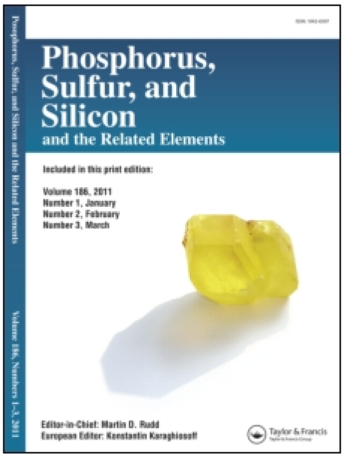

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NOVEL MOLECULAR PHOSPHORUS SULFIDES WITH S/P HIGHER THAN 2.5. I. GENESIS AND CHARACTERIZATION BY PHYSICAL AND CHEMICAL METHODS

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PS_x alloys ($x = 2.75$ to 71.5), prepared by heating P_4S_{10} with excess sulfur at 300–312°C, have been extensively extracted by carbon disulfide at room temperature. The solutions have been shown by ^{31}P NMR to contain, besides P_4S_{10} and P_4S_9, a number of novel species, hereafter called soluble Phosphorus Poly-(or Per-)sulfides (PPS). Electronic and IR spectra are reported. All attempts at separating pure individual PPS have failed. Soluble PPS are metastable, with a definite tendency to polymerize. They are selectively desulfurized by Ph_3P. They decolorize Diphenylpicrylhydrazyl instantly. NMR monitored experiments led to a classification of soluble PPS according to their rate of hydrolysis.

PS_x melts, with x between ~3 and ~50 form glasses upon cooling, especially when quenched. The physical properties of these materials have been reported.[1–6] Their solubility in carbon disulfide or benzene was said to be maximal near the borders of the vitreous domain—where the content of elemental S or P_4S_{10} is expected to be substantial—but very low near $x = 6$;[3,5] accordingly, glassy PS_x with $x >$ ~3—hereafter called glassy Phosphorus *Poly-* (or *Per-*)*sulfides* (PPS)†—were described in the past as cross-linked statistical polymers, containing P–S_n–P bridges, more or less mixed with sulfur and/or P_4S_{10}.[2,4–7] A quite recent patent[8] however, states that the soluble phase contained in solid PS_x ($x = 2.62$ to 4) may incorporate P–S_n–P links as well, in addition to P_4S_{10} and elemental sulfur.

RESULTS[9]

Characterization of Soluble PPS by Physical Methods

We found it feasible, using prolonged stirring with carbon disulfide at room temperature, to dissolve large amounts of any one glassy PPS, whatever its P content (Table I). That the solutions thus obtained contain novel species, namely soluble PPS, besides P_4S_{10} and P_4S_9, was clearly established by ^{31}P NMR; Table II details the ten major PPS signals, which were all seemingly devoid of simple (first order) P–S–P coupling. No pairing between these signals was evident too, as indicated by the apparently independent variation of their integrals.

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† The proposed term *Persulfide*, implying the presence of S–S bonds, is more specific than the more general term *Polysulfide*.

TABLE I

Dissolution of glassy PS_x in CS_2

Glassy PS_x x	Extraction step No	CS_2 ml/g PS_x	Stirring h	Dissolved fraction % wt basis	Dissolved fraction % P basis	S/P
3.5	1	249	1	28.8	26.1	4.0
	2	176	13	69.3	68.4	3.6
	total	425	14	98.1	94.5	
4.0	1	1000	24	54.3	40.0	5.8
6.0	1	168	54	60	50	7.3
	2	75	56	30	24	7.7
	total	243	110	90	74	
15.0	1	1000	74	88.5	48.3	28.2
15.0	1	36	16	28.7	11.4	39.3
	2	16	39	12.3	13.1	14.1
	3	8	54	4.2	5.2	12.1
	4	8	95	7.9	6.9	17.3
	5	16	99	5.1	5.4	14.2
	total	84	303	58.2	42.0	
71.5	1	13.2	18	76.2	28.5	191
	2	5.9	47	7.1	8.1	
	total	19.1	65	83.3	36.6	

TABLE II

^{31}P NMR signals of dissolved phosphorus persulfides (solvent CS_2)

Original solid PS_x	S/P	2.75[a]	3.5	4.5	6	10	15	19.75	71.5
Dissolved fraction	%, P basis	60	58.5	32.8	50	23.5	11.4	24.3	28.5
	S/P	2.76	3.61	5.85	7.3	17.4	39.3	39.8	191
δ (ppm)		Relative integral (%)[b]							
130.05	(6)[b]	—	—	2	4	—	13	15	16
116.32	±0.05	0.3	2	8	11	~30	13	13	10
89.54	±0.05	0.8	22	35	33	~28	14	9.5	—
88.64	±0.02	—	—	—	—	—	5	8.5	12
61.7	(4)[b]	—	—	—	5	—	9	13	10
55.4 to 63.8	P_4S_9[c]	27	21	7	—	—	—	—	—
56.3	P_4S_{10}	70	20	12	—	—	—	—	—
54.9	(6)[b]	—	—	6	4	~15	15	4	9
49.5	(4)[b]	—	—	—	—	—	8	12	13
36.9	(3)[b]	1.5	4	13	21	~27	19	20	30
33.8	(2)[b]	—	2	—	—	—	4	4	—
18.54	±0.06	—	20	17	22	—	—	1	—
weak signals at δ (ppm)		113.1	102.5 102.0 93.8 40.8		71				

[a] Crystalline solid; all other solid PS_x were vitreous.

[b] The signal was frequently wide or multiple (in brackets: maximum number of observed lines), or its chemical shift somewhat variable.

[c] Second order spectrum.[16]

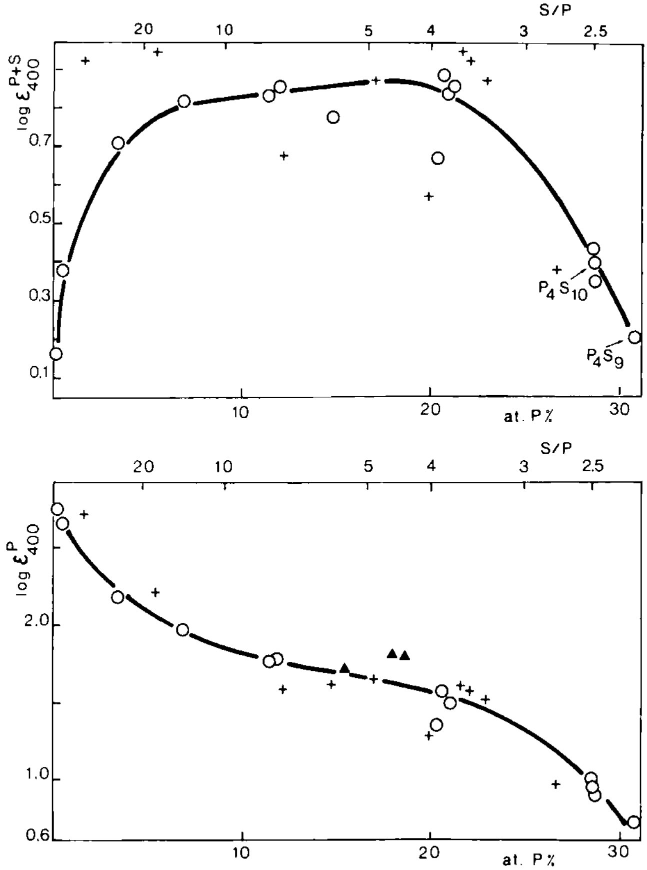

FIGURE 1 Absorption at 400 nm of PPS dissolved in CS_2. Atomic absorptivities ε are in l (g-at.) cm^{-1}. Circles refer to solutions afforded by exhaustive extraction of the original solid PS_x; crosses refer to partial or stepwise dissolution. Black triangles represent the absorptivity of PPS on their own i.e. after deducting the contribution of P_4S_{10} and P_4S_9 (see text).

Further evidence came from the electronic spectra. The crude PPS solutions were deep yellow, whereas those of P_4S_{10}, P_4S_9 or sulfur are pale to very pale yellow. More specifically, the atomic extinction coefficient at 400 nm, expressed either in terms of P (ε_{400}^{P}) or of P + S (ε_{400}^{P+S}), was much stronger than could be anticipated from any simple mixture of P_4S_{10}, P_4S_9 and S_8 (Figure 1); the contribution to ε_{400}^{P} of PPS was calculated (black triangles in Figure 1) to be as high as 63 l (g-at.)$^{-1}$cm^{-1}, to be compared to 8.9 for P_4S_{10} and 5.2 for P_4S_9. However, no specific UV or visible absorption frequency of PPS was evident. Thus, a partial solution in hexane, obtained from glassy $PS_{3.5}$ exhibited strong absorption at 217 nm and two shoulders at ~250 and ~315 nm; nearly identical spectra are afforded by solutions of P_4S_{10} and P_4S_9 (*cf* Exp. Part).

The IR spectra of PPS solutions were consistent both with NMR data and published IR spectra of glassy PPS.[1j,1k,6] E.g., a solution of $PS_{3.79}$ (ex vitreous

$PS_{3.5}$) absorbed at 720 (w), 695 (s), 545 (w), 535 (m), and 480 (w) cm^{-1}, i.e. at the frequencies of P_4S_{10} and P_4S_9.[10,11] At S/P higher than ~6, when P_4S_{10} and P_4S_9 have vanished, and most P–S–P bridges, responsible for vibrations in the vicinity of 540 cm^{-1}, are likely to have been replaced by $P{-}S_n{-}P$ bridges, a single band at ~698 cm^{-1} was observed (with shoulders at ~690 and ~715 cm^{-1}); this band is probably still associated with $\nu(P{=}S)$ vibrations, although it was about 3.5 to 7 times weaker than the corresponding band (695 cm^{-1}) in P_4S_{10}.

Genesis of Soluble PPS from P_4S_{10} and S_8

In carbon disulfide, no reaction was observed between P_4S_{10} and S_8 on boiling—even in the presence of iodine, a recognized catalyst for the production of phosphorus sulfides from the elements[12]— or between P_4S_{10} or P_4S_9 and S_μ in the cold. In the absence of solvent, no reaction took place at 120°C, but at 160°C PPS were produced, as shown by the NMR spectra. At ~300°C, equilibrium was reached in 30 min or less.

The NMR analysis of solutions obtained from the products of incomplete reaction between P_4S_{10} and S_8 (overall S/P = 19.75 or 71.5), indicated that, when present at equilibrium (Table II), signals at 116.32, 36.9, and 33.8 ppm appeared first, followed by those at 130.05, 61.7, and 49.5 and later by those at 88.54 and 54.9 ppm; signals at 18.54 and 89.54 ppm remained absent, as they were in the end products (Table II).

Solubility of PPS

Our measurements point to the following sequence of solubilities, on a P basis, in carbon disulfide (data in brackets, in m g-at. P/l at 20°C): P_4S_9 (65) > mixed PPS with S/P = 3.5 to 4 (~50) > P_4S_{10} (31) > mixed PPS with S/P ≥ 20 (~10).

In accord with the literature,[3,5] the weight solubility appears to go through a minimum (~3·9 g/l, in the vicinity of S/P = 17). This again can be explained by the growing content of elemental sulfur when the average S/P value is increased (crystals of sulfur could actually be isolated from solid $PS_{71.5}$).

Fractionation of PPS Mixtures in Solution

Adding hexane precipitates PPS from their solutions in carbon disulfide; in line with the above solubilities, this was easier for PPS having a low P content (Table III). No crystals were obtained, but only gummy solids, with S/P not exceeding ~13 (any cyclo-S_n remaining in solution); this suggests that PPS cannot accommodate more than ~8 S atoms in their $P{-}S_n{-}P$ bridges. Likewise, attempts at obtaining PPS in a crystallized form by cooling their concentrated solutions afforded gummy precipitates exclusively. Chromatographic methods (especially Gel Permeation, using Styrogel 60 Å and CS_2 or toluene as eluants) proved deceptive.

TABLE III

Fractional precipitation of PPS dissolved in CS_2

Original glassy PS_x	S/P	3.5	15	19.75	71.5	71.5
Fraction dissolved in CS_2	S/P	3.69	39.3	18.4[a]	167.5	191
	conc m g-at.P/l	22.5	6.2	10.4	9.7	9.3
Added hexane	vol% of the initial soln	300	50	50	50	50
Precipitate[b]	%, P basis	30.8[c]	15.5	47	44.8	49
	S/P	2.84[d]	4.6	4.83	12.8	10.3[e]

[a] Second extraction step (compare with Table I).

[b] No S_8 (and probably no other cyclo-sulfur) was present in any one precipitate, as ascertained by separate tests.

[c] Incomplete decantation despite a 6 days' settling.

[d] The precipitate probably contained some P_4S_{10}, as indicated by a separate test, taking account of compositions in Table II.

[e] The NMR spectrum of the mother liquor was quite similar to that of the starting solution in CS_2 (Table II, last righthand column).

Volatility of PPS.

Vitreous PPS could be sublimed to a large extent at 250–300°C under vacuum. The sublimates dissolved only in part in carbon disulfide. According to the NMR, only four soluble PPS (δ 130.05, 116.32, 88.64, and 33.8 ppm) appeared not to be volatile (Table IV). On the other hand, sublimation was probably accompanied by chemical rearrangements or polymerization, which may account for the build up of the 54.9 ppm signal, the low yield of others and the appearance of new peaks.

Chemical Reactions of Soluble PPS

(a) Soluble PPS are metastable. Gummy deposits, probably polymers, often settle on long standing of their solutions in carbon disulfide. The solids obtained from these solutions by cooling, adding of an alkane or stripping of the solvent, did not totally redissolve in CS_2. Similarly, aging a specimen of glassy $PS_{3.5}$ for seven months brought about major changes in the NMR spectrum of the soluble fraction (Table II): the P_4S_{10} signal grew, others decreased (18.54 ppm) or vanished (33.8 ppm), extra small peaks appeared (*cf* Exp. Part).

(b) PPS in solution (avg $S/P = 4.89$) could be easily desulfurized by triphenylphosphine; the reaction was fast and selective (*cf* Exp. Part). This points to the following order of reactivity with Ph_3P in apolar solvents:[13,14]

$$PPS > P_4S_{10} > P_4S_9 \gg S_8$$

(c) Selective hydrolysis was observed when PPS solutions were stirred with water. When the PPS had a relatively high P content (avg $S/P < {\sim}8$), this was accompanied by a complete bleaching of the CS_2 layer; for $S/P > {\sim}14$, the

TABLE IV

Sublimation of glassy PS_x

Original PS_x		$PS_{3.5}$		PS_{15}	
Sublimation[a]	temp, °C	247→312	none	255→298	none
	duration, min	24		28	
% Sublimed	(wt basis)	65.4	none	64.5	none
Fraction dissolved in CS_2	%, P basis[b]	38.7	58.3	20.4	11.4
	S/P	3.58	3.61	26.9	39.3
	NMR, δ (ppm)	relative integral (%)[c]			
	130.05	—	—	—	—
	116.32	—	0.6	—	1.5
	89.54	1.9	11.7	0.8	1.6
	88.64	—	—	—	0.6
	61.7	—	—	1.5	1.0
	P_4S_9	6.6	11.1	—	—
	P_4S_{10}	11.6	11.1	0.8	—
	54.9	9.7	—	3.6	1.7
	49.5	—	—	1.0	0.9
	36.9	0.4	1.8	1.3	2.2
	33.8	—	1.2	—	0.5
	18.54	2.7	10.5	0.8	—
	new peaks (together)	5.4[d]		11.1[e]	

[a] p = 18 mm Hg; liquid N_2 condenser.
[b] % of the original (unsublimed) solid PS_x.
[c] % of the total P in the original solid PS_x.
[d] 120, 113, 93.5, 46.9 (triplet), 45.6 (triplet) ppm.
[e] 127, 120, 113, 77.7, 66.7, 65.4, 30.5 ppm.

organic phase remained bright yellow. The NMR analysis of this phase, supported by the acidimetric titration of the aqueous layer (*cf* Exp. Part), points to the following classification of the NMR signals, according to the rate of hydrolysis of the corresponding individual PPS (or P sites):

very fast: 89.5 ppm, P_4S_9, 54.9, and 18.54 ppm
fast: 116.32, 61.7, and 36.9 ppm.
slow: 130.05, 88.64, 56.3 (P_4S_{10}), 49.47, and 33.8 ppm.

(d) Purple solutions of Diphenylpicrylhydrazyl (DPPH) in carbon disulfide were instantly decolorized by soluble PPS (avg S/P = 3.4, 17.3). P_4S_{10}, P_4S_9, and S_8 were ineffective, S_μ moderately active and thiophosphoric acid—a potential contaminant, even with stringent precautions to exclude moisture[10]—very slowly active.[15]

DISCUSSION

In view of the complexity of PPS mixtures in solution and their poor stability, it is not surprising that no definite component could be isolated and characterized. A complete unravelling of PPS mixtures appears in fact to be a formidable task. However, from consideration of physical and chemical features of individual PPS, it is possible to get some insight into their molecular structure. This will be discussed in the second part of this report.

EXPERIMENTAL PART

Materials

P_4S_{10} was twice recrystallized from CS_2 and purity was checked by NMR. Elemental S was CP grade, further recrystallized from toluene. CS_2 was a CP grade, further purified by Ph_3P[10] (a convenient substitute for Hg, to free CS_2 from S-containing impurities), dried with P_2O_5 and fractionally distilled.

Procedures

Solid PPS were obtained by heating a gently stirred mixture of P_4S_{10} and S at 300–312°C for ~30 min under dry nitrogen, followed by air cooling. They were ground either in a mortar, in a dry-box, or—especially with plastic PPS, i.e. having high S/P values—by cooling the reaction tube in liquid nitrogen and tapping it on a wooden piece. Dissolution in CS_2 was achieved by magnetic stirring or mechanical shaking in a dry atmosphere. PPS with $S/P \leq 6$, which are hard, crumbly solids, reduced to a fine powder during this process; those with $S/P \geq 15$, which are rubber-like, tended to agglomerate.

^{31}P NMR

Chemical shifts are expressed from external 85% H_3PO_4; for the sake of consistency, however, P_4S_{10} in CS_2 was ascribed a conventional $\delta = 56.3$ ppm and used as an internal reference; when P_4S_{10} was not naturally present, the 116.32 ppm signal was used instead.

Electronic Spectra

A saturated solution of P_4S_{10} in hexane (42 mg/l at 20°C) was found to absorb at 215, 260, and ~310 nm, with $\varepsilon = 9480$, 1400, and ~180 $l\,mol^{-1}cm^{-1}$ resp.; the spectrum of P_4S_9 was very similar, with a major peak at 213 nm.

Incomplete Reaction between P_4S_{10} and Sulfur

A mixture of P_4S_{10} and sulfur (overall $S/P = 71.5$) was heated at 183°C for 20 min, then quenched in liquid nitrogen. The solid was ground and extracted by CS_2 (12 ml/g, 90 min). NMR: δ 130.0 (6%), 116.3 (7%), 61.7 (5%), 56.3 (P_4S_{10}, 68%), and 36.9 ppm (14%). A similar experiment, with $S/P = 19.75$ (20 min at 193°C) gave: 130.0 (5%), 116.3 (18%), 61.7 (6%), P_4S_{10} (41%), 49.5 (5%), 36.9 (16%), 33.8 (5%) and 23.5 ppm (4%).

Aging Experiment

A seven-month-old specimen of glassy $PS_{3.5}$ was ground and stirred with CS_2 (55 ml/g, 50 h); dissolved material = 67.2% (P basis), with $S/P = 3.37$. NMR: 116.3 (0.7%), 113.1 (1%), 102.5 (3.6%), 99.3 (0.5%), 93.5 (1.6%), 89.5 (18.5%), 82.0 (trace), 78.9 ppm (trace); P_4S_9 (20.5%), P_4S_{10} (32.4%); 54.9 (trace), 46.9 (triplet?, 1.1%), 45.6 (triplet?, 0.8%); 51.2 and 43.5 (doublet of triplets, $J \sim 30$ Hz, probably P_4OS_9, 3.8%); 36.9 (1.1%), 27.4 (doublet, $J \sim 29$ Hz, 0.5%), and 18.5 ppm (13.9%).

Desulfuration by Triphenylphosphine

Ph_3P was gradually added to a solution of $PS_{4.89}$ in CS_2, with NMR signals at δ 116.3 (4%), 89.5 ppm (31%); P_4S_9 (6%), P_4S_{10} (13%); 54.9 (14%), 36.9 (11%), and 18.5 ppm (7%). P_4S_{10} started reacting (as made conspicuous by the solution transiently becoming cloudy) only after ~2 moles Ph_3P per P atom of the mixed PPS had been added, i.e. after the removal of $100 \times 2 : (4.89-2.5) \approx 84\%$ of the formal "excess sulfur"—the latter including some elemental S, probably much less reactive; at this point, the initially deep yellow colour of the solution was almost fully discharged. NMR: fading of the 54.9 ppm peak, disappearance of all other PPS signals.

Selective Hydrolysis of PPS

In a standardized test, a solution of PPS in CS_2 (25 ml) was stirred with water (100 ml) at 25°C for a definite time. The recovered aqueous layer was reduced in volume by boiling to ~10 ml, then, after addition of 50 ml methanol, titrated to the first inflexion ($pH \approx 7$). The overall % of hydrolysis (calculated on the basis of one atom of "hydrolyzed P" for every one equivalent of strong acidity) levels off after ~15 min, in fair agreement with the NMR analysis:

PPS in solution	Stirring with water (min)	Overall % of hydrolysis, by acidimetry	Fast + very fast hydrolysable PPS (%), by NMR (see text)
$PS_{3.79}$	12	82.3	78
	60	82.5	
$PS_{14.1}$	12	71.6	70.5
	60	76.5	
$PS_{39.8}$	5	51.5	60.5
	17	63	

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