Reports of the Academy of Sciences of the USSR

Academician of the Academy of Sciences of the Kazakh SSR S. R. RAFIKOV, M. E. ERGEBEKOV

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 160, No. 6

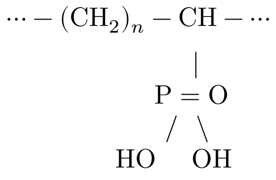
CHEMISTRY

Academician of the Academy of Sciences of the Kazakh SSR S. R. RAFIKOV,
M. E. ERGEBEKOV

SYNTHESIS AND STUDY OF POLYALKYLENEPHOSPHONATES OF CERTAIN METALS

Element-organic polymers of linear or three-dimensional structure, containing several heteroatoms simultaneously in the macromolecule, have been studied extremely little. Meanwhile, in a few cases—as, for example, in the study of polymetalloorganosiloxanes—polymers of this type possess very interesting and technically important properties ([1]). It seemed to us that element-organic polymers of the indicated type could also be obtained starting from oligomeric and high-molecular-weight polyalkylenephosphinic acids (PAPhA), formed during the hydrolysis of products of oxidative chlorophosphination of polyolefins ([2]) and solid paraffins ([3]).

In the present work are given the results of an investigation of the process of formation of polymeric salts of polyalkylenephosphinic acids with various metals and of the study of the properties of the resulting polyalkylenephosphonates (PAPh), with the aim of establishing their structure. As the starting polymers, polyalkylenephosphinic acids of the general formula were taken



$$\cdots-(CH_2)_n-\underset{\underset{HO\quad OH}{\overset{|}{P=O}}}{CH}-\cdots$$

Mainly, polymers with the following characteristics were used: high-molecular-weight PAPhA with phosphorus content 14.0% ($n = 9$), with characteristic viscosity in 0.1 N NaOH solution equal to 0.70 dl/g, and oligomeric PAPhA with phosphorus content 20.7% ($n = 4$), molecular weight ~ 2000. For X-ray diffraction studies, in addition, high-molecular-weight PAPhA with phosphorus contents of 2.9% ($n = 70$), 6.5% ($n = 27$), and 9.0% ($n = 18$) were taken.

Polyalkylenephosphonates of alkali metals were obtained by mixing aqueous solutions of PAPhA and alkalis containing calculated amounts of the components,

Fig. 1

Figure 1: Fig. 1

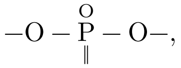
followed by evaporation of the reaction mixture to dryness on a water bath. PAPh of alkaline-earth and heavy metals were also obtained in aqueous solutions, by an exchange reaction between acetates or nitrates of the corresponding metals and PAPhA or their K and Na salts. The precipitate formed in this process was separated, thoroughly washed with water from excess nitrates and acetates, as well as from water-soluble fractions of PAPh, and dried at 70° in vacuum. Mixed PAPh were obtained in two stages: first an aqueous solution of PAPhA (about 2%) was titrated with alkali to pH 7, and then the calculated amount of nitrate or acetate of a heavy or alkaline-earth metal was added. The precipitate formed was separated, washed with water, and dried. PAPh insoluble in water of PAPhA were obtained by prolonged heating of their aqueous solutions of nitrates or acetates of the corresponding metals; the capacity of the samples was preliminarily checked by potentiometric titration with 0.1 N alkali.

It should be noted that the yield of practically water-insoluble PAPh depends on the molecular weight of the starting PAPhA and on the nature of the metal.

In the case of high-molecular-weight PAPAs, the yields of lead, calcium, barium, nickel, cobalt, cadmium, zinc, tin, iron, copper, and magnesium PAPAs, as well as mixed PAPAs of the indicated metals with sodium, were about 75-80%. In the case of oligomeric PAPAs, the yields of water-insoluble PAPAs were considerably lower, with the exception of calcium and lead PAPAs and mixed sodium PAPAs with calcium, lead, magnesium, and iron. Acidic PAPAs lost their solubility in water upon heating at a comparatively low temperature (100°). In all cases, the metal content in the PAPAs obtained was 10-15% lower than the theoretically calculated value, which indicated incomplete substitution of the protons in the PAPAs taken under the conditions studied. This was also indicated by the persistence of a weak line at 2300-2400 cm^{-1} in the IR spectra, characteristic of P—OH groups. The PAPAs obtained were subjected to comprehensive study: elemental analysis was performed, IR spectra, thermograms, and derivatograms were recorded, thermomechanical properties, strength characteristics of pressed specimens, solubility and swelling in organic solvents (4), and dielectric properties were determined.

Fig. 1. IR absorption spectra:
a —polyethylene; **b** —PAPA containing 14% phosphorus; **c** —lead PAPA

Comparison of the IR spectra of polyethylene (Fig. 1a) and the PAPA obtained from it (Fig. 1b) shows that the spectrum of the latter contains a broad absorption band in the region of about 900-1100 cm^{-1}, characteristic of the grouping



$$-O-\underset{\|}{\overset{O}{P}}-O-,$$

a broad diffuse band in the region 1600-1700 cm^{-1}, apparently due to moisture that is difficult to remove, and an intense broad band in the region 2300-2400 cm^{-1}, which may be assigned to vibrations of –OH groups bonded to phosphorus. The intensity of this band is greatly weakened on passing to polyalkylene phosphinates (for example, lead, Fig. 1c), although it does not disappear completely.

It is of great interest to compare the Debye-Scherrer diagrams of PAPAs and PAPs (Fig. 2), which have different compositions. If the initial polyethylene has a clearly expressed crystalline structure (Fig. 2a), then as the content of phosphinic acid groups in the macromolecule increases, the interference rings become increasingly diffuse and disappear completely at a phosphorus content of 9% or more (i.e., $n \leq 18$). For the corresponding PAPs of heavy metals, a completely opposite picture is observed: the crystallinity of the structure increases with increasing content of phosphonate groups (Fig. 2c′, b′, g′, d′). The most clearly expressed crystalline structures are those of lead PAPs with $n = 9$ and 18 (Fig. 2e′, d′). At the same time, it may be noted that zinc and calcium PAPs have an amorphous structure (Fig. 2e, e′). The same is characteristic of all PAPs of monovalent and divalent metals.

This phenomenon can be explained by the fact that, at a certain statistically average frequency of phosphinic acid groups, the crystalline lattice of polyethylene is disrupted, while at a sufficient concentration of phosphonate groups a crystalline lattice appears that is characteristic of the corresponding phosphates. Thus, for example, in the Debye-Scherrer diagrams of lead PAPs, lines appear at 2.9799; 2.0702; 1.3285, characteristic of lead phosphates (5).

The difference in the structure of polyvalent heavy metals (Pb, Sn, Co) and mono- and divalent metals is apparently associated with the fact that in the

To the article by S. R. Rafikov and M. E. Ergebekov

[Figure 2]

Fig. 2. X-ray diffraction patterns: *a*—polyethylene; PAFK with phosphorus content: —2.9%; —7%; —9%; —14%; ′, ′, ′, ′—the corresponding lead polyalkylene phosphonates; —zinc PAF and ′—calcium PAF from PAFK containing 14% phosphorus.

the latter are dominated by intramolecular bonds (type I), whereas the former are dominated by intermolecular bonds (type II):

[chemical structural scheme labeled **Type I**]

[chemical structural scheme labeled **Type II**]

Most of the PAF obtained are very heat-resistant polymers, as can be seen from the thermomechanical curves shown in Fig. 3. With the exception of barium PAF, they soften at about 200° and do not melt, although they are capable of deformation, and by pressing them under pressure strong films, disks, and bars can be obtained.

Fig. 3. Thermomechanical curves: **1** –polyethylene; **3** –PAFK containing 14% phosphorus (from polyethylene); polyalkylene phosphonates: **2** –lead; **4** –barium; **5** –calcium; **6** –1/2 calcium (acidic).

The strength characteristics of PAF depend both on the ratio of the organic and inorganic parts of the macromolecules and on the nature of the metal (Table 1).

Table 1

Mechanical properties of polyalkylenephosphinic acids (PAFK) and salts (PAF)

Polymers	Phosphorus content in PAFK, %	n	Tensile strength, kg/mm^2	Relative elongation, %
Polyethylene	0	> 2000	150	565
PAFK	9	18	150	250
Lead PAF	9	18	200	40
Barium PAF	9	18	220	95
Calcium PAF	9	18	190	40
PAFK	6.5	27	150	390
Lead PAF	6.5	27	185	100
Calcium PAF	6.5	27	175	110

Table 2

Swelling of PAFK and PAF in benzene at 70°

Phosphorus content in PAFK, %	n	PAFK, %	Polyalkylene phosphonates, % Pb	Polyalkylene phosphonates, % Ba	Polyalkylene phosphonates, % Ca	Polyalkylene phosphonates, % Ni
2.9	70	410	–	–	–	–
6.5	27	220	250	–	270	100
9.0	18	200	280	–	320	150
14.0	9	50	10	40	20	50
20.0	4	–	–	–	10	–

The ratio of hydrocarbon and nonhydrocarbon segments of the macromolecule has an especially sharp effect on the ability of PAFK and PAF to swell in benzene at 70°, i.e., under conditions in which a pure polymeric hydrocarbon (high-density polyethylene) dissolves completely (Table 2). The introduction of phosphinic-acid groups, even in the amount of one group per 70 methylene units, completely suppresses solubility, apparently owing to the formation of strong intermolecular hydrogen bonds. The swelling of the polymer decreases sharply with a reduction in the relative fraction of the hydrocarbon part of the macromolecule, regardless of whether the free acid or its salt with various metals is present (Table 2).

On the thermogravimetric curves of PAF and PAFK with a high content of methylene groups there are no clearly expressed peaks indicating phase transitions, which is in agreement with the X-ray data. The small peaks that are present reflect the evaporation of bound water, while the exothermic peaks in the high-temperature region reflect the most intense decomposition.

Table 3

Weight losses during thermooxidative destruction

Temp., °C	Polyethylene %	Polyethylene-phosphinic acid (14% P), %	Pb	Ni	Zn	Ba	Na
100	0	0	0	0	0	0	0
200	0	4.3	1.0	5.5	3.7	6.8	11.6
300	2.6	6.5	1.0	9.2	5.6	11.3	17.5
400	23.9	43.9	4.2	12.9	13.2	18.1	23.3
500	97.4	57.1	24.5	49.9	43.4	54.5	46.7

In Table 3 are given the relative weight losses under conditions of thermooxidation with continuous increase of temperature, found in thermogravimetric measurements of various PAF samples. As is evident from these data, PAFK and PAF begin to lose weight at comparatively low temperatures (about 200°), when polyethylene is still quite stable. However, it should be noted that the weight losses at these temperatures are due to the removal of bound water. At higher temperatures (400° and above), PAF are more thermostable than polyethylene.

In view of the presence in the macromolecule of polar groups capable of ionization, the dielectric properties of PAFK and PAF are lower than those of polyethylene (Table 4). However, it may be noted that deterioration of the dielectric properties occurs only at a considerable content of polar groups.

Table 4

Electrical properties of polyalkylenephosphinic acids and their salts

Polymer	n	Sample thickness d, mm	Specific volume resistivity, ohm • cm	Dielectric-loss tangent, 10^6 Hz	Dielectric constant	Breakdown voltage, kV/mm
Polyethylene	>2000	1.30	$2.9 \cdot 10^{15}$	0.00073	2.5	29.2
PAFK, 1.7% P	120	1.40	$4.4 \cdot 10^{15}$	0.0030	2.6	27.8
PAFK, 2.9% P	70	1.28	$9.6 \cdot 10^{15}$	0.0028	2.6	30.4
PAFK, 6.5% P	27	1.20	$3.3 \cdot 10^{9}$	0.0951	3.5	22.5
PAF, Ca	27	1.37	$1.2 \cdot 10^{13}$	0.0113	3.1	22.7
PAF, Pb	27	1.40	$1.8 \cdot 10^{10}$	0.0371	3.8	25.0

The data presented show that polyalkylenephosphinic acids obtained from polyethylene by a comparatively simple method are highly reactive polymeric compounds, and that on their basis organoelement polymers of linear or spatial structure can be synthesized, containing simultaneously phosphorus and various metals and possessing valuable properties.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Institute of Chemical Sciences
Academy of Sciences of the Kazakh SSR

Received
2 July 1964

CITED LITERATURE

1. K. A. Andrianov, *Polymers with Inorganic Main Chains of Molecules*, monograph, Publishing House of the Academy of Sciences of the USSR, 1962; S. R. Rafikov, K. A. Andrianov et al., *High-Molecular Compounds*, **4**, 1581 (1962).
2. I. R. Schroeder, W. P. Sopchak, *J. Polym. Sci.*, **49**, 417 (1960).
3. I. P. Shreter, V. P. Soshak, *Chemistry and Technology of Polymers*, No. 12, 3 (1961).

4. Engl. pat. 648328, *Chem. Abstr.*, **45**, 7136 (1951).
5. A. A. Dontsov, B. A. Dogadkin, *Kolloidnyi zhurnal*, **23**, 346 (1961).
6. L. I. Mirkin, *Handbook of X-ray Structural Analysis of Polycrystals*, 1961.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.