations were performed in standard Schlenk-ware under an argon atmosphere. Water used was OmniSolv and was thoroughly degassed prior to use. Ethanol was used absolute (AAPER) and was also thoroughly degassed prior to use. 4,4'-Azobis(4-cyanovaleric acid) was purchased from Aldrich. This product was supplied as a 75 wt % (remainder water) solid solution. The reported catalyst weights include the weight of water (e.g., 200 mg is 200 mg of a 75 wt % catalyst solution = 150 mg = 0.535 mmol of actual initiator). NaH (97%) was purchased from Aldrich. Diphenylchlorophosphine (technical grade) was purchased from Strem and used as delivered. Both dimethyl sulfoxide and benzaldehyde were slurried over CaH$_2$ for 24 h, thoroughly degassed, and freshly vacuum distilled prior to use.

Molecular weight measurements were carried out on a Waters 150C GPC instrument, using a Waters Ultrastyragel Linear column (1 000–2 000 000 MW). Measurements were carried out at room temperature, at a 1.0 mL/min flow rate, and using a 10:1 (v/v) mixture of chloroform/dimethyl sulfoxide as eluting solvent to prevent adsorption of these polar polymers on the GPC column. All molecular weights are relative to polystyrene. Monodisperse samples of the latter (polydispersity ≤ 1.05) were purchased from Polysciences, Inc.

Melting points were determined on a Büchi melting point apparatus. All determinations were performed in sealed capillaries and are uncorrected.

Preparation of Diallyldiphenylphosphonium Bromide (DAPP-Br). A 250 mL three-necked, round-bottomed flask, equipped with a mechanical stirrer and appropriate septa was purged thoroughly with argon and charged with 100 mL of freshly distilled, degassed benzene and 22.0 g (0.097 mol) of freshly distilled allyldiphenylphosphine[28] via cannula. To the resulting solution was added, all at once via syringe, 12.6 mL (17.6 g, 0.146 mol) of freshly distilled, thoroughly degassed allyl bromide. The mixture was stirred vigorously under argon at room temperature. The reaction mixture should not be heated due to the ease of isomerization of the allyl groups of product. Onset of cloudiness was observed within 5 min, but the reaction was not noticeably exothermic. Stirring was continued for 48 h under argon. A large amount of white, microcrystalline precipitate formed. The reaction mixture was filtered through a glass frit. The solid was washed with two 100 mL portions of dry benzene and then with two 100 mL portions of dry petroleum ether (30–60 °C). The solid was transferred to a dry 250 mL Schlenk flask while still saturated with petroleum ether and dried under vacuum at room temperature for 24 h, yielding 31.0 g (0.089 mol, 92%) of a white, microcrystalline, hygroscopic solid, mp 175–177 °C (lit.[2] mp 173–176 °C). No evidence of isomerization was ever observed under these conditions.

Anal. Calcd for C$_{18}$H$_{20}$PBr: C, 62.26; H, 5.81. Found: C, 62.27; H, 5.72.

FAB MS (glycerol): 267.2 (100.00%, $[M - Br^-]^+$); 268.2 (22.21%); no other prominent ions.

^{1}H NMR (DMSO-d_6): δ 4.09 (dd, 4H, J_{HP} = 15.4, J_{HH} = 7.2 Hz, PCH_2, exchangeable); 5.25–5.45 (m, 4H, $CH_2{=}$); 5.55–5.80 (m, 2H, $CH_2{=}CH$); 7.50–8.20 (m, 10H, arom).

$^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 24.8 (d, J_{CP} = 48.4 Hz, PCH_2); 117.9 (d, J_{CP} = 82.3 Hz, arom); 124.4 (broad, apparent d, apparent J_{CP} = 8.9, $PCH_2CH{=}CH_2$, superimposed; see $[Ph_2P(CH_2CH{=}CH_2)_2]^+PF_6^-$, section below, where these resonances are separable, but close in chemical shift); 129.7 (d, J_{CP} = 11.2 Hz, arom); 133.2 (d, J_{CP} = 9.0 Hz, arom); 134.5 (d, J_{CP} = 4.1 Hz, arom).

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 23.5.

Observations Concerning the Allyl to 1-Propenyl Isomerization of DAPP-Br and Its α-C-H/D Exchange. (a). Isomerization of DAPP-Br to 5 and 6. DAPP-Br is indefinitely stable at room temperature in water, ethanol, methanol, and dimethyl sulfoxide. However, as was shown by some control experiments, simply heating it in any of these solvents in base-washed glassware slowly isomerizes it to a mixture of **5** and **6**. The mass spectrum of the typical isomerized material clearly shows the material to be of the same molecular starting weight as DAPP-Br. ^{31}P NMR spectroscopy showed that this isomerized material was a complex mixture, by multiple resonances from 7 to 25 ppm. Similar observations are made with DAPP-PF_6, which excludes the possibility that the counterion is involved in these isomerizations. No isomerization was observed when DAPP-Br was heated in any of the solvents above in fresh, newly purchased glassware that had not been base-washed. However, even when fresh glassware was used in a polymerization, isomerization still was observed, so it is possible that radical sources under polymerizing conditions can cause isomerization. Finally, the rate and extent of isomerization for a given condition have been observed to be variable, presumably depending upon the amount of base that is in the glassware.

^{1}H NMR (DMSO-d_6) of a partially isomerized sample: δ 2.0–2.2 (compl m, $PCH{=}CH(CH_3)$, **5** and **6**); 4.0–4.5 (usually, two dds, DAPP-Br and **5**); 5.2–5.4 (m, $PCH_2CH{=}CH_2$, DAPP-Br and **5**); 5.6–5.8 (m, $P\text{-}CH_2CH{=}CH_2$); 6.6–7.1 (compl m, $PCH{=}CH(CH_3)$, **5** and **6**); 7.6–8.0 (compl m, arom).

FAB MS (3NBA) of a partially isomerized sample of DAPP-Br: 267.2 [$(M - Br^-)^+$, 100.00%); 268.2 (20.69%); 285.2 (DAPP-Br + H_2O, 8.93%); 286.3 (1.96%); no other prominent ions.

(b) Exchange of the α-Hydrogens of DAPP-Br, Producing $[Ph_2P(CD_2CH{=}CH_2)_2]Br$. The α-hydrogens of DAPP-Br exchange when the monomer is heated at 80 °C in D_2O. Such deuteration occurs regardless of whether base-washed or fresh glassware is used. No incorporation of deuterium occurs in the γ-position after 24 h, as shown by ^{1}H NMR spectroscopy.

^{1}H NMR (DMSO-d_6) of ca. 50% deuterated sample: δ 4.0–4.2 (compl m, $PCH(D)CH{=}CH_2$, ca. 2H); 5.2–5.4 (m, $PCH(D)\text{-}CH{=}CH_2$, 4H); 5.5–5.8 (m, $PCH(D)CH{=}CH_2$, 2H); 7.6–8.0 (m, arom, 10H).

FAB MS (3NBA) of ca. a 50% deuterated sample: 267.2 (26.35%); 268.2 (75.55%); 269.2 (100.00%); 270.3 (66.03%); 271.3 (22.91%); 272.3 (4.42%); no other prominent ions.

Diallyldiphenylphosphonium Hexfluorophosphate (DAPP-PF_6). To a 2 L Erlenmeyer flask containing a magnetic stir bar and 600 mL of distilled water was added 30.0 g (0.0864 mol) of diallyldiphenylphosphonium bromide. A saturated solution of KPF_6 was prepared by adding 60.0 g (0.326 mol) of KPF_6 to 600 mL of distilled water. To the phosphonium bromide solution was added the aqueous KPF_6 solution (save some 5–6 g of undissolved KPF_6), all at once with stirring. Immediately, a white precipitate formed which was filtered and washed with distilled water and then with ether. The solid was transferred while still wet with ether to a 250 mL Schlenk flask and was dried under vacuum at room temperature for 48 h, yielding 34.3 g (96%) of a white, microcrystalline solid, mp 135–137 °C. The infrared spectrum of this compound showed the absence of water, and the salt did not appear to be hygroscopic.

Anal. Calcd for $C_{18}H_{20}P_2F_6$: C, 52.44; H, 4.89; P, 15.03. Found: C, 52.47; H, 4.97; P, 14.81.

FAB MS (3NBA): 267.1 (75.96%, $[M - PF_6^-]^+$); 268.1 (16.01%); no other prominent ions.

^{1}H NMR (DMSO-d_6): δ 4.06 (dd, 4H, J_{HP} = 16.2 Hz, J_{HH} = 7.0 Hz, PCH_2); 5.24–5.44 (m, 4H, $CH_2{=}$); 5.58–5.80 (m, 2H, $CH_2{=}CH$); 7.75–8.00 (m, 10H, arom).

$^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 24.7 (d, J_{CP} = 48.3 Hz, PCH_2); 117.9 (d, J_{CP} = 82.1 Hz, arom); 124.1 (d, J_{CP} = 11.5 Hz, C=C); 124.6 (d, J_{CP} = 12.5 Hz, C=C); 129.8 (d, J_{CP} = 11.1 Hz, arom); 133.1 (d, J_{CP} = 9.2 Hz, arom); 134.7 (d, J_{CP} = 4.0 Hz, arom). See Br^- salt, above.

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 23.3 (P^+); −143.0 (septet, PF_6^-, J_{PF} = 712 Hz).

Poly(diallyldiphenylphosphonium bromide). 4,4′-Azobis(4-cyanovaleric acid)-Initiated Polymerization. (a) Typical Preparation in Water. A 250 mL Schlenk flask equipped with a magnetic stir bar was charged with 15.0 g (0.043 mol) of $[Ph_2P(CH_2CH{=}CH_2)_2]^+Br^-$ and 600.0 mg of 4,4′-azobis(4-cyanovaleric acid) (azo-CNV) (Aldrich, 75 wt % = 1.61 mmol of actual initiator). A septum was placed on the flask and the contents were degassed via three 10 min pump-down cycles, backfilling with argon each time. To this flask was added, all at once at room temperature, 15.0 mL of thoroughly degassed water via syringe. The flask then was placed on a preheated oil bath at 75–80 °C, and the mixture was stirred under argon. Within 1 min, the solution became homogeneous and within 10–15 min, polymerization was apparent, as the solution became opaque with precipitating polymer. Heating was continued under argon for 20 h and then the oil bath was removed and the reaction mixture was allowed to cool to room temperature. The resulting heterogeneous mixture appeared slightly blue (on other runs, the color ranged from yellow to pinkish blue/blue). The solvent was removed under reduced pressure with mild warming (never above 80 °C). The crude product then was ground in a mortar and pestle. ^{1}H NMR spectroscopy showed it to consist of the polymer, some isomerized monomer **5** (**6**), and a small amount of unreacted monomer. The crude mixture was extracted with acetone in a Soxhlet extractor for 72 h. The ^{1}H NMR spectrum of the extract showed that no polymer was present, only isomerized monomer. The solvent was removed from the polymer at room temperature under reduced pressure for 24 h, and the product was ground with a mortar and pestle (11.3 g yield at this point). The polymer was placed into a 100 mL Schlenk flask and dried under vacuum under IR heat (60–70 °C) for 24 h, yielding 10.4 g (69%) of a white, extremely hygroscopic solid. Note that this polymer also holds tenaciously onto acetone and, occasionally, ^{1}H NMR spectroscopy showed that a small amount of acetone remained with the polymer after purification. This can be removed by grinding with a mortar and pestle and further drying. The IR spectrum showed a strong, broad band at ca. 3400 cm^{-1}, due to water.

Anal. Calcd for $\{C_{18}H_{20}PBr\}_n$: C, 62.26; H, 5.81; P, 8.92. Anal. Calcd for $\{C_{18}H_{20}PBr(^1/_2H_2O)\}_n$: C, 60.69; H, 5.94; P, 8.69; H_2O (wt %), 2.53%. Found (sample 1): C, 60.72; H, 5.98; P, 8.73; H_2O, 2.67% (Karl Fischer). Found (sample 2 (different batch)): C, 60.95; H, 6.18.

^{1}H NMR (DMSO-d_6): δ 0.0–4.5 (broad aliphatic resonances, consisting of 3 broad humps); 7.0–9.0 (broad aromatic resonances); no olefinic resonances detected (5.2–7.1 ppm).

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 14.0–23.0 (broad single resonance due to six-membered ring repeat units); 23.0–35.0 (very weak, broad, diffuse resonances due to linear and/or seven-membered ring repeat units); 38.0–49.0 (two broad resonances due to five-membered ring repeat units; multiplicity due to *cis–trans* stereochemistry in ring).

(b) Typical Preparation in Absolute Ethanol. A 250 mL Schlenk flask equipped with a magnetic stir bar was charged with 15.0 g (0.043 mol) of $[Ph_2P(CH_2CH{=}CH_2)_2]^+Br^-$ and 600 mg of azo-CNV (Aldrich, 75 wt % = 0.00161 mol of actual initiator). A septum was placed on the flask and the contents were degassed via three 10 min pump-down cycles, backfilling with argon each time. To this flask was added, all at once at room temperature, 15.0 mL of degassed absolute ethanol via syringe. The flask then was placed in a preheated oil bath at 75–80 °C, and the mixture was stirred under argon. Heating was continued under argon for 20 h (the solution remained homogeneous throughout the polymerization). Upon cooling to room temperature, the homogeneous solution appeared slightly blue (on other runs, the color ranged from yellow to pinkish blue/blue). Workup as described in (1) above gave 9.0 g (60%) of a white, extremely hygroscopic solid. Spectroscopically, the polymer is identical to that prepared in water above. ^{1}H NMR spectroscopy showed that there were no olefinic resonances (5.2–7.1 ppm).

Anal. Calcd for $\{C_{18}H_{20}PBr(^1/_2H_2O)\}_n$: C, 60.69; H, 5.94. Found: C, 59.45; H, 6.05.

(2) γ-ray-Induced Polymerization. Solution irradiations were carried out in Pyrex, single-use, thick-walled sealing ampules (ca. 20 bar maximum pressure tolerance, 40 mL maximum volume), purchased from Chemglass, using a ^{60}Co γ-radiation source that delivered a dose rate of 1.2 Mrad/24 h.

(a) Typical Preparation in Water. A thick-walled, Pyrex sealing ampule was charged with 4.0 g of $[Ph_2P(CH_2CH{=}CH_2)_2]^+Br^-$. By means of a T-tube, the solid was degassed by three 10 min pump-down cycles, backfilling with argon each time. To this was added 40.0 mL of thoroughly degassed water via syringe (these concentrations are near the solubility limit of DAPP-Br in cold water). The ampule was frozen in liquid N_2, sealed under vacuum, and then allowed to thaw. After thawing, the mixture was shaken to dissolve the salt and then placed in the ^{60}Co chamber. A 10.0 Mrad dose was applied (approximately 200 h at 1.2 Mrad/24 h). During this time, the polymer precipitated from solution, and the tube itself had browned, as is usual when glassware is exposed to large radiation doses. The ampule then was frozen in liquid N_2 and opened. After thawing, the polymer was washed from the ampule with a minimum amount of methanol. The solvent was removed by trap-to-trap distillation with mild warming (never above 80 °C). The slightly yellow solid which remained was extracted with acetone for 72 h in a Soxhlet extractor. Further workup as in (1) gave 3.1 g (78%) of a slightly yellow, hygroscopic solid. The IR spectrum of this polymer showed that it contained water.

Anal. Calcd for $\{C_{18}H_{20}PBr\}_n$: C, 62.26; H, 5.81. Anal. Calcd for $\{C_{18}H_{20}PBr(^1/_2H_2O)\}_n$: C, 60.69; H, 5.98. Found (sample 1): C, 61.14; H, 6.18. (sample 2): C, 60.98; H, 5.93.

^{1}H NMR (DMSO-d_6): δ 0.0–4.5 (broad alipatic resonances); 7.0–7.9 (broad aromatic resonances); no olefinic resonances in the range 5.2–7.1 ppm). ^{1}H NMR spectroscopy also showed that the acetone washings contained a small amount of polymer (ca. 5–10% of total weight). Presumably, this was lower molecular weight material, and the fact that the ^{1}H NMR resonances were not as broad as those in the ^{1}H NMR spectrum of the bulk, purified polymer seems to be consistent with this explanation.

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 14.0–23.0 (two broad resonances due to the six-membered ring repeat units; multiplicity due to *cis–trans* stereochemistry in ring); 23.0–35.0 (resonances due to linear and/or seven-membered ring repeat units); 38.0–49.0 (two broad resonances due to five-membered ring repeat units; multiplicity due to *cis–trans* stereochemistry in ring).

(b) Typical Preparation in Absolute Ethanol. The procedure here was identical in every way (including concentrations) to the preparation in water above. The differences are that the polymer produced in ethanol did not precipitate from solution, and a dose of 10.0 Mrad took the polymerization only to ca. 80% conversion. As was observed above, 1H NMR spectroscopy showed that there was some polymer in the acetone washings, presumably, lower molecular weight polymer. The IR spectrum of this polymer also showed the presence of water, and the ^{1}H NMR and $^{31}P\{^1H\}$ NMR spectra were identical to those reported above.

Poly(diallyldiphenylphosphonium Hexafluorophosphate). A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 10.0 g (0.024 mol) of diallyldiphenylphosphonium hexafluorophosphate and 800 mg of azo-CNV (75 wt %), remainder water; 600 mg of actual initiator). The flask was closed off with a septum and the contents of the flask were degassed via three 10 min pump-down cycles, backfilling with argon each time. To the hexafluorophosphate/initiator was added 10.0 mL of freshly distilled, thoroughly degassed DMSO via syringe. The mixture was heated at 75–80 °C and within 2 min, the solution was completely homogeneous. The solution yellowed over time and heating was continued for 20 h. The oil bath was removed and the flask was opened to the atmosphere. The polymer was precipitated by addition of 250 mL of THF with stirring. The solvent was decanted from the polymer and the polymer was washed with 250 mL of THF. Again, the THF was decanted and then the polymer was washed with an additional 100 mL of THF. This procedure caused the product to change from an oil to a solid material. The solid polymer was dissolved in 20 mL of acetone and precipitated by the addition of ca. 250 mL of diethyl ether. The resulting solid was broken up and washed thoroughly with ether. The polymer was filtered, washed thoroughly again with ether, and then dried under vacuum for 72 h at 60–70 °C to give 6.4 g (64%) of a slightly yellow powder. Identically effected experiments using 500 mg (375 mg actual) of initiator and 400 mg of initiator (300 mg actual) gave polymer in 55 and 59% yield, respectively. The IR spectrum of the polymer showed the absence of water. The ^{1}H NMR spectrum was identical to that reported for the analogous cyclophosphonium bromide polymer and showed the absence of unsaturation. Note that sometimes the polymer contains a small amount of monomer and isomerized monomer, but these can be removed by redissolving in acetone and reprecipitating by addition of ether.

Anal. Calcd for $\{C_{18}H_{20}P_2F_6\}_n$: C, 52.44; H, 4.89. Found: C, 52.66; H, 4.85.

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −143.0 (PF_6^-, sharp, $J_{PF} = 712$ Hz); 14.0–22.0 (broad multiple resonances due to six-membered ring repeat units; multiplicitly due to stereochemistry in ring); 22.0–30.0 (very weak, broad, diffuse resonances due to linear and/or seven-membered ring repeat units); 37.0–48.0 (broad multiple resonances due to five-membered ring repeat units; multiplicity due to stereochemistry in ring).

Preparation of the Phosphine Oxide Cyclopolymer (Typical Procedure). The DAPP-Br-derived cyclopolymer (via azo-CNV initiation in water), 2.0 g (5.6 mmol unit), was placed in a 250 mL Schlenk flask equipped with a magnetic stir bar and dissolved in 20 mL of 85% methanol (15% water v/v, not degassed). Potassium hydroxide, 1.6 g (0.029 mol) in 15 mL of 85% methanol, was added to the polymer solution at room temperature. The resulting homogeneous solution turned bright yellow. The flask was closed off with a septum, and the solution was heated under argon in an oil bath at 60 °C with stirring for 96 h. The reaction mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure until the solution became opaque. Then, with stirring, 100 mL of distilled water was added at room temperature, causing a white solid to precipitate. The resulting polymer was filtered, washed with two 50 mL portions of distilled water, dried under vacuum at room temperature for 24 h, ground with a mortar and pestle, and placed in a 100 mL Schlenk flask. Subsequently, it was dried at 60–70 °C under vacuum for 24 h to give 0.93 g (78%) of an off-white, hygroscopic solid. The IR spectrum (KBr) showed a strong P=O at 1177 cm^{-1}.

Anal. Calcd for $\{C_{12}H_{15}PO\}_n$: C, 69.89; H, 7.33; P, 15.03. Anal. Calcd for $\{C_{18}H_{15}PO(^1/_2H_2O)\}_n$: C, 66.97; H, 7.49; P, 14.39. Found: C, 67.37; H, 7.71; P, 14.28.

^{1}H NMR (DMSO-d_6): δ 0.5–3.0 (broad aliphatic resonances); 7.0–8.3 (two broad aromatic resonances).

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 31.0–37.0 (two broad resonances due to the six-membered ring repeat units; multiplicity due to relative stereochemistry in ring); 50.0–60.0 (three broad resonances due to the five-membered ring repeat units; multiplicity due to relative stereochemistry in ring).

Essentially the same procedure was used in the basic hydrolysis of the DAPP-PF_6-derived cyclopolymer. At the beginning of the reaction, the solution was heterogeneous, since the polymer is only slightly soluble in the reaction solvent mixture. After 24 h at 60 °C, however, the solution was completely homogeneous. The reaction mixture was heated for 120 h at 60 °C. Most of the methanol was removed until the reaction mixture became opaque and then the cyclophosphine oxide polymer was precipitated from solution by addition of water. Additional workup as above resulted in a slightly yellow, hygroscopic polymer in 70% yield.

^{1}H and ^{31}P NMR spectroscopy showed that this polymer was identical to that described above.

In general, molecular weights of the phosphine oxide cyclopolymer (and thus of the phosphonium salt cyclopolymer) were moderately low. Peak maximum molecular weights of the phosphine oxide cyclopolymer were ca. 11 000 (relative to monodisperse polystyrene) and polydispersities were in the range 2.0–2.5. The initial concentration of the initiator, azo-CNV, in the range 4–8 wt % (based on monomer), appeared to have a negligible effect on the molecular weight or polydispersity of the resulting polymer. However, yields increased slightly if more initiator was used in a polymerization run, all else being equal.

Preparation of the Phosphorus Ylide Cyclopolymer and Its Reaction with Benzaldehyde. (1) Via the DAPP-Br-Derived Cyclopolymer. A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 0.101 g (4.2 mmol) of NaH. The polymer, 1.00 g (2.8 mmol unit), was placed in a 25 mL one-necked, round-bottomed flask. To the flask containing the NaH was added 10 mL of dry, freshly distilled DMSO via syringe. This mixture was heated in an oil bath at 80 °C with stirring under argon until the solution was homogeneous and slightly yellow and hydrogen gas evolution had ceased. To the flask containing the phosphonium bromide cyclopolymer was added 10 mL of dry, freshly distilled DMSO via syringe. The polymer dissolved with mild warming and the resulting solution, after it had cooled to room temperature, was added to the carbanion solution via cannula. The resulting bright orange, heterogeneous mixture was stirred under argon for 30 min at room temperature. Subsequently, 0.285 mL of dry, freshly distilled benzaldehyde (2.8 mmol) was added all at once at room temperature via syringe. The reaction mixture, which immediately turned homogeneous and golden brown, was heated at 80 °C under argon for 72 h with stirring and then allowed to cool to room temperature, resulting in a red/brown, homogeneous solution. Thirty milliters of distilled water was added to precipitate the polymer which was filtered, washed with distilled water, and dried in the air under aspirator, giving a brown solid. It then was dissolved in THF, precipitated by adding ether, and filtered in air. This process was repeated several times. The polymer was dried under vacuum at room temperature for 24 h. Finally, it was dissolved in anhydrous THF, precipitated with anhydrous ether, and then transferred via cannula to a frit, washed thoroughly with anhydrous ether, and dried at 60–70 °C for 24 h under vacuum. After this final purification step, the polymer no longer was soluble in THF but freely soluble in many other solvents. (The fact that the polymer is soluble in THF when impure is probably the result of the presence of DMSO (and/or water) in the impure polymer (a cosolvent effect). The off-white polymer (0.8 g, 80%) was hygroscopic. Its IR spectrum showed it to be free from water and showed a strong P=O band at 1192 cm^{-1}.

Anal. Calcd for $\{C_{25}H_{25}PO\}_n$: C, 80.62; H, 6.77; P, 8.32. Found: C, 75.47; H, 6.90; P, 8.38. Difference arises from some hydrolysis to the cyclic phosphine oxide unit.

^{1}H NMR (DMSO-d_6): δ 0.0–3.0 (broad aliphatic resonances); 5.4 (broad resonance, C*H*=CH(Ph)); 6.1 (broad resonance, CH=C*H*(Ph)); 6.5–8.4 (broad aromatic resonances).

^{31}P{^{1}H} NMR (DMSO-d_6): δ 30.5 (broad single resonance); *hydrolysis* at 31.0–37.0 (broad resonances due to the six-membered ring repeat units); 50.0–60.0 (broad resonances due to the five-membered ring repeat units).

(2) Via the DAPP-PF$_6$-Derived Cyclopolymer. Essentially the same procedure was used in the reaction of 6.7 mmol of $NaCH_2S(O)CH_3$ (from 160 mg, 6.7 mmol of NaH) and 2.50 g (6.1 mmol unit) of the DAPP-PF$_6$-derived cyclopolymer in 35 mL of DMSO. The resulting orange-red, heterogeneous mixture was treated with 0.78 g (7.3 mmol) of benzaldehyde at room temperature, which gave a golden-brown, homogeneous solution which was heated under argon for 22 h. Subsequently, it was added at room temperature to 100 mL of distilled water to precipitate the polymer. The polymer was filtered, washed with water, and then washed from the frit with a minimum amount of THF. To the polymer solution was added ether, causing the polymer to precipitate. This process was repeated once more and then the polymer was filtered and dried for 72 h at 60–70 °C under vacuum to give 1.0 g (35%) of a tan, slightly hygroscopic polymer. The pure polymer is not soluble in THF but is freely soluble in many other solvents.

Anal. Calcd for $\{C_{25}H_{25}PO\}_n$: P, 8.32. Found: P, 9.01.

^{1}H NMR (DMSO-d_6): δ 0.0–3.0 (broad aliphatic resonances); 5.4 (broad resonance, C*H*=CH(Ph)); 6.1 (broad resonance, CH=C*H*(Ph)); 6.5–8.4 (broad aromatic resonances).

^{31}P{^{1}H} NMR (DMSO-d_6): δ 31.0 (broad single resonance); slight hydrolysis was indicated by weak resonances at 32–36 and 51–57 ppm. A small amount of PF_6^- was detectable (without associated phosphonium resonances).

Allylation of the Polymeric Phosphorus Ylide. To a solution of the poly(phosphorus ylide), prepared by the identical procedure as above (identical weights of reagents), was added 1.1 mL (1.5 g, 0.012 mol) of freshly distilled, degassed allyl bromide via syringe at room temperature. The resulting solution rapidly became homogeneous and nearly colorless. After 1 h, the solution was very slightly yellow. Stirring was continued for 48 h at room temperature under an argon atmosphere. At the end of this time, the solution was homogeneous and yellow/orange. The polymer was precipitated by the addition of 400 mL of distilled water, filtered, and washed with water and then with ether. Finally, the polymer was dried for 24 h at room temperature under vacuum to give 1.9 g (ca. 70%, based on 100% Pf_6^- counterion) of a slightly yellow/orange solid that did not appear to be hygroscopic.

Anal. Calcd for $\{C_{21}H_{24}P_2F_6\}_n$ (assuming 100% PF_6^- counterion): C, 55.76; H, 5.35; Br, 0.00. Found: C, 54.53; H, 5.56; Br, 1.22 (titration); Br$^-$, 1.14 (ion chromatography) [measured against starting polymer blank with Br$^-$ = 0.00].

^{1}H NMR (DMSO-d_6): δ 0.0–4.0 (broad aliphatic resonances); 4.2–6.0 (broad allylic resonances); 7.0–8.6 (broad aromatic resonances).

^{31}P{^{1}H} NMR (DMSO-d_6): δ −143.0 (PF_6^-, J_{PF} = 712 Hz); 12–50 (broad multiple resonances; such resonances are not easily interpreted due to the complicated mixture of diastereomers); 50–60 (possible resonances due to slight hydrolysis of the five-membered repeat unit).

Metalation of the Polymeric Wittig Reaction Product. A 100 mL Schlenk flask was charged with 0.053 g (2.2 mmol) of NaH and a 10 mL round-bottomed flask with 0.75 g (2.0 mmol unit) of the polymeric Wittig reaction product (above). To the NaH was added 10 mL of freshly distilled, degassed DMSO via syringe at room temperature. This heterogeneous mixture was heated at 80 °C under argon for 30 min, resulting in a slightly yellow, homogeneous solution of the carbanion. The polymer was dissolved in 2 mL of freshly distilled, degassed DMSO via syringe, and the resulting solution was added to the carbanion solution at room temperature over ca. 1 min via syringe. At the end of addition the solution was blood red/brown and homogeneous. The mixture was stirred for an additional 15 min at room temperature, and then 290 μL (0.33 g, 2.4 mmol) of freshly distilled *p*-anisaldehyde was added at room temperature. The color immediately turned a bluish green and the solution remained homogeneous. It was heated under argon at 80 °C for 24 h. The addition of 50 mL of distilled water at room temperature caused the precipitation of a solid which was filtered and washed from the frit by the addition of a small amount of THF. Addition of light petroleum ether (30–60 °C) precipitated solid polymeric product which was filtered and washed with ether and then with light petroleum ether. Finally, it was dried at room temperature for 72 h, resulting in 0.52 g of a slightly yellow solid polymer. ^{1}H and ^{31}P NMR spectroscopy showed that it contained the β-OH phosphine oxide polymer unit and the starting phosphine oxide polymer unit and that little or no elimination of Ph_2PO_2Na had occurred to yield the polyunsaturated polymer.

Anal. Calcd for $\{C_{33}H_{33}PO_3\}_n$: P, 6.09. Found: P, 7.92.

^{1}H NMR (DMSO-d_6): δ 0.0–3.3 (broad aliphatic resonances); 3.5–3.9 (broad multiple resonances, *p*-CH_3OC_6H_4); 4.6–5.1 (very broad, diffuse resonances; vinyl protons; C*H* and O*H* protons); 6.0–9.0 (broad aromatic resonances and vinyl resonances [overlapping]; no aldehydic protons.

$^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 30.0 (broad single resonance); 34.0 (broad single resonance); slight *hydrolysis* δ 50–60 (broad, multiple resonances).

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References and Notes

(1) (a) Butler, G. B.; Bunch, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 3120. (b) Butler, G. B.; Ingley, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 895. (c) Butler, G. B.; Goette, R. L. *J. Am. Chem. Soc.* **1952**, *74*, 1939. (d) Butler, G. B., Bunch, R. L.; Ingley, F. L. *J. Am. Chem. Soc.* **1952**, *74*, 2543. (e) Butler, G. B.; Goette, R. L. *J. Am. Chem. Soc.* **1954**, *76*, 2418. (f) Butler, G. B.; Angelo, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 4797. (g) Butler, G. B.; Angelo, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 3128. (h) Butler, G. B.; Cranshaw, A.; Miller, L. W. *J. Am. Chem. Soc.* **1958**, *80*, 3615. (i) For a review of the cyclopolymerization process, see: Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370 and *Cyclopolymerization and Cyclocopolymerization*; Dekker: New York, 1992.

(2) Butler, G. B.; Skinner, D. L.; Bond, W. C., Jr.; Roger, C. L. *J. Macromol. Sci.—Chem. A* **1970**, *4*, 1437.

(3) (a) Boothe, J. E.; Flock, H. G.; Hoover, F. M. *J. Macromol. Sci.—Chem. A* **1970**, *4*, 1419. (b) Topchiev, D. A.; Malkanduev, Y. A.; Yanovsky, Y. G.; Oppengeim, V. D.; Kabanov, V. A. *Eur. Polym. J.* **1989**, *25*, 1095.

(4) Keough, P. T.; Grayson, M. *J. Org. Chem.* **1964**, *29*, 631.

(5) Büchi, G.; Wuest, H. *Helv. Chim. Acta* **1971**, *54*, 1767.

(6) Our experiments with $[Ph_2P(CH_2CH{=}CH_2)_2]Br$ showed it to be stable indefinitely in solution in water, ethanol, methanol, and dimethyl sulfoxide at room temperature in any kind of glassware. However, isomerization occurred when solutions of this salt in any of these solvents were heated in base-washed glassware (but not in "virgin" or acid-washed glassware). Thus the "thermally-induced isomerization" most likely was a base-catalyzed reaction.

(7) Volodina, V. I.; Tarasov, A. I.; Spasski, S. S. *Russ. Chem. Rev. (Engl. Transl.)* **1970**, *39*, 140.

(8) Laible, R. C. *Chem. Rev.* **1958**, *58*, 807.

(9) Budd, P. M. In *Comprehesive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon: New York, 1989; Vol. 1, pp 215–230.

(10) A reviewer has pointed out that the polymerization kinetics determine the course of a cyclopolymerization reaction: "Several factors would be important in predicting the size of the rings and relative rates of cyclization vs intermolecular propagation steps. First, an Arrhenius plot of ln (k_c/k_p) vs $1/T$ would yield information about the relative activation energies and the preexponentials. For classical cyclopolymerizations the formation of 5- vs 6-membered rings and the faster rate for the cyclization step is due to an increased *A* factor, probably sterically controlled for the approach of the double bond to the radical. The lower activation energy for the intermolecular step would be expected due to the increased potential energy of the primary radical in the ground state even if the transition states of both (cyclization and propagation) were similar. The phosphorus-containing heterocycle would be expected to offer different pre-exponential values as compared to nitrogen or carbon analogs, particularly with regard to ring size". See: McCormick, C. L.; Butler, G. B. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1972**, *C8*, 201.

(11) Gorenstein, D. G. In *Phosphorus-31 NMR: Principles and Applications*; Gorenstein, D. G., Ed.; Academic: New York, 1984; Chapter 1, pp 7–36.

(12) Corfield, G. C.; Monks, H. H. *J. Macromol. Sci.—Chem.* **1975**, *A9*, 1113.

(13) Masterman, T. C.; Dando, N. R.; Weaver, D. G.; Seyferth, D. *J. Polym. Sci., B: Polym. Phys.* **1994**, *32*, 2263.

(14) Kasler, F.; Tierney, M. *Mikrochim. Acta* **1981**, *2*, 301.

(15) For the application of high-energy radiation (γ-rays, electron beam) to initiate polymerization of C═C unsaturated compounds, see: Stannett, V. T.; Silverman, J.; Garnett, J. L. In *Comprehesive Polymer Science*; Eastmond, G. C., Ed.; Pergamon: Oxford, 1989; Vol. 4, pp 317–336. Unsaturated phosphonium salt have been polymerized in this manner: Rabinowitz, R.; Marcus, R. *J. Polym. Sci.; Part A* **1965**, *3*, 2063.

(16) Gray, T. F., Jr.; Butler, J. B. *J. Macromol. Sci.—Chem.* **1975**, *A9*, 45.

(17) Seyferth, D.; Robison, J. *Macromolecules* **1993**, *26*, 407.

(18) Dubin, P. L.; Principi, J. M. *Macromolecules* **1989**, *22*, 1891.

(19) Scheuing, D. R. *J. Appl. Polym. Sci.* **1984**, *29*, 2819.

(20) Omorodion, S. N. E.; Hemielec, A. E.; Brash, J. L. *J. Liq. Chromatogr.* **1981**, *4*, 1903.

(21) Sasse, K. *Methoden der organischen Chemie (Houben-Weyl)*; Müller, Ed., Ed.; *Organische Phosphor-Verbindungen*, Part I; Georg Thieme: Stuttgart, 1963; pp 144–146.

(22) This stereochemical basis for peak multiplicitly seems to conform with the literature. See, for example: Gallagher, M. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 9, pp 297–330.

(23) Chapiro, A. In *Polymer Science Overview*; Stahl, G. A., Ed.; ACS Symposium Series 175; American Chemical Society: Washington, DC, 1981; pp 233–252.

(24) Guyot, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ed.; Pergamon: Oxford, 1989; Vol. 4, pp 261–273.

(25) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(26) Polymeric phosphorus ylides, in the form of insoluble, cross-linked gels, have been reported previously[27] and used as reagents for carbonyl olefinations. However, this is the first report in which a soluble organophosphorus polymer is converted to an ylide which is reacted with an aldehyde, yielding a new, soluble polymer that presumably could be further functionalized.

(27) Campa, C.; Font, J.; Sanchez-Ferrando, F.; Virgili, A. *Anal. Quim.* **1986**, *82*, 46.

(28) Prepared by reaction of chlorodiphenylphosphine with allylmagnesium bromide in diethyl ether.

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