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Tetrasubstituted bi(phosphine sulfides) as free radical photoinitiators

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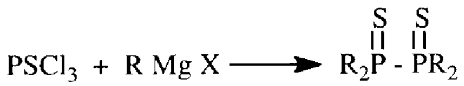
Summary

Photolysis of tetrasubstituted bi(phosphine sulfides) at 254 nm yields disubstituted thiophosphinyl radicals that initiate the polymerization of methyl methacrylate. The phosphorus-containing chain ends of the polymers produced in these polymerizations were easily measured and characterized using ^{31}P-NMR spectroscopy. These measurements showed that thiophosphinyl radical additions to methyl methacrylate are regiospecific. The yields obtained in bi(phosphine sulfide)-initiated MMA polymerizations compare favorably with yields obtained using a commercially available photoinitiator, Lucirin TPO, but the reaction times required are considerably longer. The molecular weights of PMMA samples obtained from bi(phosphine sulfide)-initiated polymerizations are lower than those of TPO-initiated samples, due to the ability of bi(phosphine sulfides) to also act as chain transfer agents.

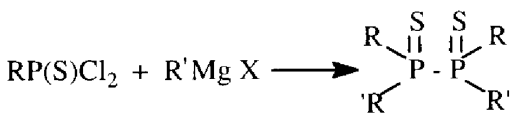
Introduction

Bi(phosphine sulfides) are compounds that are easily prepared from Grignard reagents and thiophosphoryl halides or thiophosphonic halides as shown below [1-6].

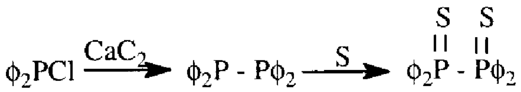


$$PSCl_3 + R\,Mg\,X \longrightarrow R_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}R_2$$

(1)



(2)



$$\phi_2PCl \xrightarrow{CaC_2} \phi_2P-P\phi_2 \xrightarrow{S} \phi_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}\phi_2$$

(3)

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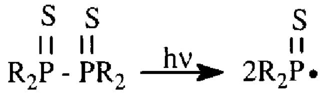
Photolysis of tetramethyl bi(phosphine sulfide) at 254 nm has been shown to yield dimethylthiophosphinyl radicals exclusively [7]. These radicals were detected and characterized by electron spin resonance (ESR) spectroscopy, but no attempts were made to use them in any chemical process. It seemed that tetrasubstituted bi(phosphine sulfides) might be useful as photoinitiators for polymerization reactions. Several tetrasubstituted bi(phosphine sulfides) were therefore investigated as photoinitiators for the polymerization of MMA in bulk at room temperature. In addition, the phosphorus-containing chain ends of the polymers produced in the polymerization experiments were characterized using ^{31}P-NMR spectroscopy.



$$R_2\overset{\overset{S}{\|}}{P} - \overset{\overset{S}{\|}}{P}R_2 \xrightarrow{h\nu} 2R_2\overset{\overset{S}{\|}}{P}\bullet \qquad (4)$$

Experimental

Materials

The bi(phosphine sulfides) were synthesized using accepted procedures [1-6]. Methyl methacrylate was purified by a two-fold washing with equal volumes of sodium hydroxide followed by a two-fold washing with equal volumes of distilled water. It was then dried over calcium hydride, vacuum distilled and stored in a refrigerator until used.

Photopolymerizations

Polymerization mixtures were exposed to an ultraviolet radiation source (Spectronics Corp., model Spectroline XX-15NF) having a wavelength maximum at 254 nm and an intensity of 1100 W/cm^2 at 12 inches. Each polymerization was carried out in a 100 ml single neck quartz flask which was sealed with a rubber septum. The monomer and initiator were syringed into the flask, which was then sealed and sparged with nitrogen for two minutes. The flask was placed two inches from the lamp and irradiated. All polymerizations were in bulk at room temperature and taken to high conversion. Yields were determined after three precipitations from THF into methanol and vacuum drying at 60°C overnight. Prior to purification, the polymers had the odor of trivalent phosphorus compounds, indicating that a portion of the thiophosphinyl radicals had abstracted hydrogen atoms from MMA.

Molecular weight determination

Sample molecular weights were measured by size exclusion chromatography on a Waters 150-C ALC/GPC with a 6-column set having pore sizes 10^6, 10^5, 10^4, 10^3, 500 and 100 A°. THF was chosen for the mobile phase and the flow rate was 1 ml/min. UV (254nm) and refractive index detectors were used and monodisperse PMMA standards were used for calibration.

Phosphorus NMR spectroscopy

Phosphorus NMR measurements were performed on samples in $CDCl_3$ on a Varian XL-400 spectrometer using a resonance frequency of 161.91 MHz. A 90° flip angle was used with a 2 second delay and an acquisition time of 0.3 s with 30012 data points. Solution concentrations were 10-15% (w/v). Samples were filtered through clean cotton into 10 mm NMR tubes and 3 mg of Lucirin TPO was added as internal standard (chemical shift of 11.0 ppm). The number of transients varied from 15,000-20,000. All chemical shifts were measured relative to 85% ortho-phosphoric acid, which was employed as an external standard with a chemical shift set at 0.0 ppm.

Results and discussion

An extensive study of the polymerization of methyl methacrylate using various bi(phosphine sulfides) as photoinitiators was conducted. The amount of bi(phosphine sulfide) employed varied from 0.015 to 0.06 moles per mole of MMA and the solutions were irradiated at 254 nm for 12-48 hours. Table 1 lists the yields and molecular weights of polymers obtained. For comparison, polymer yields obtained when MMA was irradiated alone for various times are also provided along with results obtained using a commercially available photoinitiator, diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (Lucirin TPO) [8-11]. The data clearly indicate that bi(phosphine sulfides) are photoinitiators for the polymerization of MMA; the yields of polymer obtained when MMA-bi(phosphine sulfide) mixtures are irradiated are considerably higher than those obtained when MMA is irradiated alone under the same conditions. It is interesting to note that irradiation of MMA for 41 hours yields crosslinked gel but that a gel is not obtained when mixtures of MMA and bi(phosphine sulfide) are irradiated for 44-48 hours under similar conditions. The crosslinking seems to result from the gradual coupling of PMMA radicals that are generated by an unknown process since Mn values for polymers prepared in the absence of bi(phosphine sulfides) increase with radiation extent.

Table 1. Results of MMA polymerization initiated by bi(phosphine sulfides) at 254 nm

Photoinitiator	ε_{254}*	Initiator Conc. (Mole%)	Time (Hr)	Polymer Yield(%)	Mn	%P
$[(CH_3)_2P=S]_2$	420	1.5	12	65	63,700	0.0608
$[(CH_3CH_2)_2P=S]_2$	562	5.4	44	65	39,000	
$[(CH_3CH_2CH_2)_2P=S]_2$	720	3.6	44	66	39,000	
$[(CH_3)(Ph)P=S]_2$		0.5	12	67	41,500	
		1.5	16	71	32,200	
		3.0	12	62	14,000	0.276
		6.0	48	68	4,700	
$[(Ph)_2P=S]_2$		3.0	3	Partially Crosslinked		
TPO		3.0	3	73	100,000	
None			3	0.4	100,000	
			6	0.7		
			12	7		
			17	33	220,000	
			19	38		
			27	49		
			41	Crosslinked		

*liter mole^{-1} cm^{-1}

Monomer conversions were in the 60-70 percent range – similar to that obtained in a TPO-initiated MMA polymerization. The molecular weights of the polymers varied from 4,700 to 63,700 g/mole, depending on the amount and structure of the initiator employed. Increasing initiator concentration had the effect of reducing polymer molecular weight. This can be a result of the higher rate of initiation that is obtained at higher initiator concentrations or it can be due to the bi(phosphine sulfides) acting as chain transfer agents as well as initiators (inifers). We have previously reported that the chain transfer constant for tetramethyl bi(phosphine sulfide) in MMA polymerization is 0.14 [12]. If molecular weight is influenced primarily by rate of initiation, the number average molecular weight should be inversely proportional to the square root of the initiator concentration. Figure 1 shows a plot of number-average molecular weight (Mn) versus the reciprocal of the square root of the initiator concentration ($1/I^{1/2}$) for polymers initiated by 1,2-dimethyl-1,2-diphenyl bi(phosphine sulfide). Mn increases somewhat regularly with $1/I^{1/2}$, but the curvature noted probably reflects the simultaneous operation of chain transfer processes.

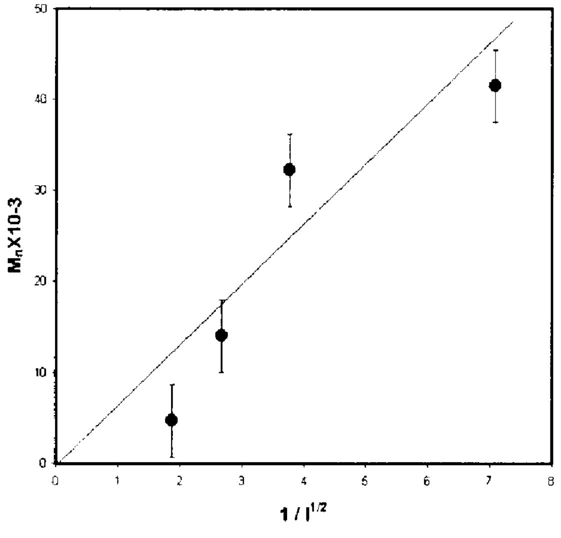


Figure 1. Relationship of Mn to $1/I^{1/2}$ for MMA polymerizations initiated by 1,2-dimethyl-1,2-diphenyl bi(phosphine sulfide)

Tetraphenyl bi(phosphine sulfide) was not effective as a photoinitiator for MMA polymerizations. When a mixture of tetraphenyl bi(phosphine sulfide) and MMA was irradiated at room temperature for 40 hours, a mixture of soluble and insoluble polymers was produced. The soluble portion was analyzed by ^{31}P-NMR spectroscopy but no peaks were observed. It is concluded from this information that tetraphenyl bi(phosphine sulfide) did not initiate the polymerization of MMA and that the polymer produced was a result of the auto-initiated polymerization of MMA.

Compared to polymerizations initiated by Lucirin TPO, bi(phosphine sulfide)-initiated polymerizations require longer irradiation times and yield lower molecular weight polymers. The extinction coefficients of bi(phosphine sulfides) are approximately one-third that of Lucirin TPO and they do not absorb appreciably in the visible region. They are thus not as effective as acylphosphine oxides for radical generation, but are of interest as sources of thiophosphinyl radicals for radical selectivity studies [13]. A reviewer has kindly suggested that bi(phosphine sulfides) may be more efficient than our results indicate if chain transfer reactions reduce their concentrations appreciably. The reviewer also noted that chain transfer reactions may contribute to initiator photobleaching, which is a desirable characteristic when thick samples are irradiated.

Chain End Characterization

Phosphorus-containing chain ends in the polymers were characterized by elemental analysis and by ^{31}P-NMR spectroscopy. Depending on the termination mechanism and whether or not the bi(phosphine sulfides) act also as chain transfer agents, the number of phosphorus-containing chain ends should be between one and two when bi(phosphine sulfides) are used as initiators. If polymerization is initiated by a phosphorus-containing radical and termination occurs by disproportionation, the polymers produced should contain one phosphorus atom per molecule. When termination occurs by coupling or when the bi(phosphine sulfides) behave as chain transfer agents the polymers produced will contain two atoms per molecule.

The phosphorus contents of several polymers were determined by elemental analysis and used in combination with number average molecular weights to estimate the average number of phosphorus atoms per molecule. Based on these calculations, it was determined that poly(methyl methacrylate) prepared by tetramethyl bi(phosphine sulfide) and 1,2-dimethyl-1,2-diphenyl bi(phosphine sulfide)-initiated polymerizations contained 1.2 phosphorus atoms per molecule. This result, which suggests that termination occurs by disproportionation 60 percent of the time, agrees with results reported by Bevington, et al. who found that PMMA prepared by photochemical polymerization at 25°C using radioactive AIBN contained ~ 1.2 initiator fragments per chain [14].

Table 2. ^{31}P-NMR chemical shifts of peaks observed in bi(phosphine sulfide)-initiated PMMA samples.

	Chemical Shift (Relative Area)	
Initiator	Peak 1	Peak 2
$[(CH_3)_2P{=}S]_2$	29.3 (0.73)	30.2 (0.27)
$[(CH_3CH_2)_2P{=}S]_2$	45.8 (0.74)	46.5 (0.26)
$[(CH_3CH_2CH_2)_2P{=}S]_2$	41.9 (0.73)	41.0 (0.27)
$[(CH_3)(Ph)P{=}S]_2$	31.0 (0.73)	32.0 (0.27)

The ^{31}P-NMR spectra of the polymers consist of two resonances having an approximately 3:1 ratio of relative intensities. Based on the fact that the ^{31}P-spectra of polymers prepared in the presence and absence of 1-octyl mercaptan are the same, and on the fact that similar spectra are observed for PMMAs initiated with diphenylphosphinyl radicals, where regiospecific addition of the radicals to the unsubstituted carbons of MMA has been established [13], the resonances are attributed to $R_2P(S)$-MMA-MMA chain ends having racemic and meso MMA-MMA dyads. Figure 2 shows the ^{31}P-resonance patterns observed for PMMAs prepared using several bi(phosphine sulfides). The relative ordering of the resonance patterns seems to be influenced by effects analogous to those responsible for chemical shifts in C^{13}-NMR spectroscopy [15]. Thus, the presence of carbons β- and γ- to the phosphorus atom causes shifts of ~8.2 and ~(-2.5) ppm, respectively. In the case of C^{13}-NMR spectra, neighboring β- and γ-carbons cause shifts of carbon resonances of 9.8 and –2.9 ppm, respectively. Table 2 summarizes the chemical shifts and relative areas of the ^{31}P-resonances observed for the polymers. The proportion of resonance in each lower field signal, which

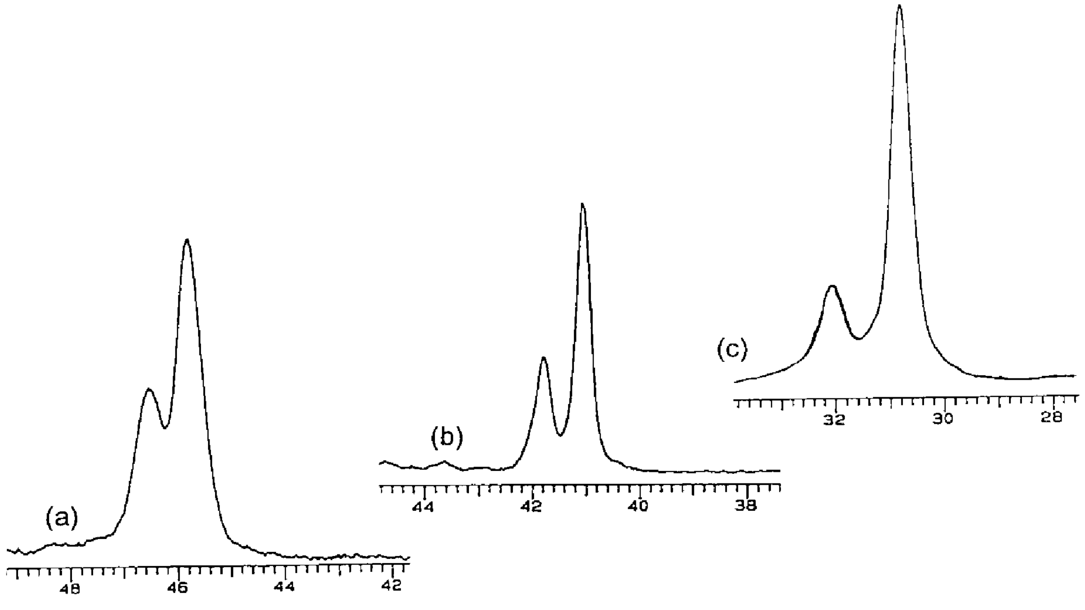


Figure 2. ^{31}P-resonance patterns observed for PMMAs prepared using (a) tetraethyl bi(phosphine sulfide),(b) tetra(n-propyl) bi(phosphine sulfide) and (c) 1,2-dimethyl-1,2-diphenyl bi(phosphine sulfide) photoinitiators.

we attribute to meso MMA-MMA enchainments at the chain ends is ~0.27, which is slightly higher than the value (0.23) that prevails throughout the rest of the polymer chain [16,17].

Conclusions

Bi(phosphine sulfides) are effective photoinitiators for MMA in the UV but are not as effective as Lucirin TPO, a commercially available photoinitiator. In addition, the thiophosphinyl radicals produced in the photolysis of bi(phosphine sulfides) appear to be regiospecific in their addition to the carbon-carbon double bond of MMA, adding exclusively to the unsubstituted carbon.

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