

The Synthesis and Characterization of Cationic Photoinitiators Bearing Two and Three Photoactive Triarylsulfonium Groups in the Same Molecule

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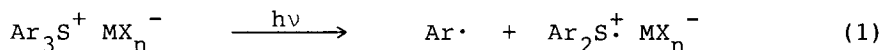
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Summary

A novel series of photoinitiators for cationic polymerization have been prepared which bear two and three photoactive triarylsulfonium groups in the same molecule. These compounds have been fully characterized by means of their UV and ^{13}C -NMR spectra and liquid chromatography as well as by their elemental analyses. The multifunctional triarylsulfonium salts have been compared among themselves and against monofunctional triarylsulfonium salts in the photoinitiated cationic polymerization of dl-limonene dioxide.

Introduction

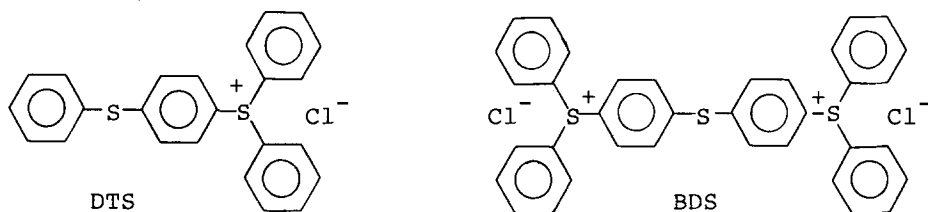
In several publications from this laboratory (CRIVELLO AND LAM 1979a-c), we have reported that triarylsulfonium salts possessing counterions of low nucleophilicity are efficient photoinitiators of cationic polymerization. On UV irradiation, these compounds undergo photolysis with the cleavage of one of the carbon-sulfur bonds as shown in equation 1 to produce an aryl radical and a diarylsulfonium cation-radical. In subsequent reactions, the diarylsulfonium cation-radical generates



strong Brønsted acids which initiate the polymerization of most cationically polymerizable monomers. Current work in this laboratory centers about the synthesis of triarylsulfonium salt photoinitiators with higher photosensitivity and broader spectral response.

The condensation of benzene with sulfur monochloride in the presence of chlorine and aluminum chloride has been reported (PITT 1957) to give triphenylsulfonium salts. Recent investigations in this laboratory (CRIVELLO AND LAM 1980) have shown that the reaction is, in fact, quite complex and that a number of triarylsulfonium salt species are formed. The distribution of products appears to depend greatly upon the stoichiometry of the starting materials as well as the way and rate at which the reactants are introduced. Among the chief products which have been identified in commercial "triphenylsulfonium chloride" was diphenyl-4-thiophenoxyphenylsulfonium

chloride, DTS.



In a recent communication (WATT et al 1984), another related compound, bis-[4-(diphenylsulfonio)phenyl]sulfide-bis-chloride, BDS, was isolated as its bis-hexafluorophosphate salt from the triarylsulfonium chloride mixture prepared by the Pitt method. Previously (CRIVELLO and LAM 1980), we had also published the ^{13}C -NMR spectrum of this compound from an inadvertently fractionated mixture of triarylsulfonium salts; however, we did not correctly assign its structure. While this work was in progress, efforts in this laboratory were also continuing in an attempt to unambiguously prepare the BDS cation as well as other photoinitiators bearing multiple triarylsulfonium groups in the same molecule and to evaluate their photoactivity in cationic polymerization. We report in this communication the results of those investigations.

Experimental

All reagents and starting materials used in the synthesis of the sulfonium salts were reagent grade and were used without purification. The arylsulfides were prepared by condensing equivalent amounts of the appropriate dibromo or dichloro compound with two equivalents of potassium thiophenoxide in dimethylacetamide (CRIVELLO and LAM 1980). Diphenyliodonium hexafluorophosphate was prepared as described previously (CRIVELLO and LAM 1977). dl-Limonene dioxide (dipentene dioxide) was a gift of the SCM Corporation and was purified by drying over CaH_2 then fractionally distilling.

General Procedure for the Arylation of Aromatic Sulfides

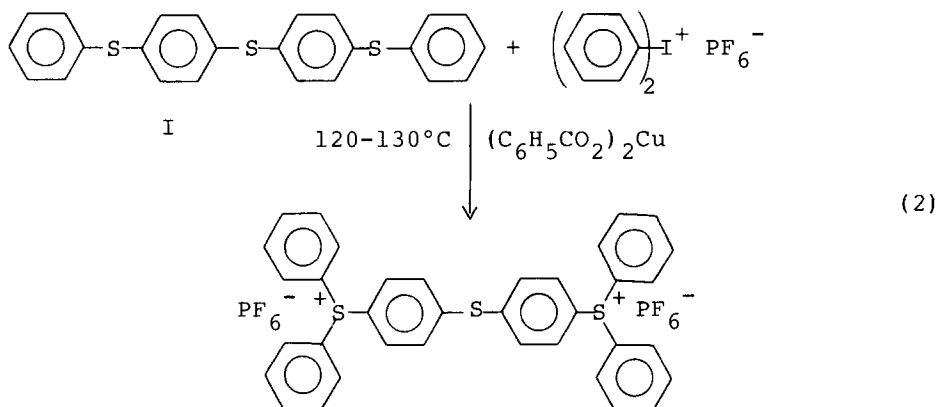
The preparation of the multifunctional triarylsulfonium salts by the arylation of aromatic sulfides is typified by the following synthesis of BDS bishexafluorophosphate. Into a 50 mL round bottom flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet were placed 4.03 g (0.01 mol) 4,4'-(bisthiophenoxy)diphenyl sulfide (prepared by the condensation of 4-bromophenyl sulfide with two equivalents of potassium thiophenoxide), 8.95 g (0.021 mol) diphenyliodonium hexafluorophosphate, 0.1 g cupric benzoate and 10 mL chlorobenzene. Nitrobenzene was used as the solvent in some of the other arylation reactions. The reaction flask was heated by means of an oil bath at 120-130°C for 3 hours. After cooling the reaction mixture was poured into approximately 100 mL ethyl ether. The tan crystalline solid was collected by filtration, washed with three 10 mL portions of fresh ethyl ether and then air dried. The pure BDS bishexafluorophosphate was obtained in 39% yield after recrystallization from ethanol.

Photomicrocalorimetry

The apparatus and techniques employed for the photomicrocalorimetric study of the cationic ring opening polymerization of dl-limonene dioxide using the initiators described in Table 1 have been described in previous communications (MOORE et al 1976ab). Stock solutions of each of the photo-initiators were prepared at the following concentrations: 0.01M for TPS and DTS, 0.005M for BDS, BPDS and DS, and 0.0033M for TS. Aliquots (13-17mg) were taken from these stock solutions and transferred to standard aluminum sample cups. Analysis was performed on a specially modified Perkin Elmer DSC II differential scanning calorimeter under isothermal conditions at 300°K. Data were collected by integrating the areas under the curves at various times and calculating the cumulative heats of polymerization which are proportional to the extents of conversion of the monomer.

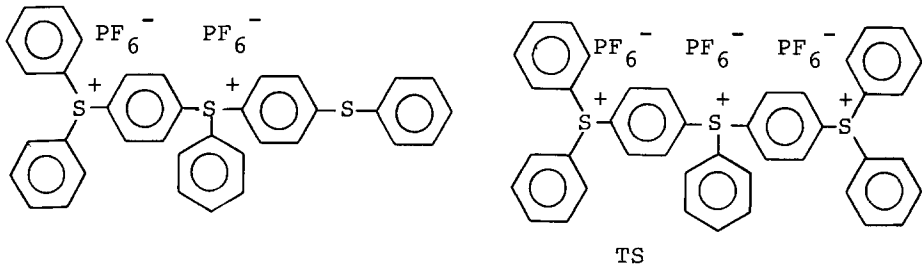
Results and Discussion

The copper catalyzed arylation of a diarylsulfide with a diaryliodonium salt (CRIVELLO, LAM 1978) is a convenient, high yield route to the synthesis of triarylsulfonium salts. We have employed this method in the past (CRIVELLO, LAM 1980b) for the preparation of the DTS cation as well as other related compounds in excellent yield. Using this same method, the 4,4'-(bisthiophenoxy)diphenyl sulfide, I, shown in equation 2 can be doubly arylated to give BDS as the major product. The pure bis salt is obtained as a colorless crystalline compound on recrystallization from ethanol.



BDS bishexafluorophosphate prepared in this manner corresponds in all respects with that reported by Watt. In addition to BDS, the HPLC chromatogram of the product mixture indicates that two other products are formed in minor amounts. The first structure shown below has been tentatively assigned to one of the two products and is an isomer of BDS. The second product, present in very small amounts, has been positively identified as the tristriarylsulfonium salt, TS, which can be isolated as the sole product when I is treated with a slight excess over three moles of diphenyliodonium hexafluorophos-

phate in the presence of a catalytic amount of cupric benzoate.



In a similar manner, we have prepared two other aromatic bithioethers and carried out their arylation to give compounds containing two triarylsulfonium salt moieties in the same molecule. The structures, elemental analyses and properties of these new compounds are shown in Table 1. $^{13}\text{C-NMR}$ was used to verify the structure of these compounds and the peak assignments are also shown in Table 1. Included in this table for comparison are the appropriate data for the monosulfonium salts TPS and DTS. In Figure 1 is given a composite UV spectrum which shows the absorption characteristics for the compounds in Table 1.

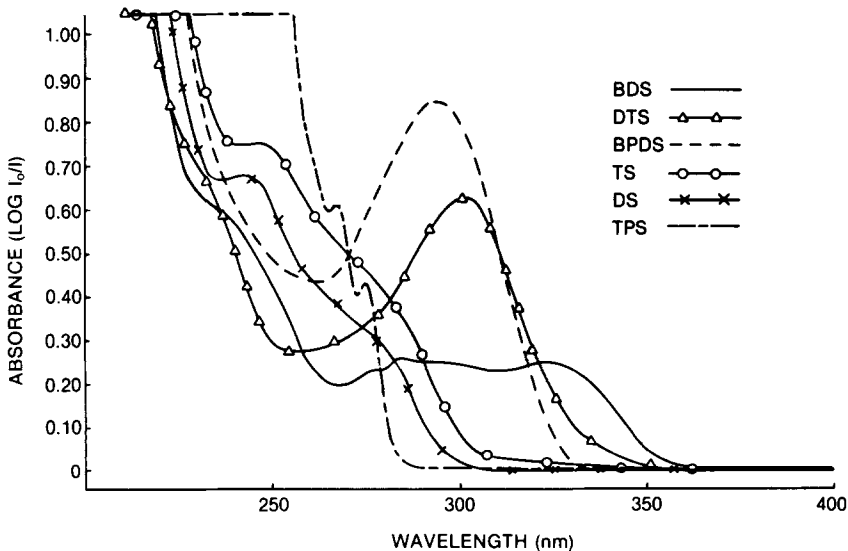


Figure 1. Composite UV spectra of various triarylsulfonium photoinitiators in methanol (TPS, 1.82M; DS, 0.200M; TS, 0.165M; BPDS, 0.209M; DTS, 0.348M; BDS, 0.142M)

It is interesting to note that BDS, DTS and BPDS have strong absorption bands in the 300-310 nm region whereas TPS, DS and TS do not. In the former three cases, the extended conjugation

Table 1
Structure and Properties of Triarylsulfonium Salt Photoinitiators

Structure ^a	Abbrev.	m.p. (°C)	¹³ C	¹ H	¹⁹ F	³¹ P	C ^{1b} (C ⁷)	C ² (C ⁸)	C ³ (C ⁹)	C ⁴ (C ¹⁰)	C ⁵ (C ¹¹)	C ⁶ (C ¹²)
	TPS	201-203	calc: 52.94 fnd: 53.29	3.70 3.80	7.85 8.07	7.58 7.26	135.0	131.9	131.6	125.1		
	DTS	78-81	calc: 55.81 fnd: 55.87	3.71 3.89	12.42 12.62		135.3 (135.2)	132.1 (149.1)	131.6 (135.3)	125.7 (130.8)	120.9 (129.2)	132.5 (130.5)
	BDS	245-247	calc: 51.06 fnd: 50.80	3.33 3.71	11.36 11.47	7.32 7.09	135.3 (132.9)	132.2 (142.7)	131.8	125.3	124.5	133.5
	BPDS	317-320	calc: 53.20 fnd: 53.17	3.47 3.46	7.64 8.32	7.62 7.14	135.2 (130.7)	132.0 (144.5)	131.7	125.2	125.8	132.5
	DS	266-268	calc: 48.78 fnd: 48.52	3.28 3.38	8.68 8.89	8.39 8.21	136.1	132.7	132.7	124.7	133.9	134.1
	TS	156-167	calc: 47.20 fnd: 47.16	3.11 3.61	9.00 8.73	8.69 8.02	135.7 (134.3)	132.3 (131.5)	132.3 (123.2)	124.3 (132.5)	133.2 (133.0)	133.9 (136.3)

a) All compounds as their PF₆⁻ salts; b) ¹³C-NMR spectra recorded in acetone-d₆

tion provided by the 4-thiophenoxyphenyl and 4-biphenyl chromophores accounts for the observed long wavelength absorption bands. These chromophores are entirely absent in the latter three compounds and in addition, the extreme steric crowding present in DS and TS causes each triarylsulfonium group present in these molecules to act as an independent chromophore.

A brief study of the effects of the presence in a molecule of multiple triarylsulfonium salt groups on their efficiency in photoinitiated cationic polymerization was undertaken and is depicted in Figure 2.

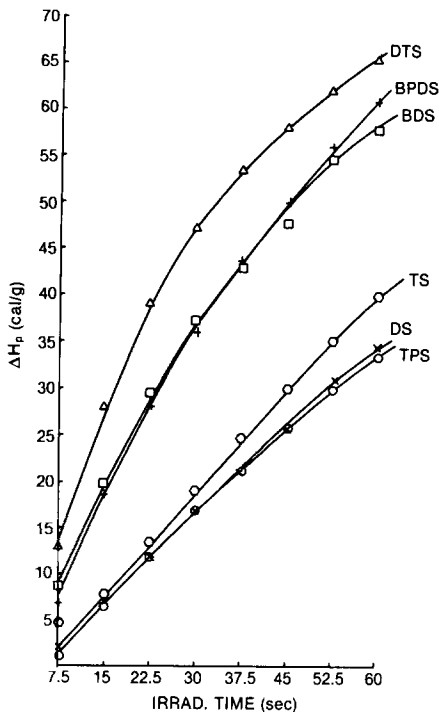


Figure 2. Comparison of the relative efficiencies of various triarylsulfonium photoinitiators in the photoinitiated ring opening cationic polymerization of dl-limonene dioxide

Here again, TPS and DTS are included for purposes of comparison. This investigation was carried out by following the evolution of the heat of polymerization using photomicrocalorimetry with dl-limonene dioxide as the subject monomer. Because of its high reactivity in ring opening cationic polymerization and low volatility, dl-limonene dioxide is an ideal monomer with which to study photoinitiated polymerizations by photomicrocalorimetric techniques. The photoinitiators were compared with each other at identical concentrations of triarylsulfonium chromophores. Thus, for example, TS was used in this study at one-third the molar concentration of TPS or DTS. As a light source, an unfiltered medium pressure mercury arc lamp was employed. As can be seen in this figure, the photoinitiators fall into two distinct classes with respect to

their efficiency of photoinitiated cationic polymerization. The most highly efficient photoinitiators are those which possess long wavelength absorption bands in the region of 300-310 nm in addition to the usual aromatic bands at 230-250 nm. This implies that the long wavelength absorption bands associated with these compounds are photoactive and result in bond cleavage reactions similar to those shown in equation 1. The higher efficiency observed in these compounds is, therefore, a consequence of their greater overall absorption of light available in the mercury emission spectrum, especially the 254 and 313 nm lines. This enhanced absorption produces more extensive photolysis of the triarylsulfonium chromophores and results ultimately in the formation of a larger number of propagating cationic centers per unit irradiation time.

The most efficient triarylsulfonium salt photoinitiator which we have yet evaluated is DTS. Only slightly less active are BDS and BPDS which exhibit nearly identical efficiency as cationic photoinitiators. The tris-triarylsulfonium salt, TS, and the bis salt, DS, are considerably less active and are about as efficient as the simple monosulfonium salt, TPS.

It is interesting to note that the photochemistry of the diphenyl sulfide trimer, BDS, appears to be similar to that reported for the corresponding dimer, DTS (CRIVELLO AND LAM 1980). Examination of the photolysis products using a 450 W unfiltered Hg arc lamp of these two compounds in acetonitrile by HPLC (Waters HPLC, μ -Bondapack CN column) showed that in both cases the major photolysis product was diphenyl sulfide.

Acknowledgement

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