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Photo- and thermal-polymerization of styrene by new sulfur-containing azoinitiators

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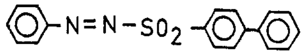
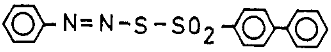
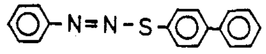
SUMMARY

New sulfur-containing azoinitiators such as: phenylazo-4-diphenylsulfone, phenylazo-4-diphenylthiosulfone and phenylazo-4-diphenylsulfide were synthetized and examined for their capability to initiate photo- and thermal-polymerization of styrene.Obtained results show that polymerization reactions caused by radicals from the decomposition of these compounds are characterized by low conversions.

INTRODUCTION

Thermal degradation and photolysis of acryloazosulfones ,arylazophenylsulfones [1] and alkylaryldiazosulphides [2,3] have been published previously. One of the advantages of these compouds is their controlled decomposition by first-order kinetics. Arylazosulfonates and arylazophenylsulfones were used as initiators for the thermal polymerization of methyl methacrylate [1] whereas organic sulphides were used for the photopolymerization of styrene and methyl methacrylate [4-6]. The last can also act as chain transfer agents [4] and as regulators of molecular weight distributions. [7,8]

In the present study,we prepared new three sulfur-containing azoinitiators:

1. Phenylazo-4-diphenylsulfone (I): 
2. Phenylazo-4-diphenylthiosulfone (II): 
3. Phenylazo-4-diphenylsulphide (III): 

and examined their photo- and thermal-initiating properties on polymerization of styrene.

EXPERIMENTAL

Sulfur-containing azoinitiators were synthetized in the following way:

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1.Phenylazo-4-diphenylsulfone (I):

0.82 g (0.012 mol) of $NaNO_2$ dissolved in 5 ml of ice-cooled water, was added dropwise to 1.17g (0.012 mol) of aniline dissolved in 10 ml of 10% hydrochloric acid. This solution was stirred for 1 hour at room temperature. 3.36 g (0.04 mol) of sodium salt of 4-diphenyl-sulphinic acid in 50 ml water-acetone (4:6) mixture was cooled to - 5°C and than added to the above solution. The yellow precipitate formed was filtered off and recrystallized from ethanol.

Yield;2.8 g (72%); m.p.114-116°C.

IR(KBr):1592 cm^{-1} (N=N),1340 and 1168 cm^{-1} (SO_2).

$C_{18}H_{14}N_2SO_2$ (322.36): Calc.: 67.08 %C; 4.34 %H; 8.51%N;9.93%S
Found: 67.00 %C; 4.20 %H; 8.45%N:9.85%S.

2.Phenylazo-4-diphenylthiosulfone (II):

1.177 g (0.012 mol) of aniline was diazotated as in(I).Excess of HNO_2 has been removed with stream of air. Solution was neutralized to pH 5-6 with Na_2CO_3. After cooling to -5°C was added 3.36g (0.012 mol) of sodium 4-diphenylthiosulphonate in 50 ml water-acetone (4:6). The yellow precipitate was filtrated and dryied under low pressure.

Yield:2.88g (67%); m.p.94-96°C.

IR(KBr):1592 cm^{-1} (N=N), 1340 and 1170 cm^{-1} (SO_2).

$C_{18}H_{14}N_2S_2O_2$ (354.42): Calc.:61.01%C; 3.95%H; 7.90%N; 18.07%S
Found:60.98%C; 3.90%H; 7.86%N; 18.00%S.

3.Phenylazo-4-diphenylsulphide (III):

2.35 g (0.025 mol) of aniline was diazotated as in (I).Excess of HNO_2 has been removed with stream of air. solution was neutralized to pH 7 with Na_2CO_3. After cooling to - 5°C was added 7.37 g (0.025 mol) of 4-diphenylsulphide and 1.0 g (0.025 mol) NaOH in 30 ml water. The yellow precipitate was filtrated and dryied under low pressure.

Yield:5.67 g (77%); m.p.75-76°C.

IR(KBr):1580 cm^{-1} (N=N),ν(str) C-S very week.

$C_{18}H_{14}N_2S$ (290.368): Calc.:74.48%C; 4.74%H; 9.65%N; 9.93%S
Found:74.13%C; 4.80%H; 9.52%N; 9.85%S.

Styrene was purified by an ordinary method. Azodiizobutyronitrile (AIBN) which was used as a thermal initiator,was purified by recrystallization from ethanol.M.p.102°C.

Photolysis of compounds I-III was made in quartz closed quvetts (1cm thick) in an argon atmosphere. The change in UV absorption during the photolysis was measured with an UV/VIS Zeiss Jena spectrometer.

Photopolymerization was carried out in closed quartz flask in an argon atmosphere at room temperature.

Thermal polymerization was carried out at 65°C in a closed reaction flask in an argon atmosphere and in absence of day light by shaking.

After photo- and thermal-polymerization polymer was precipitated by addition of an excess of methanol,washed with methanol and then dryied in a vacuum.

For UV irradiation was used a high pressure xenon lamp type CSX 150 Philips.

The intrinsic viscosity $[\eta]$ at 30°C was determined in benzene by using Ubbelohde´s viscometer. The number-average degree of styrene polymerization ($\overline{P}_{vis}$) was calculated from the equation:[9]

$$\overline{P}_{vis} = 3.205 + 1.37\log[\eta]$$

Thermoanalysis of compounds I-III has been studied using a Paulik derivatograph (Hungary) in air,heating rate 10°C per min.

RESULTS AND DISCUSSION

All the synthetized compounds I-III are yellow-orange colored and have a broad absorption between 250-350 nm (Figs 1-3).

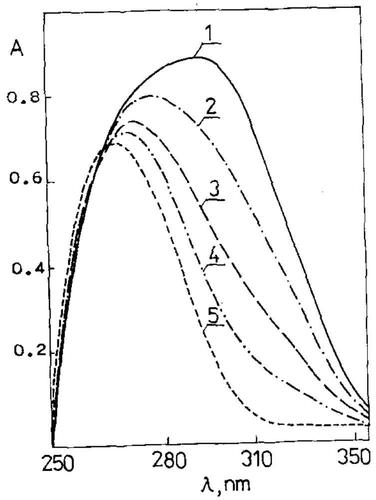


Fig.1 Absorption spectra of (I)4.5x10^{-5} M in chloroform: (1) before UV irradiation and (2) 5 min; (3) 10 min; (4) 15 min; (5) 30 min UV irradiation.

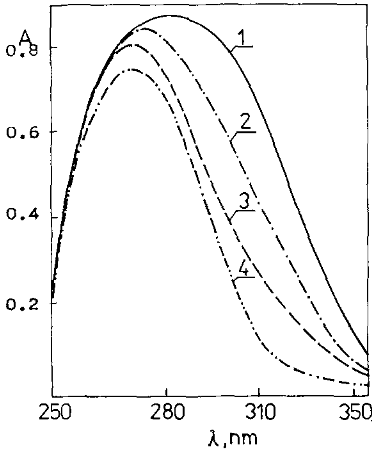


Fig.2 Absorption spectra of (II)4.3x10^{-5} M in chloroform: (1) before UV irradiation and (2) 5 min; (3) 10 min UV irradiation and (4) after 16 hours in the dark.

Under UV irradiation they are photolyzed and their absorption maxima are shifted towards the shorter wavelengths. In the case of compound II it has been observed the "dark effect",i.e.decreasing of absorption during the storage of pre-irradiated sample in the dark (Fig.2). Compounds I and II are photochemichemically stable in day light,whereas compound III decomposes quickly (Fig.4). All compounds I-III are thermally unstable and decompose in around 100°C with some exo-thermical effect (Fig.5).

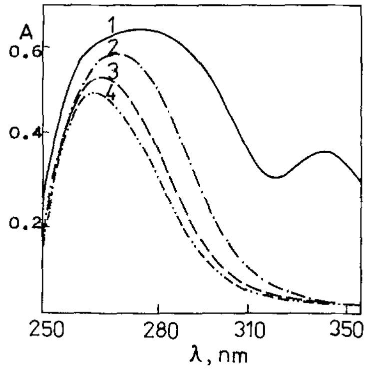


Fig.3 Absorption spectra of (III)2.9x10^{-5}M in chloroform: (1) before UV irradiation and(2) 5 min; (3) 10 min (4) 60 min UV irradiation.

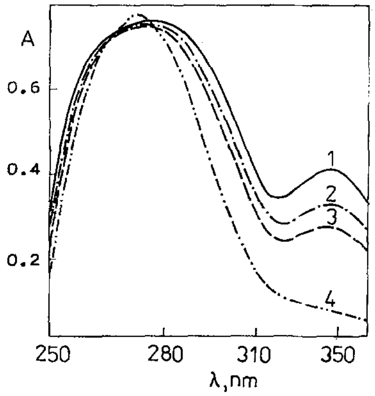


Fig.4 Absorption spectra of (III)3.5x10^{-5}M in chloroform: (1) before exposure to day light and (2) 5 min; (3) 20 min;(4) 30 min exposure to day light.

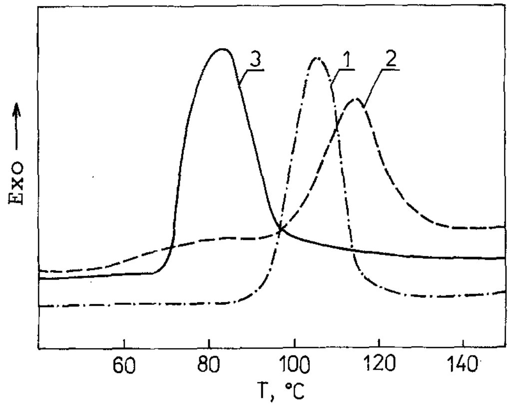
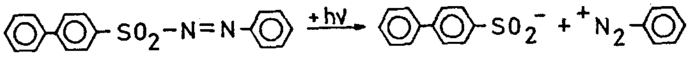


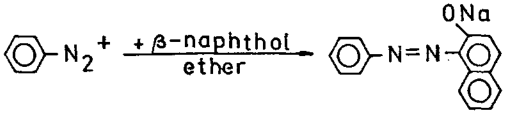
Fig.5 DTA curves for compounds: 1(I); 2 (II) and 3 (III) showing exo-thermical effect caused by the thermal decomposition of these compounds.

The photolysis mechanism of these compounds depends on the type of solvent used. In polar solvents like ethanol,photolysis of compound (I) occurs by the ionic mechanism:



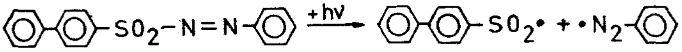
(1)

The ionic character of this reaction can be easily tested by the addition of beta-naphthol,which causes a dye red-orange colored reaction:[1]



(2)

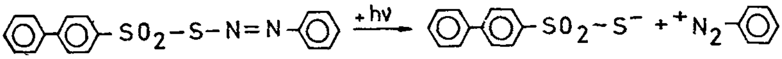
In non-polar solvents like chloroform the photolysis reaction of compound I occurs by the radical mechanism:



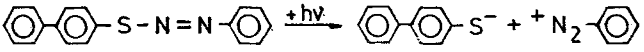
(3)

In this case addition of beta-naphthol has no effect,and does not cause coloration of the irradiated solution.

Compounds II and III are photolysed both in ethanol and chloroform,and decompose by the ionic mechanism:



(4)



(5)

Photolysis and thermolysis of compounds I-III in styrene occur by the radical mechanism. Polymerization reactions caused by radicals,formed from the decomposition of I-III,are characterized by low conversions (Fi.5 and Fig.6).

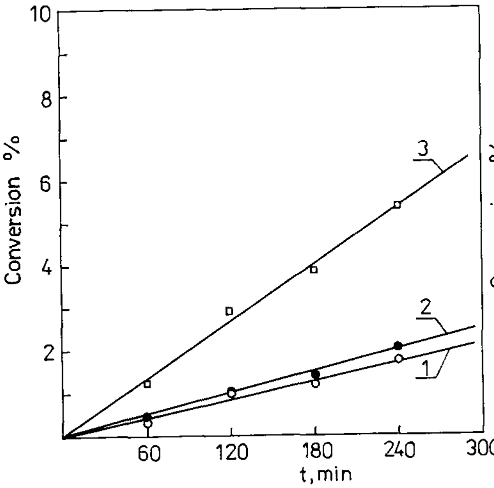


Fig.6 Photoinitiated polymerization of styrene by: 1(I),2(II) and 3(III).Conc.of compounds (I-III) was $5x10^{-3}M$.

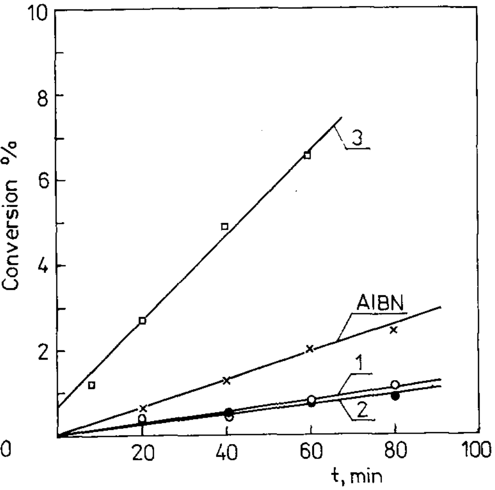


Fig.7 Thermal polymerization of styrene by: 1(I), 2(II) and 3 (III) at 65°C. Con.of compounds (I-III) and AIBN was $1x10^{-3}M$-.

Compound III used as initiator of thermal polymerization causes higher conversion of styrene into polymer,than does AIBN (Fig.7). These results show that new synthetized initiators I-III are rather poor photoinitiators for polymerization of styrene. Free radicals formed from their decomposition are probably too inactive to initiate fast polymerization of styrene to a high conversion.

Polystyrenes photopolymerized in the presence of compounds I-III have low molecular weights: $\overline{M}_v$= 5000-6000 (for I and II), and 14000 (for III). Only polystyrene thermally polymerized in the presence of compound III had $\overline{M}_v$= 510 000.

We are currently synthetized a new group of sulfur-containing photoinitiators with much better initiating properties and all kinetic data for these type photoinitiators will be present in coming papers.

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