# POLYMERS WITH INORGANIC MAIN MOLECULAR CHAINS. SYNTHESIS OF POLYORGANOPHOSPHORALUMINOXANES\*

A. A. ZHDANOV, K. A. ANDRIANOV, A. A. KAZAKOVA and T. S. BAKSHEYEVA

Institute of Hetero-Organic Compounds, U.S.S.R. Academy of Sciences

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SEVERAL papers have been published recently on the synthesis of polymers, of which the molecular chains are formed of alternate atoms of aluminium, oxygen and phosphorus. Thus, e.g. polytriethylsiloxyaluminophosphates were obtained [1, 2] by reaction of tris-(triethylsiloxy)-aluminium with triethylsiloxyphosphinic acid or tris-(triethylsilyl)-phosphate. Polymers are also described in the literature which contain main molecular chains formed of alternating organophosphorus groups such as e.g. polymethylbutoxyphosphinaluminoxanes [3]. Several investigators have studied the synthesis of certain organic compounds of aluminium containing organophosphorus substitutes [4] and the synthesis has been described of poly(phenoxymethylphosphonoxy)-aluminoxanes [5] and polyorganosiloxyphosphoraluminoxanes [6] obtained by the interaction of tris-(triethylsiloxy)aluminium with methyl- and vinylphosphinic acids.

Our interest was attracted to a study of the interaction of aluminium alkoxide with acid chlorides of methylphosphinic acid and also with diethyl, dibutyl and diphenyl esters of methylphosphinic acid.

It is known from literature data [3, 5] that aluminium butylate reacts with acid chlorides of methylbutoxyphosphinic acid or methylphenoxyphosphinic acid with separation of butyl chloride. According to our observations, during the interaction of one mole of acid chloride of methylphosphinic acid with aluminium butoxide, the reaction takes place according to the following scheme:

$$nCH_{3}POCl_{2}+nAl(OC_{4}H_{9})_{3}\rightarrow Cl \begin{vmatrix} 0 \\ 0 \\ -P-O-Al-O- \\ 0 \\ -H_{3} \\ OC_{4}H_{9} \end{vmatrix} -C_{4}H_{9}(+2n-1)C_{4}H_{9}Cl.$$

We carried out this reaction in xylene at 120-130 °C. Butyl chloride separated during the reaction was distilled from the medium. The amount of butyl chloride formed (appr. 50% of theory) and determination of Cl content of the reaction products indicate that this process leads to the formation of comparatively lowmolecular weight products which are basically dimers of trimers. By studying

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the thermomechanical properties of the product obtained (see Figure, curve 1) it was shown that it has a glass temperature  $(T_g)$  in the range of 60–70°C. The determination of molecular weight of this product by an isopiestic method gave a value of 5200. These data can be explained by the fact that, during the reaction



Temperature/deformation curves: 1, 3-polybutoxyaluminomethyl phosphinate; 2, 4-polyethoxyaluminomethyl phosphinate.

of aluminium butoxide with the acid chloride of methylphosphinic acid, in addition to low-molecular weight dimers and trimers formed with separation of butyl chloride, compounds are also obtained which contain the chlorine atom on aluminium according to the following reaction:

$$\begin{array}{c} Al(OC_4H_9)_3 + CH_3POCl_2 \rightarrow \\ O \\ \rightarrow C_4H_9OAl - O - P - Cl + C_4H_9Cl \rightarrow C_4H_9OAl - O - POC_4H_9. \\ \downarrow \\ OC_4H_9 CH_3 \\ \end{array}$$

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The substances obtained containing terminal butoxygroups, are capable of further condensation with the separation of dibutyl ether and with the formation of polymers with a higher molecular weight according to the reaction:



The polymers obtained, as is shown by elementary analysis, contain a considerable quantity of chloride which cannot solely be explained by the presence of chlorine in the terminal groups. In order to study polyorganophosphoraluminoxane formation, we investigated the interaction of aluminium alkoxide with alkyl and aryl esters of methylphosphinic acid.

During the reaction of aluminium ethoxide with diethyl ester of methylphosphinic acid, diethyl ether separates and soluble polymer forms according to the reaction:

Elementary analysis of products forming in the initial stage of the reaction, accurately corresponds to the proposed scheme of the process when n=1. During further polycondensation, products with a higher molecular weight form with an elementary unit

$$-0-Al-O-P-,$$

which, in the initial stage of the reaction, melt and dissolve in organic solvents and during further polycondensation, gradually become infusible.

A temperature/deformation curve is shown in the Figure (curve 2) for polyethoxyaluminomethylphosphinate in the initial stage of polycondensation. It can be seen from the temperature/deformation curve that the polymer has a  $T_{\rm g}$  of 90-100°C and, at this stage, is soluble in organic solvents.

During polycondensation of aluminium butoxide with dibutyl ester of methylphosphinic acid, the reaction takes place in a similar manner, with the formation of polymer products according to the following scheme:

$$\begin{array}{c} \operatorname{Al} (\operatorname{OC}_{4}\operatorname{H}_{9})_{3} + \operatorname{CH}_{3}\operatorname{PO}(\operatorname{OC}_{4}\operatorname{H}_{9})_{2} \rightarrow \\ & \circ \operatorname{C}_{4}\operatorname{H}_{9} & \circ \operatorname{O}_{4}\operatorname{H}_{9} - \operatorname{O}_{2}\operatorname{P}_{-} \\ & \circ \operatorname{OC}_{4}\operatorname{H}_{9} & \operatorname{CH}_{3}_{-} \\ & \circ \operatorname{OC}_{4}\operatorname{H}_{9} + \operatorname{CH}_{3}_{-} \\ & n \end{array}$$

Elementary analysis of polycondensation products shows that the mean value n in the polymer formed is 4-6. In the initial stage of the reaction these polymers also melt and dissolve in organic solvents (ethyl and butyl alcohols). During further polycondensation, the polymers gradually become insoluble in organic solvents, but remain fusible.

To prove the formation during the reaction of a heteropolymer chain consisting of alternating atoms of aluminium, oxygen and phosphorus, we investigated the polycondensation of aluminium ethoxide with diphenyl ester of methylphosphinic acid. In this reaction, in addition to polyethoxyaluminomethylphosphinate, ethylphenyl ether (phenetole) was separated and identified as a by-product. Diphenyl or dibutyl ether formation has not been detected under the conditions investigated. These data indicate that during the interaction of aluminium butoxide or ethoxide with esters of methylphosphinic acid, polycondensation takes place with the formation of a heteropolymer which has, in the polymer hain, an Al—O—P group, as follows from the equation of the reaction

The Figure shows the temperature/deformation curves for polybutoxyaluminomethyl phosphinate (curve 3) and polyethoxyaluminomethyl phosphinate (curve 4) obtained by polycondensation of aluminium ethylate with diphenyl ester of methylphosphinic acid. Comparison of temperature/deformation data shows that polyethoxyaluminomethyl phosphinate (obtained from aluminium ethoxide and diethyl ester of methylphosphinic acid) in the initial stage of polycondensation has a  $T_g$  of 90–100°C and with increased polycondensation,  $T_g$ (curve 4) increases to 130–150°C. Polybutoxyaluminomethyl phosphinate, with a similar degree of polycondensation, has a lower  $T_g$ , of the order of 60–80°. This is explained by the fact that the butoxyl groups which are on the aluminium atom, unlike the ethoxyl groups, set up steric hindrances, impede the dense packing of chains and reduce the forces of association between the molecules, thus reducing  $T_g$ .

#### EXPERIMENTAL

Aluminium ethoxide and butoxide were obtained by conventional methods [7] Diethyl, dibutyl and diphenyl esters of methylphosphinic acid were obtained by esterification of acid chlorides of methylphosphinic acid with appropriate alcohols or phenol in the presence of diethyl aniline as acceptor of hydrogen chloride. Freshly distilled products with the following properties were used for the work:

 $\begin{array}{c} \mathrm{CH_3PO}(\mathrm{OC}_2\mathrm{H}_5)_2\mathrm{:}\mathrm{b.p.} \ 58-62^\circ\mathrm{C}/2 \ \mathrm{mm};\\ \mathrm{Found}, \ \%: \ \mathrm{C} \ 40\cdot01; \ 39\cdot83; \ \mathrm{H} \ 8\cdot54; \ 8\cdot71; \ \mathrm{P} \ 20\cdot76; \ 20\cdot84.\\ \mathrm{Calculated}, \ \%: \ \mathrm{C} \ 39\cdot47; \ \mathrm{H} \ 8\cdot61; \ \mathrm{P} \ 20\cdot37.\\ \mathrm{CH_3PO}(\mathrm{OC}_4\mathrm{H}_9)_2\mathrm{:} \ \mathrm{b.p.} \ 100-104^\circ\mathrm{C}/3 \ \mathrm{mm};\\ \mathrm{Found}, \ \%: \ \mathrm{C} \ 52\cdot12; \ 52\cdot27; \ \mathrm{H} \ 10\cdot10; \ 10\cdot23; \ \mathrm{P} \ 14\cdot71; \ 14\cdot43.\\ \mathrm{Calculated}, \ \%: \ \mathrm{C} \ 51\cdot91; \ \mathrm{H} \ 10\cdot16; \ \mathrm{P} \ 14\cdot88.\\ \mathrm{CH_3PO}(\mathrm{OC}_6\mathrm{H}_5)_2\mathrm{:} \mathrm{b.p.} \ 188-194^\circ\mathrm{C}/10 \ \mathrm{mm};\\ \mathrm{H} \ 10\cdot10; \ 10\cdot20; \ \mathrm{P} \ 14\cdot90; \ 10\cdot10; \ 10\cdot1$ 

Found, %; C 62·31; 62·76; H 5·23; 5·39; P 12·91; 12·76. Calculated, %: C 62·90; H 5·28; P 12·48.

Reaction of aluminium butoxide with acid chloride of methylphosphinic acid.  $45\cdot3$  g (0.34 mole) aluminium butoxide dissolved in xylene was placed in the reaction flask equipped with a stirrer, reflux condenser and dropping funnel and, while stirring, a solution was added of 84 g (0.34 mole) acid chloride of methylphosphinic acid in xylene. The total amount of xylene was 350 ml. The mixture was heated for 3 hours, stirring at 120°C, the solvent and

butyl chloride separated was distilled and the butyl chloride separated from the distillate by fractionation. The amount of butyl chloride separated was 42.7% of the stoichiometric. The solid polymer obtained was heated for a further 2 hours at 150°C and dried to constant weight *in vacuo* at 100°C. 87 g polymer was obtained.

> Found, %: C 30.45; 30.35; H 6.72; 6.70; P 10.90; 11.31; Al 10.05; 10.37; Cl 11.58; 11.41.

Reaction of aluminium ethylate with diethyl ester of methylphosphinic acid. 81 g (0.5 mole) aluminium ethylate was placed in a reaction flask provided with a strirrer, reflux condenser and dropping funnel and after melting, 76 g (0.5 mole) diethyl ester of methylphosphinic acid was added dropwise while stirring. The mixture was stirred at 100-110°C, collecting the distilled diethyl ester in a container, cooled with solid carbon dioxide. After heating for 15 hours, 34.9 g diethyl ester (47.2% of the stoichiometric) was collected and identified by refraction index and boiling point. The solid polymer obtained (120 g) was dried to constant weight *in vacuo* at 100°C.

| Found,                         | %: C 34·61; | 34·90; H     | 7.57; | 7.69; | Р            | 11.76; | 11.71; A | 11.31; | 11.74. |
|--------------------------------|-------------|--------------|-------|-------|--------------|--------|----------|--------|--------|
| $C_7H_{18}O_5AlP$ . Calculated | %: C 35.00; | $\mathbf{H}$ | 7.55; |       | $\mathbf{P}$ | 12.90; | A        | 11.24. |        |

Reaction of aluminium butoxide with dibutyl ester of methylphosphinic acid. 123 g (0.5 mole) aluminium butoxide and 104 g (0.5 mole) dibutyl ester of methylphosphinic acid were placed in the reaction flask of the device. The mixture was refluxed for 15 hours at 150–180°C and the dibutyl ester separated and distilled, gradually increasing the temperature of the reaction mixture to 180–200°C. The final dibutyl ester residues were eliminated in 5 hours at 190°C *in vacuo*. The total heating time of the mixture was 30 hours. The amount of dibutyl ester collected was 75 g (57.6% of the stoichiometric). From the reaction a solid transparent polymer (148 g) with a softening temperature of 60–80°C was obtained.

| Found,                  | %: C      | 36.26; | <b>36</b> ·28; | $\mathbf{H}$ | 6·98; | <b>6</b> ∙ <b>4</b> 6; | ${\bf P}$ | 14·43; | 14.74 |
|-------------------------|-----------|--------|----------------|--------------|-------|------------------------|-----------|--------|-------|
|                         | Al        | 11.40; | 10.87.         |              |       |                        |           |        |       |
| C33H78O21Al5P5. Calcula | ted, %: C | 36.00; |                | $\mathbf{H}$ | 7.14; |                        | Р         | 14.08; |       |
|                         | Al        | 12.26; |                |              |       |                        |           |        |       |

Reaction of aluminium ethoxide with diphenyl ester of methylphosphinic acid. A mixture of 81 g (0.5 mole) aluminium ethylate and 124 g (0.5 mole) diphenyl ester of methylphosphinic acid was refluxed for 40 hours at 180–190°C and the phenetole separated and distilled, gradually increasing the temperature of the reaction mixture to 210–220°C. For complete elimination of phenetole, the reaction mixture was heated in vacuo for 10 hours at 210°C. The amount of phenetole collected was 88.2 g (72.3% of the stoichiometric). The phenetole collected was identified by refraction index (found  $n_D^{20}$  1.5098; literature data giving  $n_D^{20}$ 1.5084) and b.p. (172°C). Dibutyl and diphenyl esters in the distilled reaction products were not detected. A transparent, yellowish polymer (115 g) with a softening point of 145–150°C was obtained in the residue.

| Found,  |             | %: | $\mathbf{C}$ | <b>33</b> ·17; | 33.51; | Η            | 5.76; | 5·93; | Ρ            | 13.95; | 14.37; |
|---|-------------|----|--------------|----------------|--------|--------------|-------|-------|--------------|--------|--------|
|   |             |    | Al           | 12.46;         | 12.10. |              |       |       |              |        |        |
| C <sub>11</sub> H <sub>18</sub> O <sub>5</sub> AlP. | Calculated, | %: | $\mathbf{C}$ | 32.91;         |        | $\mathbf{H}$ | 5.52; |       | $\mathbf{P}$ | 14.98; |        |
|   |             |    | Al           | <b>13</b> ·05. |        |              |       |       |              |        |        |

### CONCLUSIONS

The polycondensation of aluminium butylate and ethylate with dibutyl, diethyl and diphenyl esters of methylphosphinic acid was investigated. It is shown that, in this reaction, simple esters separate and polymers form with an inorganic chain containing sequentially linked atoms of aluminium, oxygen and phosphorus.

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### REFERENCES

- 1. K. A. ANDRIANOV, A. A. ZHDANOV and A. A. KAZAKOVA, Izv. Akad. Nauk. SSSR, Otd Khim. n. 466, 1959
- 2. K. A. ANDRIANOV, A. A. ZHDANOV and A. A. KAZAKOVA, Zh, obshch. khiimi 29: 1281, 1959
- 3. K. A. ANDRIANOV and V. M. NOVIKOV, Vysokomol. soyed. 1: 1930, 1959
- 4. K. A. ANDRIANOV, L. M. KHANANASHVILI, A. A. ZHDANOV and A. G. SHAPATIN, Zh. Obshch. khimii 31: 224, 1961
- 5. K. A. ANDRIANOV, L. M. KHANANASHVILI, A. A. KAZAKOVA and A. N. IVANOV, Zh. obshch. khimii 31: 228. 1961
- 6. K. A. ANDRIANOV and A. A. KAZAKOVA, Plast. massy, No. 3, 24, 1963
- 7. Sintezy organicheskikh preparatov. (Synthesis of Organic Compounds.) Sb. 2, Izd. in. lit. 1949

# STUDIES IN THE FIELD OF CYCLIC POLYMERIZATION AND COPOLYMERIZATION—XXIII. STUDY OF THE RADICAL POLYMERIZATION OF DIMETHYLVINYLETHINYLCARBINOL\*

S. G. MATSOYAN and N. M. MORLYAN

Institute of Organic Chemistry, Armenian S.S.R. Academy of Sciences

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UNTIL now, there has been hardly any information available in the literature on the properties and structure of polymers of 1,3-enine systems. It is well known that the study of polymerization of vinylacetylene hydrocarbons [1] in vinylacetylene alcohols [2] was held back by the impossibility of obtaining soluble final polymers. Partial polymerization products of dimethylvinylethinylcarbinol (DMVEC) have satisfactory adhesion and have, therefore, found wide applications in engineering for joining various materials [3]. According to Nazarov and Terekhov

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