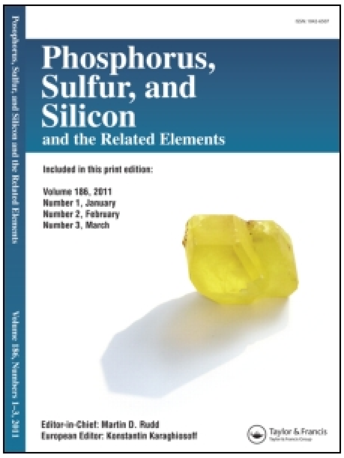

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INTITIATION OF 1,3,5-TRITHIAN3 POLYltlERIZATION BY W-IRRADIATION

Aleksander Żuk[a]; Ewa Andrzejewska[a]
[a] institute of Chemical Technology, Poznafi, Poland

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INITIATION OF 1,3,5-TRITHIANE POLYMERIZATION BY UV-IRRADIATION

Aleksander Żuk and Ewa Andrzejewska
Institute of Chemical Technology, Politechnika Poznańska,
Poznań, Poland

It is well known that 1,3,5-trithiane is polymerized to give polythiomethylene by using cationic catalysts or ionizing radiation. It has been suggested that such cyclic monomers polymerize in the solid state by an ionic addition mechanism and therefore cannot be polymerized by the ultraviolet light.
However, we have found that in definite conditions 1,3,5-trithiane polymerization can be initiated by UV-irradiation.

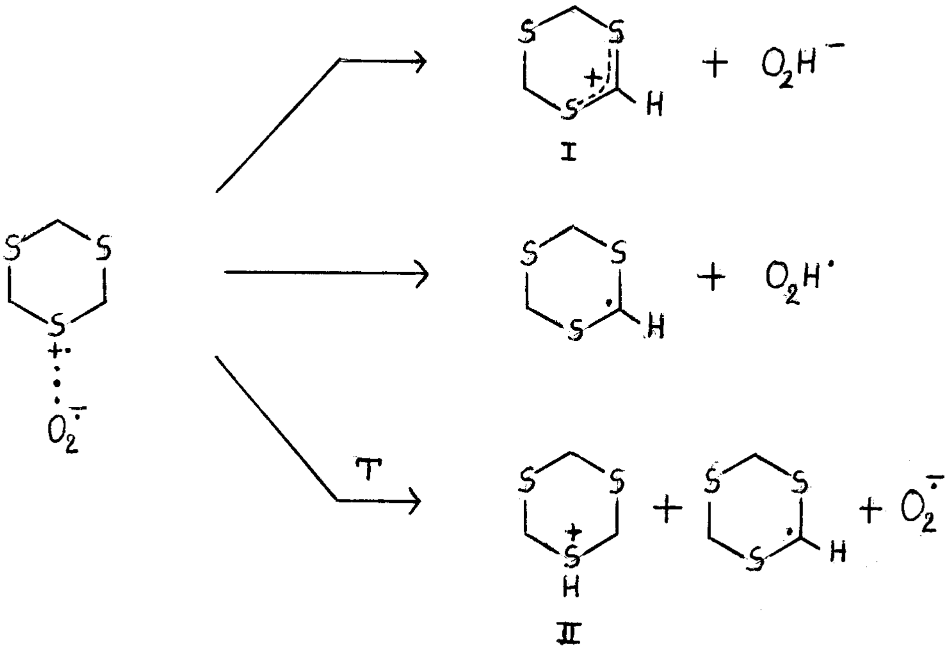
The solid monomer was irradiated by a high pressure mercury lamp and postpolymerized at 195°C.

We have discovered the essential role of oxygen in the initiation process. When the monomer was preirradiated under argon, no polymer formation was observed. Irradiation under oxygen significantly increased the polymer yield compared with the irradiation under air. Similar results were obtained by using benzophenone as the sensitizer after the elimination of monomer absorption.
Furthermore, we have found that oxygen is necessary only during irradiation.
The resulting active centres have the long life-time. No decrease in polymer yield was observed when the postpolymerization was carried out in two weeks after preirradiation.

On the basis of the observations above and the recent report on the charge-transfer complexes between oxygen and organic sulfides we propose the following scheme of the initial reaction stage.

T - 1,3,5-trithiane

$$T + O_2 \longrightarrow (T,O_2) \xrightarrow{h\nu} (T,O_2)^* \longrightarrow (T^{\dot{+}} \cdots O_2^{\dot{-}})$$



Cations I and II can be precursors of the active species initiating 1,3,5-trithiane polymerization at elevated temperatures.