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Nitroxyl radicals and nitroxylethers beyond stabilization: radical generators for efficient polymer modification

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Received 5 June 2006; accepted after revision 28 August 2006

Available online 04 October 2006

Abstract

Beyond traditional polymer stabilization, sterically hindered piperidine derivatives move into new application areas where radical functions are key elements. Recent achievements in using nitroxyl derivatives in degradation, polymerization and grafting processes are discussed together with the involved chemical reactions and the resulting material properties. The examples shown cover selected nitroxylethers (NORs) performing as flame retardants and flame retardant synergists or replacing peroxides in manufacturing controlled rheology polypropylene (PP). Furthermore, NORs and nitroxyl radicals mediate radical polymerization processes resulting in tailor-made intermediates for polymer modification via radical and condensation steps and offer access to complex polymer architecture. **To cite this article:** R. Pfaendner, *C.R. Chimie 9 (2006)*.

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Keywords: Controlled polymerization; Nitroxyl radicals; Nitroxyl ethers; Grafting; Flame retardants; Functional polymers

1. Introduction

Hindered amines (HALS) are a well-known class of powerful stabilizers that protect plastics from the negative influence of light and heat. Although there are ongoing discussions to explain completely the mechanism of stabilization, radical processes via the nitroxyl radical play an important role, for example, tetramethylpiperidine derivatives act as radical scavengers through transient formation of a nitroxylether [1].

Ciba Specialty Chemicals, with its substantial tradition in piperidine chemistry, has introduced a number of innovative products in the area of HALS chemistry:

- oligomeric or polymeric hindered amines and blends thereof contribute as excellent synergists to prolong long-term heat stability, e.g. in polypropylene and polyethylene;
- stable aliphatic nitroxyl ethers such as [®]Tinuvin NOR 371 combine excellent light stabilizer activity with resistance to aggressive environments;
- low basicity is combined with excellent light stability in Tinuvin 123;
- nitroxyl radicals such as [®]Prostab 5198 and Prostab 5415 are provided as process stabilizers in monomer distillation units and as chain stoppers to terminate polymerization reactions.

The present paper aims at reviewing the benefits of newly developed innovative nitroxyl chemistries beyond stabilization that are tailored as flame retar-

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dants, peroxide alternatives for degradation or grafting and initiators for controlled free-radical polymerization (CFRP) processes. Functional materials from CFRP are used for tailor-made modification of polymers and polymer blends.

The broad area of applications accessible by nitroxyl compounds can be adjusted by the structure and the substitution pattern adjoining the functional group. The chemical structure of the nitroxyl ether determines the stability of the N–O–C bond and consequently the thermal stability and the thermally induced split between the N–O or the O–C bond. However, the generation of radicals from nitroxyl derivatives is the key step in all these processes.

2. Nitroxylethers as flame retardants

Hydroxylamine ethers (nitroxylethers, NORs or alkoxyamines), such as Tinuvin 123, were first introduced as non-interacting UV-stabilizers with low basicity. Such stabilizers provide protection for automotive coatings and agricultural films even under severe conditions. In agricultural films pesticides generate acidic species and, therefore, deactivate conventional HALS. This problem is overcome by using NOR stabilizers.

Similarly flame retardants such as halogens or phosphorous compounds generate thermally or photochemically acidic species which result in inferior UV stability. This is solved by using NORs in combination with brominated flame retardants.

Surprisingly, it was found that the nitroxylethers do not only improve the UV stability but also contribute to flame retardancy. Even without any additional flame retardant it was demonstrated that NORs alone can achieve flame retardancy, e.g., in polypropylene fibers and films they pass industrial standards. For example, [®]Flamestab NOR 116 provides flame retardancy at a concentration of only 0.5% passing the NFPA 701 fiber test [2] on polypropylene knitted socks [3].

Moreover, the addition of NORs as FR synergist can improve the efficiency of conventional brominated flame retardants as demonstrated in Table 1, where the combination of NOR and decabromodiphenyloxide surpasses the FR alone [4].

Table 1
NFPA 701 (1996) test results in polypropylene fibers

Additive	Weight loss (%)	Drip Burn Time (s)	Rating
None	> 40	50+	Fail
4% Decabromodiphenyloxide	0.8	7	Pass
2% Decabromodiphenyloxide	5	10	Fail
1% Decabromodiphenyloxide 0.25% Flamestab NOR 116	0	4	Pass

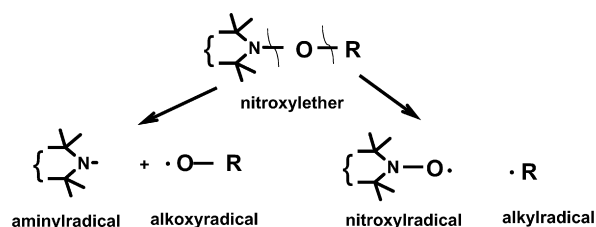


Fig. 1. Thermolysis of nitroxylethers.

Therefore, it is possible to design with NORs flame retardant polyolefin molding compositions with lower levels of halogenated flame retardants and, in addition, to eliminate antimony trioxide, which is often used as FR synergist. Low FR concentrations and no antimony trioxide result in polymers with improved processability, better mechanical properties and reduced smoke density. For example, UL 94 V-2 rating is achieved in PP injection molded plaques at concentrations as low as 3.5% of formulations containing Flamestab NOR 116 [5].

The activity of the nitroxylether as flame retardant is based on the thermolysis of nitroxyl ethers which leads to the formation of either alkoxy and aminyl radicals or alkyl and nitroxyl radicals (Fig. 1). Aminyl and alkoxy radicals are very reactive and cause, on the one hand, degradation of polypropylene (and cross-linking of polyethylene). On the other hand, they are involved in the free radical chemical reactions during the combustion process [4].

In the synergistic combinations NORs can interact with brominated flame retardants and facilitate the release of bromine, consequently increasing the overall FR performance. Additionally, ignition of a polymer creates the formation of volatile combustion products, releasing heat during burning. This heat energy from the flame is then fed back to the polymer to sustain the burning process. It is believed that the thermolysis of NOR significantly reduces the amount of thermal feedback from the flame.

3. Nitroxyls for controlled degradation of PP

Peroxides are the current products of choice for controlled degradation of polypropylene (PP), for cross-

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