

## SUBSTITUTED TRIPHENYLMETHYL CARBOCATIONS. II. TERMINATION EFFECT OF THE AZO COMPOUNDS

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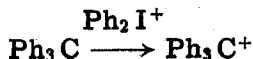
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**Abstract:** Termination effects of phenylazotriphenylmethanes on both direct and activated polymerization of tetrahydrofuran in the presence of diphenyliodonium and diphenylsulfonidiphenylsulfide salts are studied.

### 1. INTRODUCTION

As part of our continuing investigations of the azo compounds and the cationic salt combination in polymerizing systems, we have described [1, 2] the formation and the use of triphenylmethyl carbocations in cationic polymerization. Triphenylmethyl radicals which may be produced by thermal and photochemical means give rise to formation of the corresponding carbocations in the presence of suitable onium salt,



If this diversion is used in free radical polymerizing systems, the terminating effect of triphenylmethyl radicals is greatly reduced [3].

We have now undertaken studies on the termination effect of the azo compounds in combined systems, in cationic polymerization.

### 2. EXPERIMENTAL STUDY

#### 2.1 MATERIALS

Diphenyl sulfonidiphenyl sulphide hexafluorophosphate, diphenyliodonium hexafluorophosphate, phenylazodiphenyl-p-tolylmethane (PADT),

phenylazo-diphenyl-o-hydroxyphenylmethane (PADH), phenylazotriphenylmethane (PAT) and monomer (THF) were prepared and purified as described previously [2].

## 2.2 POLYMERIZATION PROCEDURES

In activated polymerization, bulk tetrahydrofuran (THF) containing given type of the azo compound and the cationic salt in 15 mm pyrex vessels were degassed in the usual manner. A 336 nm interference filter was used to eliminate direct excitation of the salt. Direct polymerizations in the presence of the azo compounds were carried out as for the activated polymerizations, except that the quartz vessels were employed in all cases. The samples were first irradiated at 1 cm from phywe 55 W mercury lamp for ten minutes, then kept in a thermostat at 40°C in the absence of light. Polytetrahydrofuran was precipitated into distilled water containing a little amount of base.

## 2.3 FLUORESCENCE QUENCHING STUDIES

They were performed in a Perkin-Elmer Model-204 spectrophotometer.

## 3. RESULTS AND DISCUSSION

The effects on the three types of the azo compounds on the polymerization of THF were shown in Table 1. The results show that all types of the azo compounds activate the polymerization, since direct polymerization via iodonium salt photofragmentation precluded by the use of interference filter which excludes wavelengths below 366 nm. In the case of PADH activation, the rate of polymerization is considerably low, probably due to high nucleophilicity of the OH group.

The sulfonium salt have not been fragmented by the azo compounds derived radicals nor by aromatic ketones such as benzophenone and 9-fluorenone. In attempts to polymerize THF utilising the sulfonium salt in the presence of the azo compounds or the aromatic ketones, we failed to produce any precipitable polymer after irradiation at 366 nm. Although several mechanisms proposed by previous reports [4-6] on photosensitization of cationic polymerization, mechanistic details still remain to be evaluated and may vary for all systems. For example, J. V. Crivello [6] showed that anthracene, pyrene and similar sensitizers were equally active for dialkylphenacylsulfonium salt. In contrast, polynuclear aromatic hydrocarbons were not active photosensitizers for dialkyl(4 hydroxyphenyl) sulfonium salts. Instead, aromatic ketones were observed to be excellent long-wave photosensitizers for these initia-

TABLE 1

Photoactivated bulk polymerization of tetrahydrofuran in the presence of  $[\text{Ph}_3\text{I}^+ \text{PF}_6^-] = 5 \times 10^{-3} \text{ M}$ , ( $\lambda = 366 \text{ nm}$ ) (Pyrex tubes)

[PAT] $\times 10^3$ (M)	[PADT] $\times 10^3$ (M)	[PADH] $\times 10^3$ (M)	Conversion (%)
—	—	—	0
0.5	—	—	1.7
1.0	—	—	4.2
3.0	—	—	7.4
5.0	—	—	8.9
10.0	—	—	8.9
20.0	—	—	10.7
—	0.5	—	3.3
—	1.0	—	5.4
—	3.0	—	7.5
—	5.0	—	8.9
—	12.0	—	9.2
—	—	1.0	2.3
—	—	3.0	3.3

tor. However, we have observed that the sulfonium salt does not quench emission from benzophenone. In this case photosensitization was not apparent. Furthermore, the fluorescence emission of anthracene is reduced on addition of the sulfonium salt, where successful photosensitization may take place (Fig. 1).

Direct polymerization occurs, when the absorption of the salt extended by the use of quartz vessels. Addition of the azo compounds causes reduction in the apparent rate of the onium salt initiated polymerization (Table 2 and 3). Then, some increase in the rate is indicating possible activation by the azo compound derived radicals up to the certain concentration even if the sulfonium salt used. Photolysis studies confirmed [2] that triphenyl methyl carbocation produced during the irradiation of this combined system, even though the azo compounds do not activate the sulfonium salt. This means that the oxidation of the triphenylmethyl radicals may also be provided by the primary photofragments of the sulfonium salt.

According to the results obtained, one may conclude that termination and activation effects of the azo compounds proceed together in these systems. Termination should be expected radicalic rather than

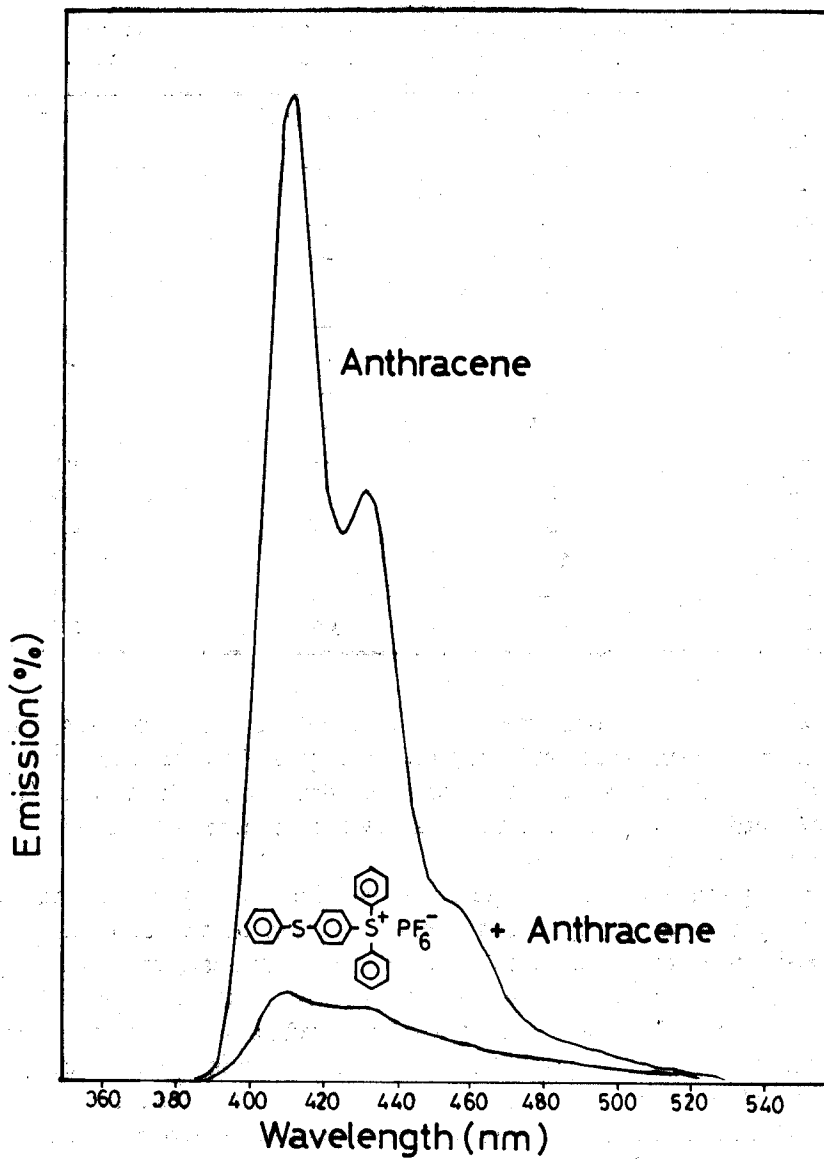


Fig. 1. Quenching of anthracene fluorescence emission by the sulfonium salt in  $CH_2Cl_2$ .

TABLE 2  
 Photoinitiated polymerization of tetrahydrofuran initiated by  
 $[\text{Ph}_3\text{I}^+ \text{PF}_6^-] = 5 \times 10^{-3} \text{ M}$  in the presence of the azo compounds  
 (quartz vessels)

$[\text{PAT}] \times 10^3$ (M)	$[\text{PADI}] \times 10^3$ (M)	$[\text{PADH}] \times 10^3$ (M)	Conversion (%)
—	—	—	8.7
1.0	—	—	5.4
3.0	—	—	8.0
5.0	—	—	9.0
15	—	—	5.6
—	0.5	—	2.0
—	1.0	—	5.7
—	3.0	—	8.4
—	5.0	—	9.2
—	—	1.0	4.8
—	—	2.2	2.9
—	—	5.0	1.4

TABLE 3  
 Photoinitiated polymerization of tetrahydrofuran initiated by  
 $[\text{Ph}-\text{S}-\text{C}_6\text{H}_4-\text{S}^+-\text{Ph}_2\text{PF}_6^-] = 5 \times 10^{-3} \text{ M}$  in the presence of the  
 azo compounds (quartz vessels).

$[\text{PAT}] \times 10^3$ (M)	$[\text{PADI}] \times 10^3$ (M)	$[\text{PADH}] \times 10^3$ (M)	Conversion (%)
—	—	—	12.8
0.5	—	—	11.8
3	—	—	13.8
5	—	—	13.2
15	—	—	7.9
—	1	—	12.8
—	3	—	12.4
—	5	—	13.5
—	—	0.5	13.6
—	—	2	7.1
—	—	5	3.3

ionic in nature assuming the terminating effect of triphenylmethyl radicals and the chain reaction, in which even aryl radicals will provide formation of cations if suitable monomers are present.

#### ACKNOWLEDGEMENT

We thank M. Acar for assistance in obtaining the fluorescence spectra.

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*Received January 27, 1984*

#### SUBSTITUTE TRIFENİLMETİL KARBOKATYONLARI II. AZO BİLEŞİKLERİNİN SONLANDIRICI ETKİSİ

**Özet:** Tetrahidrofuranın difenilyodonyum ve difenilsulfonidifenilsulfit tuzlarıyla doğrudan ve aktiflenmiş polimerleşmesi üzerine fenil azotrifenilmetanın sonlandırıcı etkisi çalışılmıştır.