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Inorganic Coordination Polymers, 20^{*)}

Zinc(II) Phosphinate Polymers and Copolymers Containing Phenyl Sulfone Side Groups

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SUMMARY:

The syntheses and characterizations of a series of new phosphinic acids and the zinc polymers and copolymers prepared from them are reported. These compositions are characterized by the presence of phenyl sulfone side groups. The zinc derivatives were found to be among the thermally most stable tractable poly(metal phosphinates) yet studied.

ZUSAMMENFASSUNG:

Über die Darstellung und Charakterisierung einer Reihe neuer Phosphinsäuren und der davon abgeleiteten Zinkpolymere und Copolymere wird berichtet. Diese Verbindungen, die durch Anwesenheit von Phenylsulfon-Seitengruppen charakterisiert sind, gehören zu den bislang thermisch stabilsten verarbeitbaren Poly(metallphosphinaten).

Introduction

As part of a general program we have investigated the effects of varying the organic moieties (R, R') on the properties of the polymeric zinc phosphinates. These polymers contain tetrahedral zinc(II) centers and symmetrical bridging $O_{,O'}$ -phosphinate groups in polymeric structures, such as A or $B^{2,3)}$.

It was found earlier that the zinc phosphinates with alkyl chains on the phosphorus were melt and solution processable (tractable)^{4,5}; however, these phosphinates also have relatively low thermal stability. More recently, in an attempt to prepare tractable polymeric zinc(II) bisphosphinates with

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improved thermal stability, we synthesized a number of phosphinic acids with organic side groups composed of short polyphenylene and poly(oxyphenylene) chains⁶⁾. Some of these materials were tractable and showed a significant improvement in terms of both thermal and oxidative stability as compared to the zinc(II) phosphinates with alkyl chain side groups. In an effort to obtain melt and/or solution processable polymeric phosphinates with even better thermal stability than those previously studied, we have prepared a series of polymeric zinc(II) bisphosphinates which contain phenyl sulfone side groups and report here our results.

The following reaction scheme shows the preparation of phenyl-4-[4-(phenylsulfonyl)phenylsulfonyl]phenylphosphinic acid (8). The phosphinic acids 9 and 10 were prepared in the same manner as 8, and 11 was prepared from 4-bromophenyl phenyl sulfone and diethylamidophosphic dichloride (mole ratio 2:1) with butyllithium (see Exptl. Part).



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Experimental Part

Miscellaneous

Elemental analyses were performed by standard methods in the Pennwalt Analytical Department.

IR spectra were recorded with a "Perkin Elmer 337" grating spectrophotometer on either Nujol or hexachlorobutadiene mulls between KBr discs. Molecular weight data were obtained at various concentrations with a thermoelectric vapor pressure molecular weight apparatus similar to that used by *Wachter* and *Simon*⁷). Thermogravimetric data were recorded on a Dupont 950 thermogravimetric analyzer. A "Bendix Time of Flight" (Model 12) mass spectrometer was used to determine the thermal decomposition products. Spectra were obtained at increasing inlet probe temperatures using an electron energy of 70 eV ($eV \approx 1,6021 \cdot 10^{-19}$ J).

Materials

All the chemical reagents and solvents employed were obtained from commercial sources unless otherwise indicated. They were of reagent quality and were used as received. A solution of tetrafluoroboric acid was prepared by dissolving 184g of boric acid in 454g of 48% hydrofluoric acid. The syntheses of bis[4-(4-biphenylyloxy)phenyl]-phosphinic acid and bis(*p*-phenoxyphenyl) hydrogen phosphate have been described earlier⁶.

4-(N,N-Dimethylthiocarbamoyloxy)phenyl phenyl sulfone (1): To a slurry of 190g (0,81 mol) of 4-(phenylsulfonyl)phenol⁸) in a solution of 32,0g (0,81 mol) of sodium hydroxide in 21 of water was added slowly with stirring a solution of 112g (0,9 mol) of N,N-dimethylthiocarbamoyl chloride in 800 ml of ether while the temp. of the reaction was maintained in the 0–10 °C range with external cooling. After the addition was complete, the basicity of the solution was adjusted to pH 8 by addition of dilute sodium hydroxide. The reaction mixture was stirred at room temp. for 2 h, and 187,5g (72%) of crude product, mp 91–110 °C, was then collected. After the analytical sample was recrystallized from ethanol, it melted at 134–135,5°C.

C ₁₅ H ₁₅ NO ₃ S ₂ (321,4)	Calc.	C 56,1	H 4,70
	Found	C 56,0	H 5,02

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4-(N,N-Dimethylcarbamoylthio)phenyl phenyl sulfone (2): Heating of crude solid 1 for 3 h at 160 °C with subsequent crystallization from ethanol gave 18 g of crude product, mp 107-111 °C. An analytical sample, which was recrystallized from ethanol, melted at 121-125 °C.

C ₁₅ H ₁₅ NO ₃ S ₂ (321,4)	Calc.	C 56,1	H 4,70
	Found	C 55.9	H 4.79

Confirmation of the rearrangement was obtained from the appearance of an amide CO band at $1640 \,\mathrm{cm}^{-1}$ in the IR spectrum.

4-(4-Nitrophenylsulfonyl)phenyl phenyl sulfone (5): The thioester 2 was hydrolyzed to 4-(phenylsulfonyl)thiophenol $(3)^{9}$ which was then reacted with 4-chloronitrobenzene to yield 4-nitrophenyl 4-(phenylsulfonyl)phenyl sulfide $(4)^{9}$. Then, a solution of 8,1 g (0,05 mol) of potassium permanganate in 150 ml of water was added slowly to a solution of 14 g (0,038 mol) of 4 in 250 ml of acetic acid. The resulting mixture was stirred for 1,5 h, warmed on a steam bath for another 1,5 h, and then the excess manganese dioxide was decomposed with sodium bisulfite. The reaction mixture was then cooled with an equal volume of ice, and 14,2 g (88 %) of product, mp 289–298 °C, was collected by filtration.

C ₁₈ H ₁₃ NO ₆ S ₂ (403,4)	Calc.	C 53,6	Н 3,25	N 3,47
	Found	C 53,4	H 3,35	N 3,68

4-(4-Aminophenylsulfonyl)phenyl phenyl sulfone (6): A warm slurry of 13,5 g (0,034 mol) of 5 in 450 ml of N,N-dimethylformamide (DMF) was hydrogenated at an initial hydrogen pressure of 60 psi (1 psi= $6,89475 \cdot 10^5$ N m⁻²) and in the presence of 10 ml of a slurry of Raney nickel in ethanol. The theoretical amount of hydrogen was consumed in 6 h. The catalyst was removed by filtration, and the filtrate was concentrated to dryness. The residue was crystallized in 50 ml of ethanol to give 10 g (79%) of product, mp 231-235 °C. An analytical sample was recrystallized from ethanol to give material melting at 234,5-237 °C.

4-[4-(Phenylsulfonyl)phenylsulfonyl]benzenediazonium tetraf luoroborate (7): To a slurry of 10g (0,027 mol) of finely ground **6** in 200 ml of tetrafluoroboric acid solution was added slowly 5,0g (0,073 mol) of sodium nitrite in 10 ml of water, with cooling to 0–10 °C. The resulting solid was collected by filtration, washed with 10 ml of cold aqueous tetrafluoroboric acid, then 10 ml of ethanol, and finally 50 ml of ether, and dried. Yield 11 g (95%); mp 120–130 °C.

Phenyl-4-[4-(phenylsulfonyl)phenylsulfonyl]phenylphosphinic acid (8): A slurry of 11 g (0,026 mol) of 7, 0,1 g of copper(I) bromide, and 5 ml (0,06 mol) of dichlorophenylphosphine in 100 ml of ethyl acetate was warmed at 40–50 °C for 30 min. The resulting solution was cooled, and 200 ml of water was added. Ethyl acetate and volatile by-products were removed by steam distillation, and the crude product was collected by filtration. This solid was partially dissolved in 500 ml of 5% potassium carbonate and reprecipitated

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with hydrochloric acid to give 3,1 g of solid, mp 125–150 °C. Recrystallization from 200 ml of ethanol gave 2,0 g (15%) of the phosphinic acid, mp 227–230 °C.

$C_{24}H_{19}O_6PS_2$ (498,5)	Calc.	C 57,8	H 3,84	P 6,21	S 12,86
	Found	C 57,6	H 4,04	P 6,17	S 12,80

Phenyl-[3-(phenylsulfonyl)phenyl]phosphinic acid (9): This acid was prepared in the same manner as 8 starting from 3-aminophenyl phenyl sulfone^{10,11)}. Recrystallization from aqueous ethanol gave a 39,5% yield of final product, mp 175–177°C.

C ₁₈ H ₁₅ O ₄ PS (358,4)	Calc.	C 60,3	H 4,23	P 8,64
	Found	C 60,3	H 4,52	P 8,47

Phenyl-[4-(phenylsulfonyl)phenyl]phosphinic acid (10): This acid was also synthesized in a manner analogous to 9 but using 4-aminophenyl phenyl sulfone^{12,13)}. The final product was crystallized from 80% ethanol to give a 45% yield, m.p. 225–228 °C.

C ₁₈ H ₁₅ O ₄ PS (358,4)	Calc.	C 60,3	H 4,23	P 8,64	S 8,95
	Found	C 60.2	H 4.49	P 8.77	S 9.49

Bis[4-(phenylsulfonyl)phenyl]phosphinic acid (11): A solution of 30 g (0,1 mol) of 4-bromophenyl phenyl sulfone¹⁴⁾ in 500 ml of tetrahydrofuran was cooled to -100 °C in a liquid nitrogen/toluene slush, and 42 ml (0,1 mol) of 2,38 M butyllithium in hexane was added. After about 10 min, 9,5 g (0,05 mol) of diethylamidophosphonic dichloride¹⁵⁾ was added, and the reaction mixture was allowed to warm slowly to room temp. After 18 h at room temp., 125 ml of 6 M HCl was added, and the reaction was heated under reflux for 4 h. The tetrahydrofuran (THF) was removed by distillation, and 7,5 g of almost white solid, mp 115–130 °C, was collected by filtration. This solid was recrystallized from tetrahydrofuran to give 7,0g (28%) of product, mp 155–165 °C.

$C_{24}H_{19}O_6PS_2$ (498,5)	Calc.	C 57,8	H 3,84	P 6,21	S 12,86
	Found	C 58,5	H 4,55	P 6,02	S 13,06

This reaction was repeated using a greater ratio of the bromide to diethyl amidophosphonic dichloride without significant increase in yield.

Syntheses of zinc phosphinate polymers

All of the zinc bisphosphinates were synthesized by the same general procedure. The phosphinic acid (or acids for a copolymer) was first neutralized with K_2CO_3 in a THF/water mixture by treating it with the stoichiometric amount of K_2CO_3 (0,5 mol per 1 mol of acid). An excess of K_2CO_3 was avoided, so that zinc hydroxy phosphinates would not be formed in the next step. The potassium phosphinate solution was then added slowly with stirring to an aqueous solution of zinc sulfate (0,5 mol of zinc sulfate per 1 mol of potassium phosphinate). After the addition was completed, the solution was heated to and held at boiling until all the THF was removed. The precipitate which formed was filtered off, washed with water, and dried in a vacuum desiccator. Yields: $\geq 85\%$.

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Analytical
Tab. 1.

Substance	Bruttoformula (Molecular weight)		Eleme	ental analy H	sis Zn	Softening point in °C	Molecular weight ^{a)} in CHCl ₃
Poly{Bis[μ-bis[4-(phenylsul- fonyl)phenyl]phosphinato] Zinc(11), (12)	(C ₄₈ H ₃₆ O ₁₂ P ₂ S ₄ Zn) _n (1060,4)	Calc. Found	54,4 54,0	3,42 3,42	6,16 6,08	> 400	(q
Poly (Bis[μ-pheny]-[4- (phenylsulfonyl)phenyl]- nhosnhinato] Zincf11% (13a)	(C ₃₆ H ₂₈ O ₈ P ₂ S ₂ Zn) _n (780,1)	Calc. Found	55,4 55,0	3,62 4,00	8,38 7,98	180	(q
Poly (Bis[μ-phenyl-4-[4-(phenyl-sulfonyl)phenylsulfonyl]phenylsulfonyl]phenylsulfonyl]phenyl	$(C_{48}H_{36}O_{12}P_2S_4Zn)_n$ (1060,4)	Calc. Found	54,4 54,1	3,42 4,06	6,16 5,72	400	(q
Poly {Bis[μ -phenyl-[3-(phenyl-sulfonyl)phenyl]phosphinato] Zinc(II)} (14)	(C ₃₆ H ₂₈ O ₈ P ₂ S ₂ Zn) _n (780,1)	Calc. Found	55,4 55,7	3,62 4,03	8,38 8,40	140	20000 (8000)
Poly{[μ -phenyl-[3-(phenyl- sulfonyl)phenyl]phosphinato] [μ -phenyl-[4-phenylsulfonyl)- phenyl]-phosphinato] Zinc(II)}	(C ₃₆ H ₂₈ O ₈ P ₂ S ₂ Zn) _n (780,1)	Calc. Found	55,4 55,4	3,62 3,94	8,38 7,93	155	28 000 (15 000)
Poly{ $[\mu$ -phenyl-[4-(phenyl- sulfonyl)phenyl]phosphinato] $[\mu$ -bis-(4-phenoxyphenyl)phos- phinato] Zinc(11) (16)	(C ₄₂ H ₃₂ O ₁₀ P ₂ SZn) _n (856,1)	Calc. Found	58,9 59,3	3,77 4,27	7,64 7,32	80	5030 (4890)
Poly{[μ -phenyi-[4-(phenyl- sulfonyl)phenyl]phosphinato] [μ -bis-(4-biphenylyloxy- phenyl)phosphinato] Zinc(II)}	(C ₅₄ H ₄₀ O ₈ P ₂ SZn) _n (976,3)	Calc. Found	66,4 67,6	4,13 3,77	6,70 6,83	140	(q

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(11)

^{a)} Values in parenthesis are for unpurified CHCl₃ (containing 0,75% C₂H₅OH); limit of error: \pm 5%. ^{b)} Insoluble in CHCl₃.

Tab. 1 gives analytical and softening point data for the seven polymeric zinc bisphosphinates prepared and molecular weights for the three polymers that are soluble in chloroform. The analytical data for copolymer 17 suggests that it is not exactly a 1:1 copolymer but contains a slight excess of bis(4-biphenylyloxyphenyl)phosphinate groups.

Results

Structure and properties of the polymeric zinc bisphosphinates

The structure of the new zinc phosphinates 12, 13a, b, 15, 16 and 17 probably consists of tetrahedral zinc atoms held together by symmetrical



O,O'-phosphinate groups **A** and **B** as do all of the previously studied zinc polymers of this type²⁻⁶⁾.

Except for 13b and 17 all of these zinc phosphinates are soluble in organic solvents such as dimethylformamide, tetrahydrofuran, and/or chloroform. The molecular weights of those that are soluble in chloroform were measured and indicate that the chain lengths vary from 6 to 36 units in this solvent. The molecular weight values obtained in unpurified chloroform (which contains 0,75% ethanol) for 14 and 15 are considerably lower than in chloroform which contains no ethanol. This phenomenon is caused by the dissociation of the polymeric chains due to the presence of coordinating molecules of ethanol and similar effects have been observed in molecular weight studies of various beryllium phosphinates¹⁶. The low molecular weight observed for 16 and the observation that this value is practically unaffected by the presence of ethanol suggests that a coordinating impurity may be present in the bulk solid.

The softening points of the polymers tend to be higher than those of the copolymers, a result which is similar to that found for other zinc phosphinate copolymers⁴). All of these materials, when fused, were brittle glossy solids at room temperature.

Stability Studies

The thermal stabilities of the various zinc phosphinates were measured in both nitrogen and air, and the results are given in Tab. 2.

It is apparent from these data that the zinc phosphinates containing phenyl sulfone groups are among the thermally most stable metal phosphinates studied to date. Several trends in thermal stability were found both in these polymers and the polymers containing polyphenylene and poly(oxyphenylene) side groups⁶. Increasing the size of a side group beyond two phenyl groups causes a marked decrease in thermal stability irrespective of whether the phenyl groups are attached directly to one another or through an O or SO₂ group. In addition, the polymers with *ortho*- or *meta*-substituted side groups were less stable than those with para substituted groups, a behaviour that can be explained by the fact that free rotation of the groups is hindered in the case of both *ortho*- and *meta*-substitution, thus making more thermal energy available for bond breaking.

The presence of sulfonyl groups in the backbone of various poly(aryl sulfones) has been reported to impart resistance to air oxidation at high temperatures¹⁷.

Substance	Atmosphere ^{a)}	Tem	Temp. in °C for indicated weight loss ^{b)}				
	•	Initial	2%	5%	10%		
12	N	440	450	485	495		
	Α	440	450	480	500		
13a	N	440	450	465	475		
	А	450	460	495	500		
13b	Ν	385	400	440	460		
	А	350	400	450	470		
14	Ν	410	415	440	455		
	А	355	400	440	455		
15	А	365	400	450	460		
16	А	140	150	310	350		
17	А	155	165	300	360		

Tab. 2. Thermogravimetry of zinc phosphinate polymers and copolymers

^{a)} Atmosphere during the run: N = nitrogen, A = air.

^{b)} Heating rate: 5°C/min.

In these polymers the sulfonyl groups act as electron sinks and deactivate the aromatic chain units. It is probable that a similar effect occurs in the aryl sulfone side groups of the zinc phosphinates. Indeed, the thermal decomposition of the zinc phosphinates with aryl sulfone groups in nitrogen is nearly the same as that in air.

Several of these thermal decompositions were followed by mass spectra, and the results are given in the following scheme.

Decomposition scheme:

Primary products in the upper lines



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In general the decomposition products consisted of non-phosphorus-containing organic groups derived from the side groups of the phosphinate. Thus, the decomposition of these polymers begins with the breaking of P—C and C—S bonds, leaving the polymer backbone intact. The degradation of the polysulfone side groups appears to involve elimination of sulfur dioxide similar to that observed for other polymeric aromatic sulfones¹⁸⁾.

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