



SULFIDES AND DISULFIDES OF S-TRIAZINE AND S-HEPTAZINE: FLAME RETARDANCY

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INTRODUCTION

Flame retardancy is a key property of polymer materials. One of the most efficient flame retardant mechanisms of a compound is the thermal release of species which are able to inhibit radical reactions occurring in a flame: so-called flame poisoning. Especially pure hydrogen-carbon-based polymers with a low charring tendency, such as polypropylene, and applications of these polymers which do not allow high flame retardant amounts, such as foils or foams, have to be protected against ignition by suitable flame retarding radical generators. Sulfur compounds, including organic disulfides, are one example.

In our current study, phenyl thiocyanurate, phenyl dithiocyanurate and phenyl thiocamelurate (see Figure 1) are studied as possible radical generators with flame retardant properties.

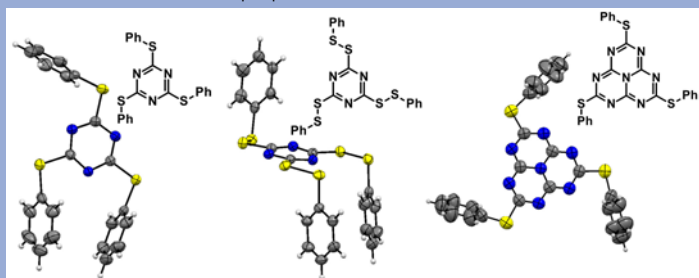


Figure 1. Molecular structure of the studied s-triazines and s-heptazine.

SYNTHESIS

The synthesis of triithiocyanuric acid and its alkyl- and aryl-derivatives are well-known in literature. By adding thiols or sodium thiolates to a solution of cyanuric chloride $C_3N_3Cl_3$, alkyl- and arylsulfides of s-triazine can easily be synthesized. Alkyl- and aryldisulfides of s-triazine are synthesized by adding an alkyl- or aryl sulfonylchloride to a dispersion of sodium thiocyanurate.

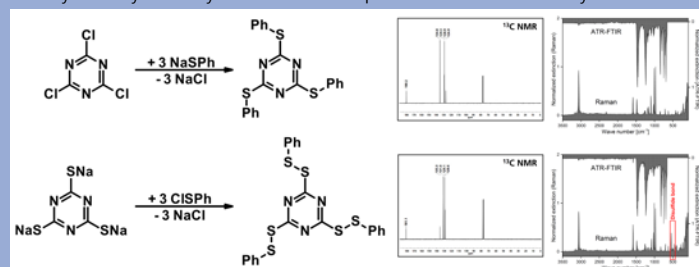


Figure 2. Synthesis path of thiocyanurates and dithiocyanurates.

While cameluric chloride reacts with arylthiols to form arylthiocamelurates, the synthesis of alkylcamelurates requires an auxiliary base like *N,N*-diisopropylamine (DIPEA) to obtain alkylthiocamelurates. In our recent studies we reported the preparation of alkyl- and aryl-substituted thiocyanurates and dithiocyanurates^[1] as well as thiocamelurates^[2].

FLAME RETARDANCY

Phenyl dithiocyanurate and phenyl thiocamelurate degrade by releasing sulfur species whereas phenyl thiocyanurate show no thermal decomposition in the condensed phase (see Figure 3).

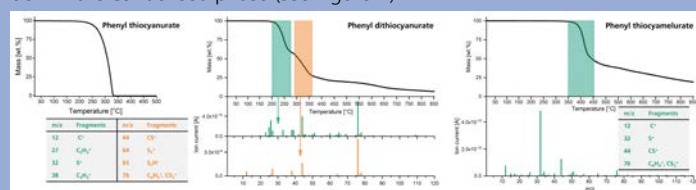


Figure 3. Thermogravimetric analysis combined with mass spectrometry.

For flame retardant investigations, the three components were incorporated into polypropylene (PP) and studied by the limiting oxygen index (LOI) test and thermogravimetric analysis (see Figure 4). Weak flame retardant effects are observed for phenyl thiocyanurate. However, phenyl thiocamelurate shows increasing flame retardant effects up to 7.5 wt. % (ΔLOI : 2.3 $O_2\%$) which are comparable to the flame retardant effects reported for organic disulfides like diphenyl disulfide. Phenyl dithiocyanurate shows unusually high flame retardant effects for organic disulfides in PP. The highest efficiency is observed at 5.0 wt. % (ΔLOI : 5.9 $O_2\%$).

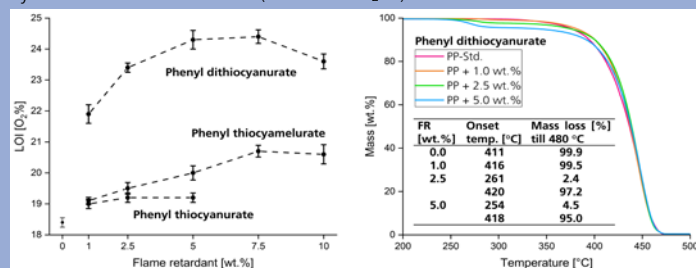


Figure 4. LOI results (left) and TGA of phenyl dithiocyanurate in PP (right).

Based on these results, several aryl- and alkyl-substituted dithiocyanurates and thiocamelurates were studied. The flame retardant efficiency (measured according to LOI in PP) can be classified as follows: dithiocyanurate >> thiocamelurate > thiocyanurate and aryl group > alkyl group.

CONCLUSIONS

Phenyl dithiocyanurate has proved to be a sulfur compound with an unexpectedly strong flame retardant effect. Phenyl thiocamelurate also provides flame retardancy. Both compounds are able to release sulfur species during thermal degradation. However, phenyl thiocyanurate releases no fragments during thermal degradation and only weak flame retardancy is observed.

For references see

- [1] C.-C. Höhne, C. Posern, U. Böhme, E. Kroke, *Chem. Eur. J.* **2018**, 24, 13596.
- [2] C. Posern, U. Böhme, J. Wagler, C.-C. Höhne, E. Kroke, *Chem. Eur. J.* **2017**, 23, 12510.