

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Linear Polymers from Diene Monomers by the Cyclic Polymerization Mechanism. XI. Polyphosphonium Salts via Cyclopolymerization

George B. Butler^a; David L. Skinner^{ab}; William C. Bond Jr.^{ac}; C. Lawson Rogers^a

^a Department of Chemistry, University of Florida, Gainesville, Florida ^b Jim Walter Corporation, St. Petersburg, Florida ^c Copolymer Corporation, Baton Rouge, Louisiana

To cite this Article Butler, George B. , Skinner, David L. , Bond Jr., William C. and Rogers, C. Lawson(1970) 'Linear Polymers from Diene Monomers by the Cyclic Polymerization Mechanism. XI. Polyphosphonium Salts via Cyclopolymerization', Journal of Macromolecular Science, Part A, 4: 6, 1437 – 1451

To link to this Article: DOI: 10.1080/00222337008081736

URL: <http://dx.doi.org/10.1080/00222337008081736>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Linear Polymers from Diene Monomers by the Cyclic Polymerization Mechanism. XI. Polyphosphonium Salts via Cyclopolymerization

GEORGE B. BUTLER, DAVID L. SKINNER,* WILLIAM C. BOND, JR.,†
and C. LAWSON ROGERS

*Department of Chemistry,
University of Florida,
Gainesville, Florida 32601*

SUMMARY

A wide variety of diunsaturated phosphonium salts have been synthesized in order to determine whether or not such structures undergo cyclopolymerization. As intermediates for these monomers, a number of previously unreported unsaturated phosphines have been prepared and characterized. Polymerization studies using a wide variety of free radical initiating conditions led to polymers in those cases which were predicted to undergo cyclopolymerization leading to five-, six-, or seven-membered rings with one exception. The properties of the polymers are consistent with the cyclopolymerization mechanism. The conversion of poly(diallyldiphenylphosphonium bromide) to poly(diallyldiphenylphosphine oxide) offers additional evidence for cyclopolymerization. Di-3-butenyldiphenylphosphonium bromide, a monomer functionally capable of forming a polymer containing an eight-membered ring, did not polymerize. Divinylphenylphosphine was found to undergo copolymerization with acrylonitrile in accordance with the cyclopolymerization mechanism.

*Present address: Jim Walter Corporation, St. Petersburg, Florida.

†Present address: Copolymer Corporation, Baton Rouge, Louisiana.

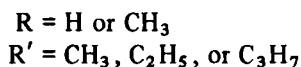
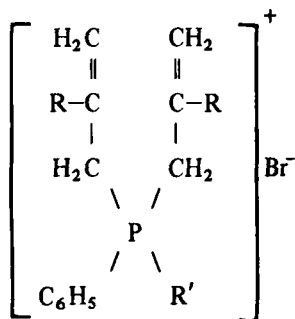
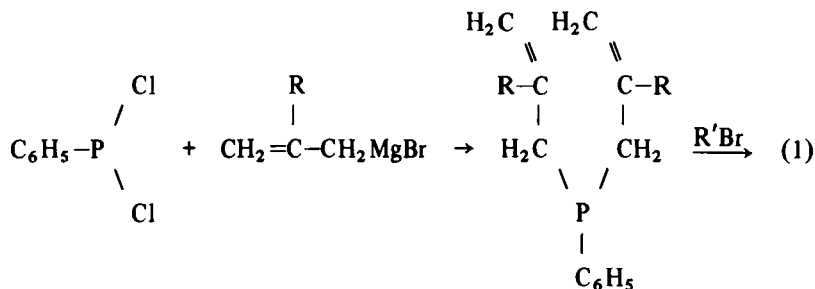
INTRODUCTION

The purpose of this investigation was to determine whether or not 1,6-heptadienes containing the phosphonium substituent in the chain would undergo cyclopolymerization as so many other 1,6-heptadienes do [1], and if so, to investigate the properties of the polymers produced. As intermediates for the phosphonium salts, a number of unsaturated phosphines were synthesized. These were synthesized by reaction of the allyl, methallyl, vinyl, or 3-butenyl Grignard reagents with phenyldichlorophosphine or diphenylchlorophosphine. Thus a variety of unsaturated phosphines were obtained that could be converted to the required diene structure containing the phosphonium substituent in the chain. Reaction of appropriate phosphines with appropriate alkyl or alkenyl halides made it possible to synthesize 1,5-, 1,6-, 1,7-, and 1,8-dienes having the diphenylphosphonium or the phenylalkylphosphonium substituent in the chain. Such structures possess the functional capability of leading to five-, six-, seven-, and eight-membered ring structures, respectively, via cyclopolymerization.

RESULTS AND DISCUSSION

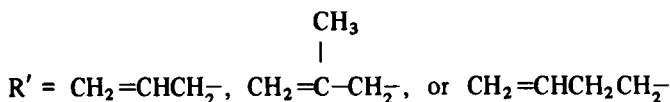
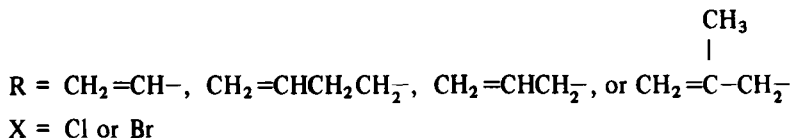
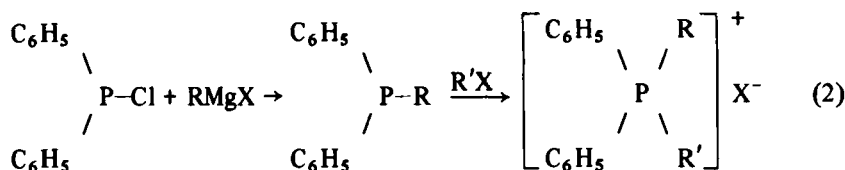
Phosphines, as a group, are very reactive substances, which is characteristic of all derivatives of trivalent phosphorus. The low aliphatic substituted derivatives are, in fact, spontaneously combustible when exposed to atmospheric oxygen. The triaryl phosphines are, on the other hand, stable to air oxidation and can be stored for long periods of time with no special precautions. The mixed aryl-alkyl phosphines prepared lie between these two extremes. Usually, the monophenyl substituted phosphines were transferred and all open manipulations were carried out in a nitrogen flushed dry box. The diphenyl substituted derivatives were transferred under a flow of nitrogen and did not oxidize appreciably. At elevated temperatures both types of phosphines oxidized readily. For this reason, distillations were performed under nitrogen. Even small amounts of oxygen present during distillation caused hazy, impure distillates which were contaminated by the solid, insoluble phosphine oxide. After distillation the aryl substituted phosphines were usually treated immediately with an alkyl halide dissolved in ether to form the phosphonium salt.

The phosphines were synthesized either by Eq. (1) in which phenyldichlorophosphine was allowed to react with two equivalents of allyl or methallyl magnesium bromide followed by reaction of the diunsaturated



phosphine with an alkyl bromide; or by Eq. (2) in which diphenylchlorophosphine was allowed to react with allyl, methallyl, vinyl, or 3-butenyl magnesium bromide followed by reaction of the unsaturated phosphine with allyl, methallyl, or 3-butenyl halide; or by Eq. (3) in which dimethylaminodichlorophosphine was allowed to react with two equivalents of methyl magnesium bromide at -30° to yield the intermediate dimethylaminodimethylphosphine, which in turn could be converted to dimethylallylphosphine by reaction with allyl magnesium bromide at 30° . Dimethylallylphosphine was then converted to dimethyldiallylphosphonium chloride by reaction with allyl chloride.

The physical properties, analytical data, and yields of the previously unreported unsaturated phosphines are recorded in the Experimental Section. Previously reported and characterized phosphines are not recorded. The physical properties, analytical data, and yields of the previously unreported phosphonium salts prepared and characterized are recorded in Table 1.



The polymerization conditions, yields, physical properties, and analyses of the polymers obtained are recorded in Table 2.

Solution polymerization of the phosphonium salts was used throughout this study, since the monomers are very high melting solids. They are soluble in both water and dimethylformamide, and both solvents were used. Initiators were either benzoyl peroxide, *t*-butyl hydroperoxide, α, α' -azobisisobutyronitrile, or benzoin with UV irradiation. The polymers were soluble in ethanol and dimethylformamide, and showed little or no absorption in the IR region corresponding to residual unsaturation. The monomers showed infrared absorption at 1640 and 930 cm^{-1} due to olefinic unsaturation. These absorptions were absent in the polymers. The absorption at 930 cm^{-1} was particularly useful due to its sensitivity to small amounts of unsaturation. The softening points of the polymers were much higher than the melting points of the corresponding monomers. All polymers were obtained as the hydrate as indicated by analytical results. In every case, the polymer contained one molecule of water per phosphonium unit.

The properties of the polymers are consistent with the cyclopolymerization mechanism [1]. The conversion of poly(diallyldiphenylphosphonium bromide) to poly(diallylphenylphosphine oxide) by the action of sodium hydroxide [2], according to Eq. (4), offers additional proof of cyclization. Poly(diallylphenylphosphine oxide) obtained by this procedure gave an IR spectrum identical with the spectrum obtained previously by cyclopolymerization of diallylphenylphosphine oxide [3].

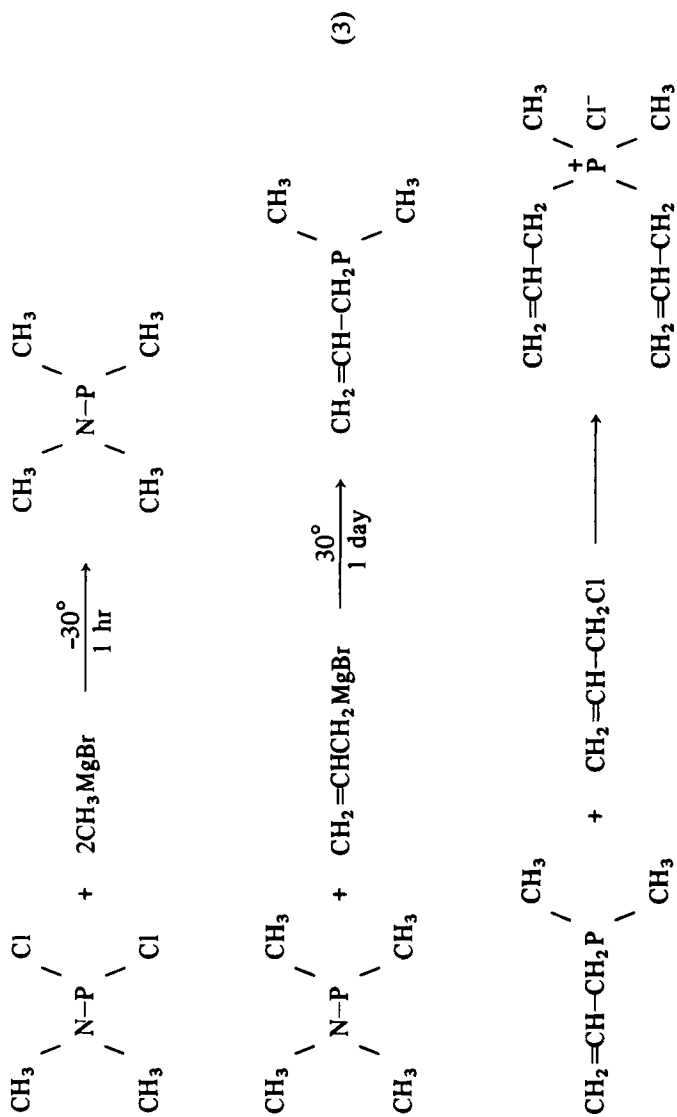


Table 1. Physical Properties, Analytical Data, and Yields of Unsaturated Phosphonium Salts

Phosphonium salt	Identification No.	Melting point (°C)	Analysis ^a	Yield (%)
Methyldiallylphenyl Br	I	98-99	Calc for C ₁₃ H ₁₈ PBr: P, 10.86; Br, 28.03 Found: P, 10.86; Br, 28.22	53
Ethyl diallylphenyl Br	XI	123-130	Calc for C ₁₄ H ₂₀ PBr: P, 10.37; Br, 26.76 Found: P, 10.31; Br, 25.87	23
n-Propyldiallylphenyl Br	XII	85	Calc for C ₁₅ H ₂₂ PBr: P, 9.90; Br, 25.20 Found: P, 9.84; Br, 25.50	30
Triallylphenyl Br	XIII	109-111	Calc for C ₁₅ H ₂₀ PBr: P, 10.12; Br, 25.63 Found: P, 9.97; Br, 25.37	47
Methyldimethylphenyl Br	II	175-178	Calc for C ₁₅ H ₂₂ PBr: P, 9.81; Br, 25.33 Found: P, 9.68; Br, 24.81	51
Ethyldimethylphenyl Br	XIV	77-79	Calc for C ₁₆ H ₂₄ PBr: P, 9.48; Br, 24.47 Found: P, 9.40; Br, 24.63	11
n-Propyldimethylphenyl Br	XV	107-110	Calc for C ₁₇ H ₂₆ PBr: P, 9.09; Br, 23.40 Found: P, 9.18; Br, 23.07	7

Allyl(methallyl)di- phenyl Br	IV	162-164	Calc Found:	for C ₁₉ H ₂₂ PBr: P, 8.59; Br, 22.18 P, 8.61; Br, 22.19	42
Dimethallyl-di- phenyl Br	V	179-180	Calc Found:	for C ₂₀ H ₂₄ PBr: P, 9.27; Br, 21.33 P, 8.39; Br, 21.39	18
3-Butenyldiphenyl- vinyl Br	VI	163-170	Calc Found:	for C ₁₈ H ₂₀ PBr: C, 62.26; H, 5.81; P, 8.72 C*, 61.07; H, 6.12; P, 8.85	61
Allyldiphenyl- vinyl Br	VII	169-171	Calc Found:	for C ₁₇ H ₁₈ PBr: C, 61.28; H, 5.44; P, 9.23 C, 61.18; H, 5.87; P, 9.18	32
Allyl-3-butenyl- diphenyl Br	VIII	139-142	Calc Found:	for C ₁₉ H ₂₂ PBr: C, 63.17; H, 6.14; P, 8.57 C, 63.15; H, 6.24; P, 8.57	88
3-Butenyldiphenyl- methallyl Cl	XVI	175-177	Calc Found:	for C ₂₀ H ₂₂ PCl: C, 72.60; H, 7.31; P, 9.36 C, 72.06; H, 7.07; P, 9.60	97
Di-3-butenyl- diphenyl Br	IX	115-117	Calc Found:	for C ₂₀ H ₂₄ PBr: C, 63.85; H, 6.45; P, 8.25 C, 63.36; H, 5.74; P, 8.57	35

(continued)

Table 1. (continued)

Phosphonium salt	Identification No.	Melting point (°C)	Analysis ^a	Yield (%)
Diallyldiphenyl Br	III	173-176	Calc for C ₁₈ H ₂₀ PBr: C, 62.25; H, 5.80 Found: C*, 62.29; H*, 5.78	88
Diallyldiphenyl Cl	X	152-160	Calc for C ₁₈ H ₂₀ PCl: C, 71.46; H, 6.64; P, 10.25 Found: C*, 71.87; H*, 6.96; P, 10.19	33
Allyldiphenyl-n-propyl Br	XVII	134-137	Calc for C ₁₈ H ₂₂ PBr: C, 61.90; H, 6.31; P, 8.88 Found: C, 61.67; H, 6.33; P, 9.01	28
Diallyldimethyl Cl	XVIII	76-82	Calc for C ₈ H ₁₆ PBr: C, 53.88; H, 9.03; P, 17.34 Calc for C ₈ H ₁₆ PBr·H ₂ O: C, 48.85; H, 9.23; P, 15.40 Found: C, 48.27; H, 9.42; P, 15.40	82

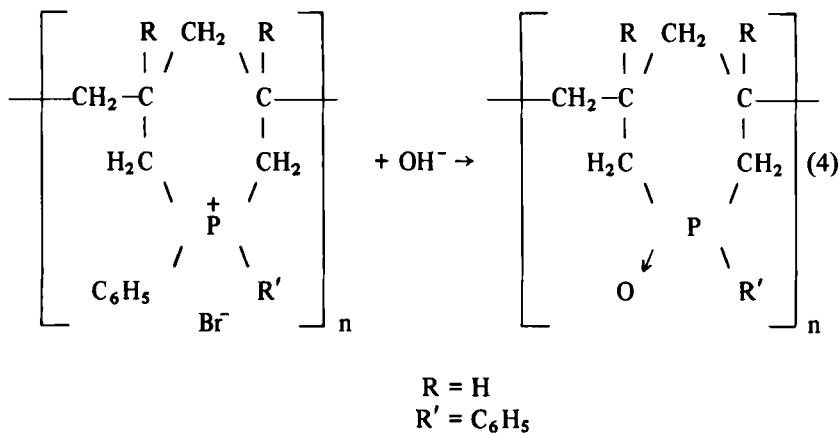
^a Analyses starred (*) were done by C. D. Miller of the Analytical Department, University of Florida.

Table 2. Polymerization Conditions, Yields, Physical Properties, and Analyses of Polyphosphonium Halides

Mon-omer	Initiator	% Solvent	Time (days)	% Yield	Soft range	[η]	Molecular formula	Analyses			
								%P		%Br	
								Calc	Found	Calc	Found
I	1,7,C	33,H	3	60	230	0.04	(C ₁₃ H ₁₈ PBr·H ₂ O) _n	10.22	10.34	26.40	26.77
II	5,B	33,H	6	95	220	0.02	(C ₁₅ H ₂₂ PBr·H ₂ O) _n	9.36	9.41	24.18	24.08
III	4,B	60,D	34	45	250	0.03	(C ₁₈ H ₂₀ PBr·H ₂ O) _n	8.50	8.59	21.90	21.80
III	0.1,A	50,H	7	80	190	0.05	(C ₁₈ H ₂₀ PBr·H ₂ O) _n	8.50	8.29	21.90	21.67
IV	4,B	60,D	34	96	240	0.04	(C ₁₉ H ₂₂ PBr·H ₂ O) _n	8.19	7.90	21.10	20.68
V	4,B	60,D	34	35	256	0.01	(C ₂₀ H ₂₄ PBr·H ₂ O) _n	7.90	8.05	20.35	20.48
VII	2,A	50,H	5	42	220	0.03	(C ₁₇ H ₁₈ PBr·H ₂ O) _n	8.82	8.71	22.76	22.43
VIII	2,A	50,H	3	58	220	0.05	(C ₁₉ H ₂₂ PBr·H ₂ O) _n	8.18	8.12	21.10	20.90
X	1,A	50,H	7	74	270	0.08	(C ₁₈ H ₂₀ PCl·H ₂ O) _n	9.67	9.41	11.08	10.77 ^a
XI	5,B	67,D	14	100	290	0.03	(C ₁₄ H ₂₀ PBr·H ₂ O) _n	9.78	9.30	25.20	24.05
XII	10,B	67,D	13	60	200	0.02	(C ₁₅ H ₂₂ PBr·H ₂ O) _n	9.36	8.80	24.10	23.34
XIII	4,B	33,H	4	100	b	b	(C ₁₈ H ₂₀ PBr·H ₂ O) _n	9.43	9.10	24.30	23.34
XIV	4,B	50,D	6	20	185	0.03	(C ₁₆ H ₂₄ PBr·H ₂ O) _n	8.98	8.63	23.18	21.50
XV	4,B	60,D	34	60	170	0.03	(C ₁₇ H ₂₆ PBr·H ₂ O) _n	8.60	8.46	22.18	21.67
XVI	2,A	50,H	3	60	210	0.04	(C ₂₀ H ₂₄ PCl·H ₂ O) _n	8.90	8.30	10.20	9.80 ^a
XVIII	1,A	50,H	1	80	b	b	(C ₈ H ₁₆ PCl·H ₂ O) _n	—	—	—	—
				5	150	—					

^aHalogen atom was chlorine.

^bInsoluble, cross-linked.



All of the diolefinic monomers synthesized produced polymers, except vinyl-3-butenyldiphenyl and di-3-butenyldiphenylphosphonium bromides. It is quite surprising that the former compound did not polymerize, if not by way of the cyclic mechanism to produce the six-membered ring structure, by way of the vinyl group. The fact that the latter compound did not polymerize is not too surprising since cyclic polymerization would require formation of an eight-membered ring. Also, the 3-butenyl double bond is not very reactive toward free radical initiators.

The viscosity data for the poly-phosphonium salts were typical of the data for polyelectrolytes in general. It is well known [4] that the viscosity curves (η_{sp}/c vs c) of polyelectrolytes are strongly concave upward, in contrast to the behavior of uncharged linear polymers. This is believed to be due to the dissociation of the ionic bond in the solution which leads to large repulsive forces between the positively charged groups remaining on the chain. These forces give rise to greatly expanded configurations and very large intrinsic viscosities. At high concentration, the molecules in the polyelectrolyte are not significantly ionized and tend to partially overlap; thus, they are not appreciably expanded. As the solution is diluted, the molecules no longer fill all the space and some of the halide ions leave the regions of the chain. This causes a development of charge and extension of the chains. The addition of a strong electrolyte suppresses the loss of halide ion and the viscosity behavior becomes more normal. However, the intrinsic viscosity is dependent on the volume of the polymer in the solution and added electrolyte compresses the hydrodynamic unit corresponding to the polyelectrolyte. The compression changes the shape

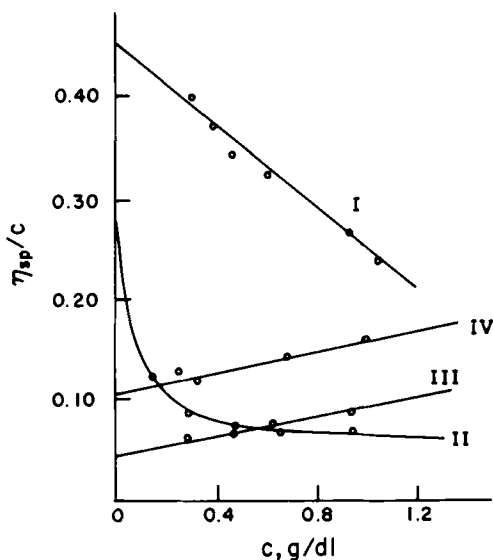
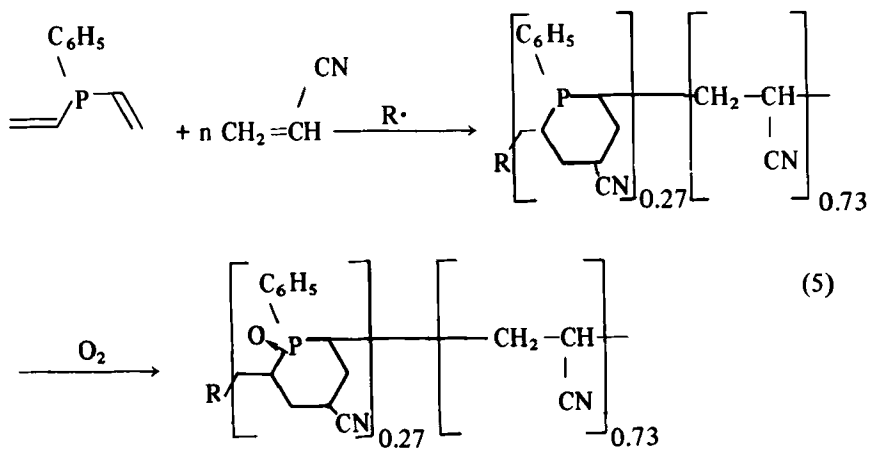


Fig. 1. Intrinsic viscosity determinations of phosphonium polymers. Plots of η_{sp}/c vs c for: (I) poly(diallyldiphenylphosphonium bromide) in 95% ethanol; (II) poly(diallyldiphenylphosphonium chloride) in a 1.0 M 1:1 ethanol-water solution of potassium chloride; (III) poly(diallyldiphenylphosphonium bromide) in 1:1 ethanol-water 0.1 M in potassium bromide; and (IV) poly(diallylphenylphosphine oxide) in 95% ethanol.

of the polymer and causes a marked decrease in the viscosity of the solution. Thus, the term intrinsic viscosity for a polyelectrolyte can not be used in the same sense as for an uncharged polymer since it is dependent largely on the concentration of added salt. This type of behavior was exhibited by the polyphosphonium compounds and is illustrated in Fig. 1. Line I represents poly(diallyldiphenylphosphonium bromide) dissolved in ethanol and, as was expected, η_{sp}/c tended to increase with dilution. Addition of a strong electrolyte, such as a potassium halide, provided a common ion effect which repressed the ionization of the polymer. At this time the viscosity behaved similarly to a linear uncharged polymer, as shown by Line III. Line II represents polydiallyldiphenylphosphonium chloride rather than the bromide; but demonstrates an intermediate change between Line I and III where insufficient common ion was present to completely repress ionization. Line IV represents the viscosity of the phosphine oxide, which was produced from the same sample of diallyldiphenylphosphonium bromide used for the determination of Line III.

Copolymers of divinyl compounds have been known for some time. Divinyl ether [5] and other 1,4-pentadienes have been copolymerized with a variety of olefins to yield cyclic copolymers. The copolymerization of divinylphenylphosphine with acrylonitrile gave a brilliant red, brittle solid which contained approximately 3 moles of acrylonitrile for each mole of divinylphenylphosphine. The per cent of acrylonitrile in the polymer increased as the concentration of that comonomer increased in the initial charge. The copolymer produced was soluble in dimethylformamide and showed no residual unsaturation. Thus, it had apparently undergone cyclocopolymerization. The excess acrylonitrile in the polymer was most likely due to its strong tendency to undergo homopolymerization. The copolymer also exhibited a broad absorption band in the IR region at 1170 cm^{-1} which corresponds with the phosphine oxide; thus, the phosphine probably was oxidized during the work-up of the polymer.

Elemental analysis indicated the copolymer contained 0.265 mole fraction of divinylphenylphosphine oxide and 0.732 mole fraction of acrylonitrile. The structure of this copolymer and the mechanism of its formation are represented in Eq. (5).



EXPERIMENTAL

Preparation of Phosphines

The tertiary phosphines were prepared by reaction of the appropriate chlorophosphine with the appropriate Grignard reagent. All operations were conducted under an anhydrous nitrogen atmosphere.

New unsaturated phosphines prepared and characterized along with their physical properties and analyses are (phosphine, molecular formula, % yield, bp/mm, n_D^{20} , d_4^{20} , anal., calc, C, H, P; found, C, H, P): 3-butenyldiphenyl, $C_{16}H_{17}P$, 82, 113-115/0.3, 1.5991, 1.028, 79.98, 7.13, 12.89; 79.80, 7.02, 12.95; di-3-butenylphenyl, $C_{14}H_{19}P$, 53, 85-88/0.3, 1.5448, 0.9467, 77.00, 8.78, 14.20; 76.39, 9.34, 14.07; and allyldimethyl, $C_5H_{11}P$, 36, 95-99/760, 58.80, 10.86, -, 58.42, 11.58, -.

Preparation of Phosphonium Salts

The phosphonium salts were prepared by adding a solution of the appropriate alkyl halide in acetone to the tertiary phosphine and allowing the solution to stand at room temperature. All operations were conducted under an anhydrous nitrogen atmosphere.

The previously unreported phosphonium salts synthesized and characterized along with their physical properties, identifying numbers, and analyses are recorded in Table 1.

Polymerization of Phosphonium Salts

Polymerizations were run in solution in H_2O (H) or DMF (D) in 5 ml sealed ampoules or in closed test tubes under a nitrogen atmosphere. The tubes were thoroughly flushed with dry nitrogen, and the initiator added before closing. The solutions in the ampoules were frozen and thawed twice under a dry nitrogen atmosphere, and the initiator added before sealing. The tubes were placed in an oven at 68° and the ampoules in an oil bath at 60° for the specified time. Initiators were: A, benzoin and UV; B, α,α' -azodiisobutyronitrile; C, t-butyl hydroperoxide; and D, benzoyl peroxide.

The polymerization conditions, yields, physical properties, and analyses of the polymers obtained are recorded in Table 2.

Poly-(diallylphenylphosphine oxide)

To 7.35 g of poly-(diallyldiphenylphosphonium bromide) dissolved in 25 ml of methanol was added a solution of 4 g of potassium hydroxide in 25 ml of water. The colorless solution immediately changed to yellow and, on heating, to orange, then red, and after 3 days at reflux a gummy brown solid separated out of the clear solution. The solution was decanted and the solid extracted in a soxhlet extractor with ethanol. The solution was evaporated until approximately 10 ml was left. This solution was then dropped slowly into stirred ether and a fine precipitate was collected. An IR spectrum showed strong absorption at 1170 cm^{-1} , thus, indicating that poly(diallylphenylphosphine oxide) was the product. A yield of 4.2 g (96%) of a light tan solid, softening at 260° and melting at 320° was collected. The intrinsic viscosity $[\eta]$, determined in ethanol, was 0.11. Anal. calc for: $(\text{C}_{12}\text{H}_{17}\text{PO}\cdot\text{H}_2\text{O})$: C, 64.39; H, 7.64; P, 13.80. Found: C, 64.89; H, 7.39; P, 12.67.

Preparation of Copolymer of Divinylphenylphosphine and Acrylonitrile

A. To a solution of 1.34 g (0.0083 mole) of divinylphenylphosphine and 0.456 g (0.0087 mole) of acrylonitrile dissolved in 5 g of dimethylformamide, in an ampoule, was added 1% (0.0183 g) of AIBN. The ampoule was sealed and allowed to stand in an oven at 60° for 4 days. The very fluid red solution was poured into 250 ml of dry ether. An orange solid precipitated, was filtered, and dried in a vacuum desiccator. A yield of 0.6 g (34%) of a brittle red solid softening at 110° and melting at 200° was obtained. The IR spectrum indicated that the phosphine had been largely converted to the phosphine oxide. The intrinsic viscosity $[\eta]$, determined in dimethylformamide, was 0.14. Anal.: P, 9.53% = 0.265 mole fraction of divinylphenylphosphine oxide; N, 11.89% = 0.732 mole fraction of acrylonitrile

B. To a solution of 1 g (0.00625 mole) of divinylphenylphosphine and 0.67 g (0.0128 mole) of acrylonitrile dissolved in 5 g of dimethylformamide, in an ampoule, was added 1% (0.0161 g) of AIBN. The ampoule was sealed and allowed to stand in an oven at 60° for 3 days. The brilliant red solution which formed was then poured into 200 ml of stirred ether and the precipitate collected and dried in a vacuum desiccator. A yield of 1.10 g (65%) of an orange solid, which softened at 120° and melted at 195° , was recovered. The IR spectrum showed that the phosphine had been converted to the phosphine oxide during the work-up. The intrinsic viscosity, determined in dimethylformamide, was 0.108. Anal.: P,

8.34% = 0.215 mole fraction divinylphenylphosphine oxide; N, 14.40% = 0.785 mole fraction of acrylonitrile.

ACKNOWLEDGMENTS

This work received financial support from the Air Force Office of Scientific Research under Contract No. AF 33(616)-5616, the Air Force Aeronautical Systems Division under Contract No. AF 33(616)-6887, and from the National Science Foundation under Grant No. 10011 for which the authors are grateful.

REFERENCES

- [1] G. B. Butler, "Cyclopolymerization" (A Review), in *Encyclopedia of Polymer Science and Technology*, **4**, 568 (1966).
- [2] M. Zanber, C. A. Vanderwerf, and E. W. McEwen, *J. Amer. Chem. Soc.*, **81**, 3806 (1959).
- [3] K. D. Berlin and G. B. Butler, *J. Amer. Chem. Soc.*, **82**, 2712 (1960).
- [4] R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**, 602 (1948).
- [5] G. B. Butler, *J. Polym. Sci.*, **48**, 279 (1960).

Accepted by editor November 18, 1970

Received for publication January 27, 1970