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# The role of hydroperoxides in the chemiluminescence of oxidized polymers reconsidered

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ABSTRACT

Chemiluminescence phenomena often occur on heating oxidized polymers in an inert atmosphere. This light emission is frequently attributed to reactions involving hydroperoxides produced during the oxidation process. The main objective of this study was to check the role played by hydroperoxides in the luminescence of three oxidized polymers: polyoctenamer, an ethylene propylene diene monomer (EPDM), and polypropylene. The hydroperoxides of pre-oxidized polymers (photo-oxidized or hydroperoxidized) were transformed using photolysis or dimethyl sulfide (DMS) treatment. The chemiluminescence of the polymer samples was measured before and after treatment and decomposition of hydroperoxides monitored with IR spectroscopy and thermal analyses. Surprisingly, all the photolysed polymers retained strong luminescence that is not entirely explained by the presence of hydroperoxides. On the contrary, two of the three polymers showed a quenching of luminescence after DMS treatment. Two conclusions can be drawn. First, the results clearly indicate that the luminescence of oxidized polymers does not only depend on the presence of hydroperoxides. The second conclusion concerns the origin of the remaining chemiluminescence after photolysis and the quenching observed after DMS treatment. As photolysis mainly leads to the formation of carbonyl compounds and DMS treatment to the production of alcohols, it is proposed that carbonyl compounds are probably involved in the chemiluminescence of oxidized polymers, especially through associations with remaining hydroperoxides.



## 1. Introduction

The auto-oxidation mechanisms of polymers [1], which are notably involved when applying thermal or photochemical stresses in the presence of oxygen, lead to the formation accumulation of hydroperoxides. These compounds play a key role in oxidation pathways [2] and are often considered as the first easily detectable oxidation species. Hydroperoxides are thermally and photochemically unstable and easily decompose to form radical species that participate in the oxidation chain reactions. Decomposition of hydroperoxides is also responsible, after several steps, for production of the final oxidation products, such as carboxylic acids, ketones or alcohols. Moreover, the reactions occurring during this process lead to the

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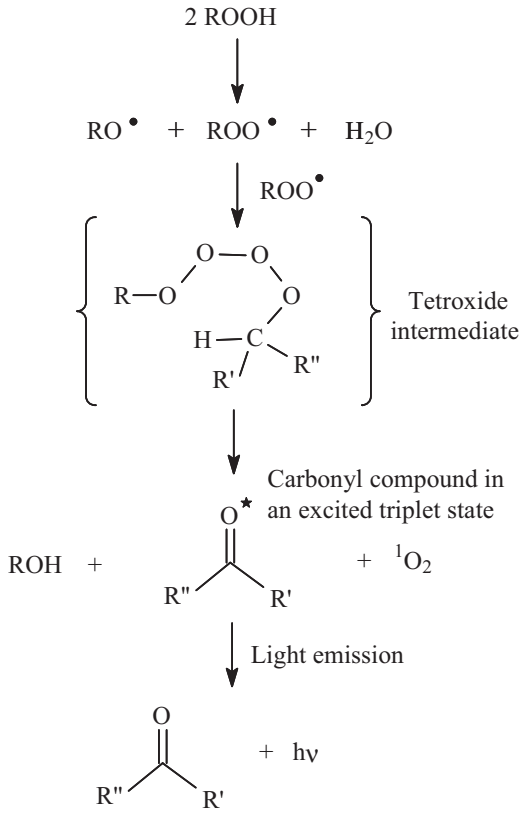


**Fig. 1.** Russell mechanism of light emission by hydroperoxides [11].

well-known and well-studied light emission called "chemiluminescence" [3–6]. This luminescence phenomenon is often ascribed in the literature to reactions involving hydroperoxides [7–10]. The pathway most postulated is the Russell mechanism [11] which involves recombination of two peroxyl radicals formed through the bimolecular decomposition of hydroperoxides (see Fig. 1). At least one of the peroxyl radicals has to be primary or secondary for the reaction to occur. Recombination of the peroxyl radicals leads to formation of a tetroxide intermediate. This intermediate's rearrangement and cleavage produces an alcohol, singlet oxygen and a carbonyl compound in an excited triplet state. The radiative decay of this carbonyl compound is considered to be responsible for the light emission. Some other more controversial pathways have been proposed to explain the chemiluminescence of oxidized polymers such as direct homolysis of hydroperoxides [3,12], disproportion of alkoxy radicals [3,13] and β-scission of alkoxy radicals [3,14]. Whatever the mechanism, hydroperoxides have been postulated to be linked, directly or indirectly, to the light emission of oxidized polymers. As hydroperoxides are considered an early oxidation species, the luminescence of oxidized polymers is often used to determine the oxidation state of the polymer and to establish correlations between the hydroperoxides contents and the measured chemiluminescence. Most chemiluminescence studies on oxidized polymers involve polypropylene [7–10], a polymer well known to be easily oxidized in the absence of stabilisers and to produce, upon oxidation, a high level of hydroperoxides, essentially in the tertiary form [15,16]. These studies were only possible thanks to the technological development of highly sensitive single-counting mode photomultipliers [7,17].

The aim of this study was to check if the presence of hydroperoxides is necessary for the luminescence of oxidized polymers. The investigations consisted in measuring the chemiluminescence of three different oxidized polymers whose hydroperoxides were previously destroyed, either chemically or photochemically. The results, discussed and considered against the more well-accepted mechanisms, yield a new insight into the origins of the light emission of oxidized polymers.

## 2. Experimental

### 2.1. Materials

The experiments were conducted using three different unstabilized polymers: a polyoctenamer, an ethylidene norbornene based ethylene propylene diene monomer (EPDM) and a polypropylene.