The Preparation and Thermal Stability Properties of Certain Silicon and Phosphorus Containing Heterocyclic Polymers

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ABSTRACT

A number of monomers containing silicon and phosphorus have been synthesized which are functionally capable of undergoing polymerization by an alternating intramolecular-intermolecular mechanism to produce soluble, linear polymers. Three different types of monomers have been prepared: (a) di-unsaturated silanes capable of closing five-, six- or, seven-membered rings, (b) di-unsaturated phosphonium salts, and (c) di-unsaturated phosphine oxides. As intermediates for the phosphorus containing monomers a number of unsaturated phosphines have been prepared. Both free radical initiators and Ziegler-type initiators have been used, when appropriate, to initiate polymerization of the monomers prepared. In addition, polyphosphine oxides of high molecular weights were obtained by alkaline degradation of appropriate polyphosphonium salts. The silane polymers tested have been found to be thermally stable up to the range of 410 – 530° C. The phosphine oxide polymers tested decompose in the range of 392 – 450° C.

I. INTRODUCTION

The purpose of this research program was to investigate the possibility of producing new and useful heterocyclic polymers containing silicon and phosphorus through use of monomers functionally capable of polymerization by an alternating intramolecular-intermolecular chain propagation. It has previously been reported[1] that such monomers as diallyldimethylsilane and diallylphenylphosphine oxide are capable of undergoing such a chain propagation to produce soluble, linear polymers containing cyclic recurring units. Reports on the diallyldimethylsilane polymer[18,19] indicate that it possesses considerable thermal stability. It is the purpose of this paper to report on additional monomer and polymer syntheses and to discuss some of the properties of the polymers.

II. MONOMERS AND POLYMERS CONTAINING SILICON

(a) Monomers

Monomers in addition to those previously reported[1] which have been synthesized include the following: diallylmethylphenylsilane, dimethallylmethylphenylsilane, diallylcyclotetramethylenesilane, diallylcyclopentamethylenesilane, dimethallylcyclopentamethylenesilane, allyltrimethylsilane, allylvinyldimethylsilane, and 3-butenylallyldimethylsilane. The synthetic method employed was reaction of an appropriate Grignard reagent with an appropriate chlorosilane.

Allyldimethylvinylsilane was prepared both by the reaction of vinyl Grignard reagent with allyldimethylchlorosilane and by the reaction of allyl

Grignard reagent with vinyldimethylethoxysilane. The products of the two reactions were identical in their physical properties and infrared spectra, providing a definite structure proof for this compound in addition to the analysis and molar refraction. The infrared spectrum of this compound exhibits two distinct peaks for the two carbon–carbon double bonds at 1635 and 1595 $cm.^{-1}$. The peak at 1595 $cm.^{-1}$ appears in the spectra of other vinylsilanes and can be attributed to the vinyl group attached to silicon. The peak at 1635 $cm.^{-1}$ appears in all of the spectra of the allylsilanes and is assigned to the allyl double bond. This shift indicated that the carbon–carbon double bond of the vinyl group is of lower energy than is that of the allyl group. This suggests a polarization of the vinyl double bond due to the presence of the silicon atom. The physical properties, analytical data, yields, and appropriate references for these monomers are summarized in Table I.

(b) Silane Polymers and Polymerization

It was decided to attempt the polymerization of the diunsaturated silanes with both Ziegler catalysts and with free radical initiators. Due to "degradative chain transfer" most free radical initiated allylic polymerizations tend to give relatively low degrees of polymerization. The Ziegler catalysts might be expected to give higher molecular weight polymers. A great deal of work has been published concerning polymerizations by use of these complex metal catalysts in the past five years. With these catalyst systems it is possible to obtain high molecular weight polymers of α-olefins which could not be polymerized with free radical initiators. There are, however, some types of α-olefins which cannot be polymerized with conventional Ziegler catalysts. It has been reported[30] that α-olefins with branching closer than the 3- or 4-position to the double bond cannot be polymerized by this method. In view of this evidence it would be unlikely that the dimethallylsilanes and possibly the vinylsilanes would polymerize with the Ziegler catalysts. If these findings hold true for these compounds it will be necessary to polymerize them by means of free radical initiators.

The Ziegler catalyst system chosen for the polymerizations was triethyl aluminum–titanium tetrachloride. This is a common catalyst system and both of these materials are readily obtainable. The free radical initiator chosen was di-t-butyl peroxide. This initiator was chosen because it is readily obtainable and is soluble in the non-polar system which will be used in the polymerizations.

Intrinsic viscosity measurements will be made on samples of the polymers obtained in order to get an approximation to the relative degree of polymerization.

The polymerization of the diallyl- and dimethallylsilanes was accomplished by two different methods. The Ziegler catalyst was effective for the polymerization of the diallylsilanes while free radical initiators were effective for the polymerization of the dimethallylsilanes.

All of the diallylsilanes gave solid, benzene soluble polymers when treated with the Ziegler catalyst. A wide variety of conditions were used in some of the polymerizations in order to obtain the best conversion of the monomer to polymer. The factors varied were: mole ratio of the co-catalyst components, reaction time, temperature, and aging time of the catalyst.

It is reported[31] that the aluminum triethyl–titanium tetrachloride mole ratio should be 2 or 3 to 1 in order to obtain the most active catalyst. It was found, in the polymerization of diallyldimethylsilane that when the catalyst was not aged, the best conversion was obtained with a mole ratio of

Table I

Physical Properties, Analytical Data and Yields of Unsaturated Silanes

Silane	Physical Properties	Analysis	Yield %	Ref.
Diallyldimethyl	B.P. 135° n_D^{20} 1.4405		76	(16) (19) (18)
Diallyldiphenyl	B.P. 137–38/1.5mm n_D^{20} 1.5742		71	(15) (19) (18)
Dimethallyldimethyl	B.P. 75–79/25mm n_D^{20} 1.4525		72	(16) (20)
Dimethallyldiphenyl	B.P. 148/0.5mm n_D^{22} 1.5650		55	(16) (8)p.14
Diallylmethylphenyl	B.P. 124/15mm n_D^{20} 1.5200		75	(16) (8)p.14
Dimethallylmethylphenyl	B.P. 138/12mm n_D^{22} 1.5180		51	(16) (8)p.14
Diallylcyclotetramethylene	B. P. 142° n_D^{20} 1.5813	Calcd. for $C_{10}H_{18}Si$: C, 72.20; H, 10.90; Si, 16.88 Found: C, 69.80; H, 11.64; Si, 17.33	79	(20)p.11 (5)p.8 (3)p.11
Diallylcyclopentamethylene	B.P. 104/24mm n_D^{20} 1.4815	$C_{11}H_{10}Si$: C, 73.28; H, 11.18; Si, 15.54 C, 72.07; H, 10.82; Si, 15.06	68	(20)p.12 (3)p.11
Dimethallylcyclopentamethylene	B.P. 95/2mm n_D^{24} 1.4900	$C_{13}H_{24}Si$: C, 74.94; H, 11.61; Si, 13.45 C, 74.01; H, 11.36; Si, 13.77	60	(20)p.14 (7)p.14
Allyltrimethyl	B.P. 85° n_D^{20} 1.4058		54	(7)p.14 (5)p.7
Allylvinyldimethyl	B.P. 111° Density: 0.7594 n_D^{20} 1.4290	$C_7H_{14}Si$: C, 66.57; H, 11.17; Si, 22.24 C, 66.61; H, 10.95	51	(20)p.15 (9)p.14 (12)p.29 (14)p.4
3-Butenylallyldimethyl	B.P. 71-2/40mm n_D^{20} 1.4436		60	(14)p.7

2.5 to 1. It was found, as expected, that the conversion was increased by raising the reaction temperature from 30 to 85°. The reaction time seemed to have only a small effect upon the yield of polymer obtained.

The effect of aging of the catalyst upon the conversion to polymer was studied for the polymerization of diallyldimethylsilane. It is reported[31] that the aging of the catalyst decreases its activity. It was found that the aging of the catalyst actually increased the conversion of this monomer to solid, linear polymer. The best conversion was obtained with a co-catalyst mole ratio of 1 to 1 and a one hour aging time for the catalyst. The conversion dropped off slowly as the catalyst was aged for a longer period.

In the polymerization of diallyldiphenylsilane it was found that the mole ratio of the co-catalyst components had a smaller effect upon the conversion, between mole ratios of 2.2 and 4.4 to 1. With this monomer the temperature and reaction time seem to have only a small effect upon the conversion.

In some polymerizations of diallyldiphenylsilane, titanium tetrachloride was replaced in the catalyst by dicyclopentadienyltitanium dichloride, to give a soluble Ziegler type catalyst. Diallyldiphenylsilane was chosen for these experiments due to the fact that good yields of solid polymer had been obtained in previous polymerizations of this monomer with the conventional Ziegler catalyst. Only small amounts of solid polymer were obtained with the soluble catalyst mixture. Natta has reported that this soluble catalyst is less active than is the conventional catalyst.

Polymerization of the remaining diallylsilanes was accomplished with the conventional Ziegler catalyst. Conditions for these polymerizations were not significantly varied and no attempts were made to obtain optimum conditions for the polymerizations.

Attempts were made to polymerize dimethallyldimethylsilane with the Ziegler catalyst but no polymer was isolated. This was not surprising in view of previously published reports of attempts to polymerize olefins with branching close to the double bond.[30]

Free radical polymerization of the dimethallylsilanes led to soluble polymers. Di-t-butyl peroxide was used as the initiator for these polymerizations. Diallyldimethylsilane and diallyldiphenylsilane were also polymerized with this initiator.

Lower melting points and lower intrinsic viscosity values for these free radical initiated polymers indicate that the polymers are of lower molecular weight than are those obtained with the Ziegler catalyst. The dimethallyl-silanes all have very low intrinsic viscosities which indicate that they have a low degree of polymerization. The low degree of polymerization is probably due to "degradative chain transfer" involving the allylic hydrogen atoms. In the dimethallylsilanes, this effect should be more important due to the greater number of allylic hydrogens. Diallylsilanes have four allylic hydrogens while the dimethallylsilanes have ten. Comparison of the results of the free radical polymerization of diallyldiphenylsilane and of dimethallyldiphenylsilane shows that although both have low intrinsic viscosity value, those for the diallyl polymers are about twice those for the dimethallyl polymers. Since these compounds are very similar it seems likely that the molecular weights for these two polymers would be in about the same ratio as are their intrinsic viscosities.

All of the diallyl- and dimethallylsilanes gave polymers which were soluble in benzene although small fractions of a few polymers were insoluble. These soluble polymers exhibited little or no residual unsaturation in the

infrared spectra. In most cases the abosrption bands for carbon–carbon double bond stretch and for terminal methylene deformation could be removed from the spectra by further purification of the polymer.

The analytical results of the polymers are in many cases rather far from the theoretical value for carbon. It is reported, that in the analysis of silicon polymers, combustion of the sample may lead to the formation of some silicon carbide which is not completely oxidized. The formation of this compound would account for the low per cent of carbon found in the analyses of these polymers. The per cent silicon would not be affected by this due to the fact that the silicon analyses are performed on a separate sample using wet oxidation methods. The silicon and hydrogen analyses of these polymers are fairly close to the theoretical values and it seems certain that the formulae assigned to the polymers are correct.

The polymerization of allyldimethylvinylsilane was attempted with several catalysts but no solid, soluble polymer was obtained. The polymerization with free radical initiators gave varying results. With di–t–butyl peroxide both an insoluble solid and a heavy oil were obtained. The infrared spectra were very similar and showed absorption for both allyl and vinyl groups. The allyl double bond absorption was decreased a great deal in the two polymers however. Benzoyl peroxide gave a low yield of heavy oil which had an infrared spectrum similar to that of the polymers above. Use of α,α'–azobisisobutyronitrile gave no polymerization.

It has been reported that vinylsilanes do not polymerize with benzoyl peroxide. The reason for this lack of polymerization can be explained by consideration of the radical which would be formed by a free radical attack on a vinylsilane. It has been mentioned earlier in this section that there is a polarization of the vinyl group attached to silicon. This polarization is due to the "electron sink" effect of silicon. This "electron sink" effect would stabilize the free radical formed above. This radical stability is apparent in the free radical chlorination of tetraalkylsilanes. The chlorination of tetraethylsilane gives the α–chloro compound exclusively. This indicates that the radical on a carbon atom adjacent to a silicon atom of a tetraalkylsilane is very stable. The stability of this radical may account for lack of polymerization through the allylic double bonds. This type of polymerization leaves a vinyl group on the chain which may, under proper conditions, react to form a crosslink leading to insoluble polymer.

Attempts to polymerize this monomer by use of Ziegler catalysts gave results similar to those obtained with free radical initiators. In this case the vinyl double bond does not take part in the polymerization due to steric factors. The allyl double bond undergoes polymerization, however, to give low molecular weight oils. It was not possible to purify the polymers obtained with this monomer to any large extent due to the fact that the polymers were non–volatile and liquid at even very low temperatures. Infrared spectra, however, indicate that the only major changes from the monomer is the decrease of allyl double bond content in the polymer.

A sample of polydiallyldiphenylsilane was fractionated and molecular weight determinations of each of the twelve fractions was done using light scattering technique. The results are shown below:

Fraction	Molecular Weight
1–6	$4–5 \times 10^4$
7	6.7×10^4
8	9.1×10^4

9	1.5×10^5
10	1.8×10^5
11	2.4×10^5
12	2.0×10^6

A molecular weight determination of Fraction 5 by the osmotic pressure method gave a value of 3.6×10^4, in fair agreement with that obtained by the light scattering method.

Differential thermal analysis of several of the polydiallyldiphenylsilane samples gave the following results:

Fraction	Decomposition
1	410–530°C
4	410–530°C
8	410–530°C

Although the sample of polydiallyldiphenylsilane did not fractionate into consistently increasing molecular weight groups in the first several fractions, a distribution is implied which appears to be consistent with the results of other workers who have used the column fractionation technique. From the values obtained it is seen that most of the sample weight, approximately 75 per cent, lies in the molecular weight range of $10^4 - 10^5$, while only about 3 per cent of the sample has a molecular weight greater than 10^6. This may be compared to molecular weight distributions determined by a similar fractionation technique at Monsanto Chemical Company on samples of polystyrene and polyethylene. The integral molecular weight curves which have been published for these polymers indicate that as much as 60 per cent – 75 per cent of the sample weight has molecular weights ranging in value over a factor of ten, with only a very small amount greater than a factor of a hundred above the lowest measured weight. The results obtained for polydiallyldiphenylsilane are in good agreement with these values, even though very little fractionation occurred among the light fractions.

In addition, the range of molecular weights serves as a confirmation of the value obtained for the average molecular weight determined on a different sample of polydiallyldiphenylsilane in the earlier part of this work. The measured average value of 6.7×10^4 is well within the limits of the range, and it is believed that this agreement indicates the methods developed for removing the micro-gel from the solutions are effective, and that the measurements are a true indication of the polymer molecular weight.

The absence of fractionation among the light fractions was probably caused by the fact that the Cellosolve used as the nonsolvent actually dissolved the light fractions, which constituted a large part of the sample weight, and was not initially present in large enough quantity to remove all of this portion. As previously stated, Cellosolve was the best non-solvent available for use at the desired temperature, and was not expected to remove material from the column. However, when heated to the operating temperature, some of the polymer dissolved and was precipitated from the Cellosolve used to keep the column wet while heating the system. The first several mixtures of Cellosolve and toluene contained only small precentages of toluene, and, with the warm Cellosolve acting as a solvent, it is possible that the toluene added did not cause a large increase in solvent power over that of the Cellosolve itself. Only a limited amount of the polymer was available, and extensive testing was not done prior to the fractionation run.

An additional complication was encountered in measuring the molecular weight of these light fractions. While performing the calculations, it was apparent that these molecular weights may have been near the lower limit which can be measured by this method. While the lower limit of molecular weights measurable by means of light scattering is usually given as around 1×10^4, it is seen that this limit depends somewhat upon the solvent–polymer pair being measured insofar as the refractive index gradient, dn/dc, is involved. In general, the measured turbidity will be greater for a given concentration in a system having a larger value for this gradient. While the value of the refractive index gradient of the system measured was not particularly low, the loss in sensitivity which was encountered caused difficulty in extrapolating the curves, so that some molecular weight separation may have occurred even though no consistent increase was obtained from the measurements.

The appearance of micro–gel upon dissolving the last, or heaviest, fraction was surprising. It had been thought that the micro–gel encountered previously was caused by the cross–linking of several polymer molecules during the polymerization process, since one characteristic of a cross–linked polymer is that it will not dissolve. However, in this case the polymer was filtered before fractionation in order to remove such insoluble material, and the eluting mixtures underwent further filtration in the column while passing over the bed of uncoated Celite and through the glass frit which held the Celite. This should have removed any micro–gel which may have been present, and it is difficult to understand how the polymer could have cross–linked after fractionation, as no catalyst was present. In addition, all of the fractions received similar treatment, and if cross–linking had occurred at this stage it should have shown up in some of the other fractions as well. Another possibility is that the polymer molecules were brought very close together in the precipitation step, and that this allowed dipole interaction between molecules strong enough to hold them together when placed again in solvent. This may have taken the form of a crystallization process, as it is known that a crystalline polymer is more difficult to dissolve than an amorphous one. The presence of dipoles in this polymer is very likely, since it contains silicon as well as carbon atoms. As the micro–gel appeared only in the fraction having the highest molecular weight, it is also possible that it is simply the result of chain entanglement occuring during precipitation. If this is the case, there should be a solvent effect, the micro–gel being less pronounced in a better solvent. It seems most likely that all of these factors contributed to the sudden appearance of micro–gel in this heaviest fraction.

The physical properties and other data for the silane polymers are reported in Table II.

III. PHOSPHONIUM MONOMERS AND POLYMERS

(a) Phosphonium Monomers

As intermediates for the phosphonium salts to be prepared, a number of unsaturated phosphines were prepared by the method of Jones and Davies.[29] The physical properties and other data for these phosphines are reported in Table III.

The phosphonium salts were prepared by reaction of the appropriate phosphine with the appropriate alkyl halide. The pronounced reactivity of the allyl and methallyl halides with phosphines was taken advantage of when possible in order to facilitate preparation of the phosphonium salts. Due to the

Table II

Physical Properties, Analytical Data and Yields of Silane Polymers

Silane Polymers	Initiator	Yield %	Analysis Calculated for:	Found:	Polymer Properties	References
Diallyldimethyl	$AlR_3/TiCl_4$	59	$(C_8H_{16}Si)_n$: C, 68.52	65.84	M.R. 115–140	(3)p.11,(17)
			H, 11.50	10.95	Decomp. 330	(8)p.16,(18)
			Si, 19.98	19.73	η = 0.13	(12)p.30,(19)
						(20)p.20
Diallyldiphenyl	$AlR_3/TiCl_4$	60	$(C_{18}H_{20}Si)_n$: C, 81.78	80.74	M.R. 142–180	(3)p.12,(18)
			H, 7.63	7.60	Decomp. 315	(8)p.16,(19)
			Si, 10.60	10.40	η = 0.08	(11)p.5
					MW = 4.5×10^4–2.0×10^6	(12)p.35
						(20)p.21
Dimethallyldimethyl	Di-t.BP[a]	38	$(C_{10}H_{20}Si)_n$: C, 71.34	71.04	Viscous liquid	(8)p.17
			H, 11.97	11.31		(3)p.13
			Si, 16.68	16.75		(20)p.21
Dimethallyldiphenyl	Di-t.BP	75	$(C_{20}H_{24}Si)_n$: C, 82.12	80.88	M.R. 110–125	(9)p.15
			H, 8.27	8.72	η = 0.030	(12)p.36
			Si, 9.60	9.43		(20)p.23
Diallylmethylphenyl	$AlR_3/TiCl_4$	56	$(C_{13}H_{18}Si)_n$: C, 77.15	71.60	M.R. 90–130	(5)p.9,(20)p.21
			H, 8.96	8.72	η = 0.12	(8)p.16,(12)p.36
			Si, 13.88	13.79		(9)p.15
Dimethallylmethylphenyl	Di-t.BP	40	$(C_{15}H_{24}Si)_n$: C, 78.18	76.31	M.R. 65.75	(8)p.18
			H, 9.62	9.38	η = 0.03	(20)p.24
			Si, 12.18	12.76		
Diallylcyclotetramethylene	Di-t.BP / $AlR_3/TiCl_4$	30–50	$(C_{10}H_{18}Si)_n$: C, 72.20	69.80	M.R. 85–87	(9)p.15,(20)p.22
			H, 10.90	11.64	M.R. 130–140	(3)p.12,(5)p.9
			Si, 16.88	17.41	Decomp. 325;n = 0.11	(8)p.16
Diallylcyclopentamethylene	$AlR_3/TiCl_4$	60	$(C_{11}H_{20}Si)_n$: C, 73.28	69.07	M.R. 95–110	(3)p.11,(8)p.16
			H, 11.18	10.58	n = 0.12	(5)p.9,(20)p.22
			Si, 15.54	15.95		(9)p.15,(12)p.36
Dimethallylcyclopentamethylene	Di-t.BP	50	$(C_{13}H_{24}Si)_n$: C, 75.64	73.68	M.R. 75–90	(8)p.18
			H, 10.74	10.84	η = 0.04	(20)p.24
			Si, 13.60	14.77		

Table II (Continued)

Allyltrimethyl–Diallyldimethyl Copolymer	$AlR_3/TiCl_4$	10		(5)p.9 (8)p.16
Allylvinyldimethyl	$\frac{AlR_3/TiCl_4}{Di\text{–}t.BP}$		$\frac{Oil}{Oil}$	$\frac{(12)p.30,(20)p.24}{(12)p.30}$

3-Butenylallyldimethyl

a. Di–t.BP = Di–tert. Butyl Peroxide

Table III

Physical Properties, Analytical Data and Yields of Intermediate Unsaturated Phosphines

Phosphine	Physical Properties	Analysis	Yield %	Ref.
Diallylphenyl	B.P. 79°/0.7mm n_D^{25} 1.5670		45	(27)p.7 (12)p.24 (29)
Dimethallylphenyl	B.P. 98°/1.5mm n_D^{25} 1.5485			(8)p.8 (10)p.3 (29)p.3
Allyldiphenyl	B.P. 114–116°/0.5mm			(9)p.7 (12)p.25
Methallyldiphenyl	B.P. 118–121°/0.45mm			(9)p.7 (12)p.25
Divinylphenyl	B.P. 48–50°/0.2mm	Calcd. for $C_{10}H_{11}P$: C, 74.07; H, 6.79; P, 19.13 Found: C, 73.96; H, 6.80; P, 18.94	66	(12)p.20 (9)p.9 (28)
Vinyldiphenyl	B.P. 104°/0.25mm $n_D^{24.5}$ 1.6260	Calcd. for $C_{14}H_{13}P$: C, 79.24; H, 6.13; P, 14.62 Found: C, 79.43; H, 6.12; P, 14.42	57	(12)p.21 (9)p.10 (13)p.6 (26)
3-Butenyldiphenyl	B.P. 142–43°/1.25mm n_D^{20} 1.5991		40	(13)p.5

hygroscopic nature of these salts, and the tendency for the intermediate phosphine to react with oxygen and to absorb water from the atmosphere, it was necessary to work under an inert atmosphere and under anhydrous conditions. Several phosphonium salts have been prepared which are functionally capable of producing other ring sizes during polymerization. The physical properties and other pertinent data on these compounds are reported in Table IV.

(b) Phosphonium Polymers

Free radical initiation was chosen as the method for polymerizing the monomers prepared. Since the phosphonium compounds are somewhat ionic in character, the use of anionic or cationic initiation is precluded. Compounds of this type are also known to poison the Ziegler catalyst system. Free radical initiation then becomes the only remaining choice. This is unfortunate because of difficulties which have been observed in attempting the polymerization of allylic materials by means of free radicals. The phenomenon known as degradative chain transfer arises due to the labile hydrogen atoms attached to the carbon alpha to the double bond. Abstraction of one of these hydrogens by a free radical leads to a new radical which is stabilized by free radical resonance. Due to this stability, the new radical is not active enough to act as a chain carrier. Although degradative chain transfer leads to a new radical, it in effect is a chain termination step.

Solution polymerization was used throughout this study. It is not known definitely if other free radical initiated systems will produce linear polymers from these compounds. Bulk polymerization has been found to yield linear polymers from 1,6-diunsaturated phosphine oxides.[24] No bulk polymerizations were attempted using phosphonium type monomers due to the high melting points of these compounds. The concentrations used for the solution polymerizations were near saturation. The solvent acted only to bring the monomer and initiator into a single phase.

The polymers prepared from the monomers discussed earlier have several things in common. All of them are soluble in ethanol and dimethylformamide. All had infrared spectra which contain very little or no absorption corresponding to unsaturation. The softening points of the polymers are higher than the melting points of the monomers. The analyses of the polymers were, in every case, consistent with the analyses calculated for the monohydrates.

The increased softening points indicate an increase in molecular weight. The analyses corresponding to hydrated products are also indicative that larger molecules were formed by the polymerization reaction. Phosphonium compounds are known to form hydrates, and water of hydration would be more difficult to remove from high molecular weight compounds. The fact that the materials formed are soluble indicates that they are linear. The cyclic mechanism accounts for the reaction of two double bonds per repeating unit in the polymer chain. The infrared data and solubility of these materials is then consistent with the formation of cyclic units, separated by methylene groups, for these materials.

Poly-(triallylphenylphosphonium bromide) was also prepared as part of this study. In the light of information gained from the polymerization of triallylammonium bromides, triallylphenylphosphonium bromide was expected to form a cross-linked material. Poly-(triallylphenylphosphonium bromide) was indeed cross-linked. The material is an amber, glass-like, insoluble solid. The similarity between the ammonium and phosphonium type polymers is strengthened by the production of this cross-linked material.

Two of the polymers prepared appeared to be highly unsaturated upon first examination. Both poly-(diallylphenylmethylphosphonium bromide) and

Table IV

Physical Properties, Analytical Data, and Yields of Unsaturated Phosphonium Salts

Phosphonium Salt	Physical Properties	Analysis		Yield %	Ref.
Diallylhydrogen-phenyl Cl	M.P. 105–110°			26	(4)p.8 (3)p.2
Diallylmethyl-phenyl Br	M.P. 98–99°	Calcd. for $C_{13}H_{18}PBr$:	P, 10.86; Br, 28.03	53	(4)p.7 (7)p.4
		Found:	P, 10.86; Br, 28.22		
Diallylethyl-phenyl Br	M.P. 123–130°	$C_{13}H_{20}PBr$:	P, 10.37; Br, 26.76	23	(8)p.7 (4)p.7 (5)p.4
			P, 10.31; Br, 25.87		
Diallyl-n-propylphenyl Br	M.P. 85°	$C_{14}H_{22}PBr$:	P, 9.90; Br, 25.50	30	(5)p.5 (6)p.2 (8)p.7
			P, 9.84; Br, 25.20		
Triallyl-phenyl Br	M.P. 109–111°	$C_{15}H_{20}PBr$:	P, 9.97; Br, 25.63		(5)p.4 (8)p.7
			P,10.12; Br, 25.37		
Dimethallyl-methylphenyl Br	M.P. 175–78°	$C_{15}H_{22}PBr$:	P, 9.81; Br, 25.32	51	(8)p.8 (23)p.31
			P, 9.68; Br, 24.81		
Dimethallyl-ethylphenyl Br	M.P. 77–79°	$C_{16}H_{24}PBr$:	P, 9.48; Br, 24.47	11	(6)p.3 (8)p.8 (7)p.3
			P, 9.40; Br, 24.63		
Dimethallyl-n-propylphenyl Br	M.P. 107–110°	$C_{17}H_{26}PBr$:	P, 9.09; Br, 23.40	7	(8)p.9
			P, 9.18; Br, 23.07		
Diallyldi-phenyl Br	M.P. 155–157°	$C_{18}H_{20}PBr$:	P, 8.94; Br, 23.01	57	(9)p.7 (12)p.25
			P, 8.75; Br, 23.14		
Dimethallyl-diphenyl Br	M.P. 179–180°	$C_{20}H_{24}PBr$:	P, 9.27; Br, 21.33	18	(9)p.8
			P, 8.39; Br, 21.39		
Allylmethallyl-diphenyl Br	M.P. 162–164°	$C_{19}H_{22}PBr$:	P, 8.59; Br, 22.18	42	(12)p.26 (9)p.8
			P, 8.61; Br, 22.19		
Di-3-butenyl-diphenyl Br	M.P. 115–117°	$C_{20}H_{24}PBr$:	C, 63.85; H, 6.45; P, 8.25	35	(14)p.6
			C, 63.36; H, 5.74; P, 8.57		
Vinyl-3-butenyl-diphenyl Br	M.P. 115–117°			35	(9)p.6 (14)p.6
Allylvinyl-diphenyl Br	M.P. 173–175°	$C_{17}H_{18}PBr$:	C, 61.28; H, 5.44; P, 9.23		(12)p.25
			C, 61.19; H, 5.59; P, 9.14		
Allylvinyl-diphenyl Cl				13	(12)p.25

poly-(dimethallylphenylmethylphosphonium bromide) gave infrared spectra which showed strong absorption in the 930 cm.$^{-1}$ region. This is the region where absorption due to terminal unsaturation was expected. All of the monomers prepared absorbed in this area. The polymers produced, however, did not absorb in this area with these two exceptions. Poly-(dimethallylphenylmethylphosphonium bromide) was catalytically hydrogenated at 25 p.s.i. in order to eliminate the infrared absorption at 930 cm.$^{-1}$. The product of the hydrogenation gave a spectrum which was identical with the spectrum of the material before hydrogenation. The failure to produce a change in the infrared spectrum leads to the conclusion that the absorption was due to some anomaly of these methyl substituted compounds rather than to unsaturation in the polymers. Infrared spectra of triphenylmethylphosphonium bromide and triphenylallylphosphonium bromide were compared with the spectra from the monomer and the polymer of dimethallylphenylmethylphosphonium bromide and diallylphenylmethylphosphonium bromide. These spectra show a strong absorption at 916 cm.$^{-1}$ which may be assigned to phosphorus-methyl bonds. Double bond absorptions for these compounds are found at 1017 and 872 cm.$^{-1}$. These two absorptions, which appear in the spectra of the methyl-substituted monomers, do not appear in the spectra of the polymers. It has been concluded from this evidence that what had appeared to be unsaturation in poly-diallyl- and poly-(dimethallylphenylmethylphosphonium bromide) is due rather to phosphorus-methyl bonds. These polymers are now thought to be saturated materials.

It has been established that amines act as inhibitors for free radical reactions. It was assumed that phosphines would act in a similar fashion. If this were true it would not be possible to polymerize diallylphenylphosphine by a free radical reaction. An attempt was made to polymerize diallylphenylphosphine using a free radical initiator in order to test this assumption. The monomer was placed in a benzene solution along with five per cent ABN and refluxed 11 days. The product, which was isolated, possessed physical properties and an infrared spectrum nearly identical with diallylphenylphosphine oxide. Since no polymeric material was isolated it was concluded that the phosphine had acted as an inhibitor.

Reference was made earlier to intrinsic viscosity values obtained for the polyelectrolyte polymers obtained. Polyelectrolyte materials behave differently in solution than non-electrolyte materials. In solution, the polyelectrolytes obtained are free to ionize. The bromide ions formed by ionization are free to move about in solution. The positive phosphonium ions formed are not free to move about as they are bound together by the polymer chain. These positive ions repel each other and force the polymer chain to uncoil. The greater the extent of ionization, the more the polymer chain is extended. Dilution of a sample of polymer causes greater ionization. Intrinsic viscosity cannot be measured under these conditions due to the change in interaction between molecules in the system. Ionization of these polyelectrolytes was held constant enough for viscosity measurements to be made through the use of added electrolyte. Intrinsic viscosity values were obtained by the usual method. These values are small when compared to values obtained for other polymer systems. The magnitude of these values may have several meanings. First, the polymers may be of low degree of polymerization. Or, the degree of polymerization is large but the added electrolyte has supressed the ionization to a point where the polymer molecules remain tightly coiled and do not act as long chains. Two polyelectrolyte polymers were degraded to give non-electrolyte polymers. This reaction and the polymers obtained by this method will be discussed later. The intrinsic viscosities obtained for non-electrolyte polymers obtained by degradation are shown in Table VII. These values are considerable larger than values obtained from the

polyelectrolytes from which they were obtained. Due to the change in intrinsic viscosity between the compounds it was thought that both types of polymers have longer chains than was indicated by the intrinsic viscosities of the electrolyte materials. It then seems that the added electrolyte is suppressing ionization and that the coiled molecules give very little indication as to their degree of polymerization in this system.

The physical properties and other pertinent data for the polyphosphonium salts are recorded in Table V.

IV. PHOSPHINE OXIDE MONOMERS AND POLYMERS

(a) Phosphine Oxide Monomers

The preparation of diallylphenylphosphine oxide was previously discussed[1] and its preparation along with that of dimethallylphenylphosphine oxide has been published.[24] Additional phosphine oxides as suitable monomers for this study are reported in this paper. The physical properties, and other pertinent data on these monomers are included in Table VI.

(b) Polyphosphine Oxides

Diallylphenylphosphine oxide could be polymerized in bulk with benzoyl peroxide; yields 15–30%. Poly–(diallylphenylphosphine oxide) was soluble in alcohol, dimethylformamide and glacial acetic acid. An intrinsic viscosity determination of a sample melting at 85–115° gave a value of 0.026 (inalcohol). An infrared examination of the polymer showed only a small peak for a carbon–carbon double bond (1640 $cm.^{-1}$). Absorption assigned to the terminal methylene group (910 $cm.^{-1}$) in the monomer did not appear in the polymer. A sample of poly–(diallylphenylphosphine oxide) lost 21.9% of its original weight when heated at 210° for four hr. It began to darken in 10 min. and had the appearance of tar after 48 hr.

Polymerization of dimethallylphenylphosphine oxide was initiated by either α,α'–azodi–isobutyronitrile or benzoyl peroxide at 75°. The yields of polymer were low (less than 30%) with either initiator. Poly–(dimethallylphenyl–phosphine oxide) was soluble in alcohol, glacial acetic acid and dimethylformamide. A value of 0.04 was found for the intrinsic viscosity of an alcohol solution of the polymer; the sample melted at 130–165°. The infrared spectrum has only a small hump to indicate a carbon–carbon double bond (1635 $cm.^{-1}$) and does not have a peak for a terminal methylene group (892 $cm.^{-1}$) as is present in the spectrum of the monomer. When heated at 210° for four hr., the polymer decreased in weight by 32.5%.

In view of the low intrinsic viscosity measurements it appears likely that the polymers are not of high molecular weight. Polymerizations involving allyl groups have been reported to terminate through degradative chain transfer which may be influential in retarding growth in samples.

A molecular weight determination of a poly–(diallylphenylphosphine oxide) by the light scattering method gave a value of 2.8×10^4.

Differential thermal analysis of two of the polyphosphine oxides gave the following results: Polydiallylphenylphosphine oxide (M.R. 165–205°), Decomp. 438–450°; Polydimethallylphenylphosphine oxide (M.R. 198–225), Decomp. 392–438°.

Treatment of dimethallylmethylphosphine oxide in bulk with catalytic amounts (up to 5%) of benzoyl peroxide apparently initiated little or no polymerization as unreacted monomer could be recovered in high yield. This is in contrast to the behavior of diallyphenylphosphine oxide and dimethallylphenyl–

Table V

Physical Properties, Analytical Data and Yields of Phosphonium Polymers

Phosphonium Salt Polymers	Initiator	Yield %	Analysis Calculated for:	Found:	Polymer Properties	References
Diallylhydrogen-phenyl Cl	t-BHP[a]				M.P. > 350°	(4)p.9
Diallylmethyl-phenyl Br	t-BHP		$(C_{13}H_{18}PBr)_n$: P,	10.88 10.34	Soft. 230°	(4)p.9, (9)p.9
			Br,	28.03 26.77	M.P. 270°;n = 0.035	(12)p.27
Diallylethyl-phenyl Br	t-BHP	95	$(C_{14}H_{20}PBr\cdot H_2O)_n$:			(5)p.4, (9)p.9
			P,	9.78 9.30	M.P. 260-300°	(8)p.9, (12)p.27
			Br,	25.20 24.05	η = 0.034	(23)p.22
Diallyl-n-propyl-phenyl Br	t-BHP		$(C_{15}H_{22}PBr\cdot H_2O)_n$:			(6)p.3, (9)p.7,9
			P,	9.36 8.80	M.P. 235°	(12)p.26,27
			Br,	24.10 23.34	η = 0.02	
Triallyl-phenyl Br	t-BHP	Quant.	$(C_{15}H_{20}PBr\cdot H_2O)_n$:		Insoluble,	(8)p.9
			P,	9.43 9.10	Cross-linked	(5)p.5
			Br,	24.30 23.34		
Dimethallyl-methylphenyl Br	t-BHP	95	$(C_{15}H_{22}PBr\cdot H_2O)_n$:		Soft. 220°	(9)p.7,9
			P,	9.36 9.41	M.P. 344°	(12)p.26,27
			Br,	24.18 24.08	η = 0.018	(23)p.33
Dimethallyl-ethylphenyl Br	AIBN,[b] BP[c] t-BHP	90	$(C_{16}H_{29}PBr\cdot H_2O)_n$:		M.P. 180-200°	(7)p.4
			P,	8.98 8.63	η = 0.025	(23)p.33
			Br,	23.18 23.40		(8)p.9
Dimethallyl-n-propylphenyl Br	AIBN	60	$(C_{17}H_{26}PBr\cdot H_2O)_n$:		Soft. 170°	(9)p.7,9
			P,	8.60 8.46	M.P. 220°	(12)p.26,27
			Br,	22.18 21.67	η =0.031	
Diallyldi-phenyl Br	AIBN	97	$(C_{18}H_{20}PBr\cdot H_2O)_n$:		Soft. 250°	(9)p.8,9
			P,	8.50 8.49	M.P. 295-315°	(12)p.26,27
			Br,	21.90 21.80	η = 0.031	
Dimethallyl-diphenyl Br	AIBN	89	$(C_{20}H_{24}PBr\cdot H_2O)_n$:		Soft. 256°	(9)p.8,9
			P,	7.90 8.05	M.P. 326°	(12)p.26,27
			Br,	20.35 20.48	η = 0.013	
Allylmethallyl-diphenyl Br	AIBN	96	$(C_{19}H_{22}PBr\cdot H_2O)_n$:		Soft. 240°	(9)p.8,9
			P,	8.19 7.90	M.P. 270°	(12)p.26,27
			Br,	21.10 20.68	η = 0.038	
Di-3-butenyl-diphenyl Br						
Vinyl-3-butenyl-diphenyl Br						
Allylvinyldiphenyl Br	AIBN					(14)p.6

a. t-BHP = tert-Butylhydroperoxide
b. AIBN = Azo-di-iso-butyronitrile
c. BP = Benzoylperoxide

Table VI

Physical Properties, Analytical Data and Yields of Unsaturated Phosphine Oxides

Phosphine Oxide	Physical Properties	Analysis	Yield %	Ref.
Diallylphenyl	M.P. 42.5	Calcd. for $C_{12}H_{15}OP$: C, 69.90; H, 7.28; P, 15.05 Found: C, 69.87; H, 7.40; P, 14.89	56	(4)p.11 (5)p.6 (24)
Dimethallylphenyl	B.P. 156–61/3mm	$C_{14}H_{19}OP$: C, 71.79; H, 8.11; P, 13.24 C, 71.89; H, 8.39; P, 13.01	47	(4)p.11 (5)p.6 (24)
Diallylmethyl	B.P. 145–52/1–3mm n_D^{22} 1.4870		43	(4)p.12 (3)p.7,8
Diallylethyl	B.P. 148–52/1–2mm n_D^{24} 1.4846		42	(4)p.14 (3)p.8,9
Dimethallylmethyl	B.P. 135–41/2mm	$C_9H_{17}OP$: C, 62.79; H, 9.88; P, 18.02 C, 62.56; H, 9.82; P, 17.98	57	(8)p.11 (4)p.13 (25) (27)p.19
Dimethallylethyl	B.P. 115–18/0.3mm	$C_{10}H_{19}OP$: C, 64.51; H, 10.21; P, 16.66 C, 64.49; H, 10.32; P, 16.46	43	(8)p.11 (7)p.4 (25)
Divinylphenyl	B.P. 133–36/0.75mm		37	(9)p.10 (12)p.20
Diphenylvinyl	M.P. 115–17	$C_{14}H_{13}OP$: C, 73.66; H, 5.70; P, 13.59 C, 73.40; H, 5.88; P, 13.60	48	(9)p.11 (12)p.21 (26)
Phenylcyclopenta-methylene	M.P. 128–29	$C_{11}H_{15}OP$: C, 68.04; H, 7.71; P, 15.97 C, 68.22; H, 7.79; P, 15.73	9	(8)p.12

phosphine oxide. The highest conversions of the trialkylphosphine oxides to soluble polymers were obtained by using azobisisobutyronitrile (5%) at a temperature of 110°. That poly(dimethallylmethylphosphine oxide) was not of high molecular weight was inferred by a low value (0.042) for its intrinsic viscosity. Infrared data demonstrated the existence of a small amount of residual unsaturation.

The small conversions of monomers with azobisisobutyronitrile as well as the negative results with benzoyl peroxide can probably be explained in part as another example of degradative chain transfer.

Diphenylvinylphosphine oxide was polymerized in presence of free radical initiators either in bulk or in solution. The polymer is soluble in dimethylformamide and alcohol, and one sample (M.P. 220-242°) in alcohol gave a value of 0.047 for its intrinsic viscosity.

Polyphosphine oxides have also been prepared by reaction of polyphosphonium salts with sodium hydroxide. When poly-(diallyldiphenylphosphonium bromide) was treated, a phenyl anion was lost. The product of the reaction was poly-(diallylphenylphosphine oxide). No reliable analysis could be obtained for this product. Poly-(diallylphenylphosphine oxide) had been prepared by the free radical polymerization of diallylphenylphosphine oxide.[24] It was found that it also was difficult to obtain an acceptable analysis on the polymer obtained in this manner. The infrared spectrum of the poly-phosphine oxide prepared by hydroxide degradation was identical with the spectrum obtained by Berlin.[24]

When poly-(diallylphenylethylphosphonium bromide) was degraded by this method, the product was found to be poly-(diallylethylphosphine oxide). The phenyl radical was eliminated rather than the ethyl radical due to its greater stability. Again, analyses obtained for the product were inconclusive. An examination of the infrared spectrum showed a strong absorption at 1180 $cm.^{-1}$ for the phosphoryl group. No absorptions appeared in the spectrum which could be assigned to the phenyl group. The spectrum was very similar in other respects to the spectrum of poly-(diallylphenylphosphine oxide).

The intrinsic viscosities of the polyphosphine oxides were considerably larger than the intrinsic viscosities of the poly-phosphonium bromides from which they were prepared, as was mentioned earlier. The intrinsic viscosity found for poly-(diallylphenylphosphine oxide) prepared by degradation was 0.109. Berlin[24] reported an intrinsic viscosity of 0.026 for the same polymer produced by the polymerization of diallylphenylphosphine oxide. It appears that the phosphonium bromide polymerized to give a product having a considerably greater degree of polymerization than the corresponding oxide.

The poly-phosphine oxides produced by both methods appear to be identical except for chain length. This is considered to constitute an alternate synthesis of this cyclic polymer and lends support, along with other evidence presented, to the theory of cyclic polymerization of 1,6-diolefinic phosphonium bromides.

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Table VII

Physical Properties, Analytical Data and Yields of Phosphine Oxide Polymers

Phosphine Oxide Polymers	Initiator	Yield %	Analysis Calculated for:	Found:	Polymer Properties	References
Diallylphenyl	t-BHP[a] NaOH on Diallyl-diphenylphos-phonium Br	20-30	$C_{12}H_{15}OP$: C, 69.90 H, 7.28 P, 15.05	68.98 7.15 14.05	M.R. 90-115 η = 0.026 MW = 28,000 M.R. 250°; n = 0.109	(3)p.9,10,(24) (4)p.14 (9)p.8,(10)p.3
Dimethallyl-phenyl	BP[b] AIBN[c]	11	$C_{14}H_{19}OP$: P, 13.24	12.96	M.R. 130-165 η = 0.04	(8)p.13,(24) (4)p.15,(27)p.19
Diallylmethyl						
Diallylethyl	NaOH on Diallylphenyl-ethylphosphonium Br				M.R. 192-310 η = 0.103	(6)p.3 (12)p.24-25
Dimethallyl-methyl	AIBN	15	$(C_9H_{17}OP\cdot H_2O)_n$: C, 59.99 H, 10.55	59.95 10.01	M.R. 162-170 η = 0.042	(7)p.5,(25) (8)p.13 (5)p.7
Dimethallyl-ethyl	AIBN	5	$(C_{10}H_{19}OP\cdot H_2O)_n$: C, 58.82 H, 9.31 P, 14.21	59.17 9.99 13.18	M.R. 165-185	(8)p.13-14 (25)
Divinylphenyl Copolymer with Malaic Anhydride	AIBN	15			White solid	(12)p.24
Diphenylvinyl	AIBN t-BHP	Quant.	$(C_{14}H_{13}OP\cdot H_2O)_n$: C, 68.29 H, 6.09 P, 12.60	67.85 5.99 11.79	M.R. 220-224 η = 0.047	(9)p.13 (12)p.23, (26)

a. t-BHP = t-Butyl hydroperoxide
b. BP = Benzoyl peroxide
c. AIBN = Azo-isobutyronitrile

Bibliography

1. Conference on High Temperature Polymer and Fluid Research, WADD, U. S. Air Force, Dayton, Ohio, May, 1959
2. Quart. Prog. Rep. No. 3, AF 33(616)-5808, Mar. 5, 1959
3. Quart. Prog. Rep. No. 4, AF 33(616)-5808, June 5, 1959
4. Final Report, AF 33(616)-5808, October, 1959
5. Quart. Prog. Rep. No. 1, AF 33(616)-5616, I, Nov. 5, 1959
6. Quart. Prog. Rep. No. 2, AF 33(616)-5616, I, Dec. 5, 1959
7. Quart. Prog. Rep. No. 3, AF 33(616)-5616, I, Mar. 5, 1960
8. Final Report, AF 33(616)-5616, I, May, 1960
9. Quart. Prog. Rep. No. 1, AF 33(616)-6887, I, Sept. 5, 1960
10. Quart. Prog. Rep. No. 2, AF 33(616)-6887, I, Dec. 5, 1960
11. Quart. Prog. Rep. No. 3, AF 33(616)-6887, I, Mar. 5, 1961
12. Pre-Print Copy, Annual Rep. AF 33(616)-6887, I, July 1, 1961
13. Quart. Prog. Rep. No. 1, AF 33(616)-6887, Sept. 5, 1961
14. Quart. Prog. Rep. No. 2, AF 33(616)-6887, Dec. 5, 1961
15. A. D. Petrov, V. F. Mironov, and V. G. Glukhotsev, Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk, 1123(1954)
16. L. D. Nasiak and H. W. Post, J. Org. Chem., 24, 489(1959)
17. A. V. Topchiev, N. S. Nametkin, S. G. Durgaryan and S. S. Dyankov, Khim i Prakt. Primenenie Kremneorg. Soedinenii, Trudy Konf. Leningrad, No. 2, 118(1958)
18. C. S. Marvel and R. G. Woolford, J. Org. Chem., 25, 1641(1960)
19. G. B. Butler and R. W. Stackman, J. Org. Chem., 25, 1643(1960)
20. R. W. Stackman, Ph.D. Dissertation, U. of Fla., Jan., 1961.
21. C. S. Marvel, J. Polymer Sci., 48, 101(1960)
22. G. B. Butler, J. Polymer Sci., 48, 279(1960)
23. D. S. Skinner, Ph.D. Dissertation, U. of Fla., Jan., 1961

24. K. D. Berlin and G. B. Butler, J. Am. Chem. Soc., 82, 2712(1960)

25. K. D. Berlin and G. B. Butler, J. Org. Chem., 25, 2006(1960)

26. K. D. Berlin and G. B. Butler, J. Org. Chem., 26, 2537(1961)

27. WADD Technical Report 59-475, I

28. L. Maier, D. Seyforth, F. G. A. Stone, and E. G. Rochow, J. Am. Chem. Soc., 79, 5884(1957)

29. W. J. Jones, W. C. Davies, et al., J. Chem. Soc., 1947, 1446

30. J. D. Stille, Chem. Revs., 58, 541(1958)

31. N. G. Gaylord and H. F. Mark, Linear and Stereoregular Addition Polymers, Interscience Publishers, Inc. New York, 1959, p.90