

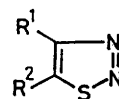
## A New Type of Photo-cross-linking

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5-Methyl-4-vinyl-1,2,3-thiadiazole can be thermally or catalytically polymerized; cross-linking of the polymer chains is possible by photochemical degradation of the thiadiazole rings leading to sulphur bridges.

Recently, photochemical processes for the cross-linking of polymer chains have increased in importance.<sup>1</sup> We have made use of the photofragmentation of 1,2,3-thiadiazoles for this purpose. 1,2,3-Thiadiazoles with  $\alpha,\beta$ -unsaturated side-chains in the 4- or 5-position are readily available;<sup>2</sup> *e.g.*, the vinyl compound (**1a**) which was a suitable starting material for thermal polymerization reactions. Three methods for the polymerization of (**1a**) were investigated: (A) bulk polymerization, (B) radical polymerization in boiling toluene initiated by dibenzoyl peroxide, and (C) cationic polymerization in dichloromethane catalysed by boron trifluoride-diethyl ether. The conditions and results of the methods A, B, and C are summarized in Table 1.

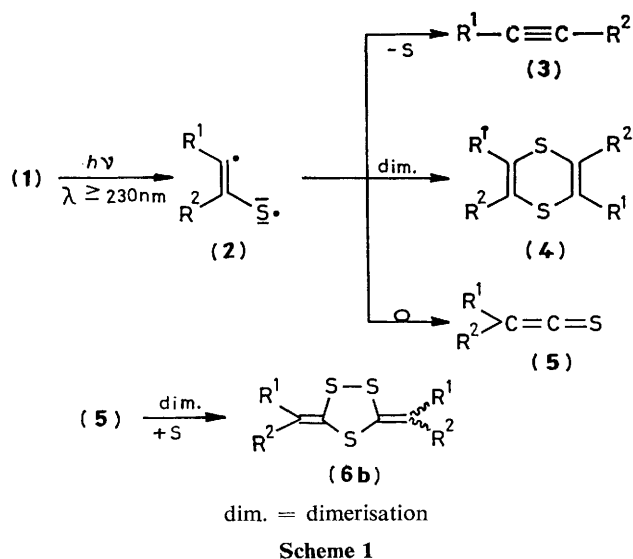


(**1**) **a**;  $R^1 = \text{CH}=\text{CH}_2$ ,  $R^2 = \text{Me}$   
**b**;  $R^1 = \text{Et}$ ,  $R^2 = \text{Me}$

Method A yields a highly viscous, rubber-like polymer, whereas the methods B and C lead to powdery solids. All three polymers are easily soluble in dichloromethane. The closely related i.r. spectra as well as the analysis data for the resultant polymers confirm that the linkage of the monomers

**Table 1.** Polymerization of 5-methyl-4-vinyl-1,2,3-thiadiazole.

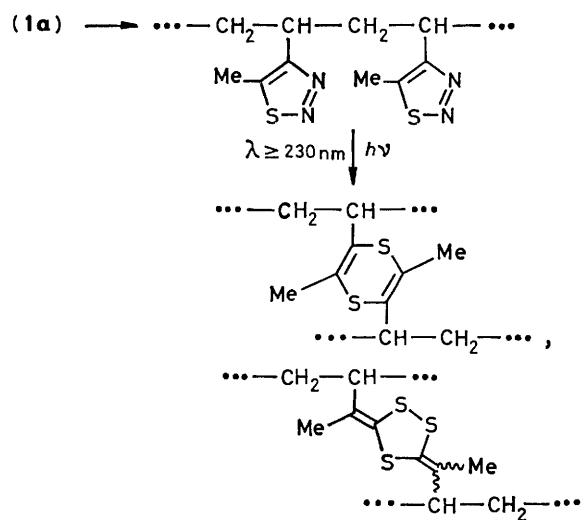
Method	Reaction time	Reaction temperature $T/^\circ\text{C}$	Yield of polymer/%	Decomposition temperature of polymer $T_d/^\circ\text{C}$
A	4 d	25	79	165
B	30 h	110	26	140
C	50 h	20—40	15	135



(1) is that found in other polyvinyl chains and show, in particular, that in all cases the 1,2,3-thiadiazole rings have not been affected. The reaction temperatures are not high enough for thermal degradation of the heterocyclic rings (compare columns 3 and 5 of Table 1).

Irradiation of the polymers (dissolved in dichloromethane,  $\lambda \geq 230$  nm, room temp.,  $N_2$  atmosphere) with a Hanovia 450 W high pressure mercury lamp leads (1 h) to a practically quantitative emission of nitrogen. Almost insoluble solids can be isolated. To determine the type of cross-linking which occurs, we have investigated the photochemistry of the related compound 4-ethyl-5-methyl-1,2,3-thiadiazole (1b).

After the nitrogen elimination a fragment with the character of a 1,3-diradical<sup>3,4</sup> remains, for which different stabilization reactions<sup>5</sup> exist: cleavage of the C-S bond leading to a thioketen (Scheme 1). In the case of (1b) mainly the 1,4-dithiin (4b) and 1,2,4-trithiolan (6b) rings are formed (Scheme 2).<sup>5</sup> Whereas (4b) can be regarded as the most obvious dimer of (2b),<sup>6</sup> the generation of (6b) involves a rearrangement of (2b) to (5b) and the addi-



tion of the previously eliminated sulphur. It is certainly justified to assume analogous photochemical behaviour of the polymer chains, because they are so closely related.

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