Chimia 47 (1993) 396

ISSN 0009–4293

Stabilization of Polymers against Photodegradation

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Light stabilizers (LS) for polymers are classified according to their stabilization mechanism. The first group of LS are those which prevent the formation of excited chromophores in the polymers, or rapidly quench them back to the ground state. These physically active LS are UV absorbers (UVA) which absorb UV energy and thereby reduce or prevent the formation of excited electronic states in the polymer, and quenchers which take over excitation energy from the excited chromophores in the polymers. The second group of LS stabilize already chemically damaged polymer molecules, before degradation under chain scission occurs. These chemically active LS are radical scavengers which cure reactive radicals, and hydroperoxide decomposers which transfer hydroperoxides to more stable species without generation of free radicals, or before polymer breakdown.

The chemistry as well as the mechanism of stabilization are discussed for various UVA (2-hydroxybenzophenones, 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxyphenyltriazines, oxalanilides, formamidines, salicylates, and cinnamates), quenchers (Ni complexes), radical scavengers (hindered amine light stabilizers = HALS, 4-hydroxybenzoates) and hydroperoxide decomposers (dialkyldithiocarbamates). Most of these LS are multifunctional, and they are usually classified just according to the mechanism which is prevailing.

LS are applied to polymers according to various technologies. They can be incorporated in concentrations of 0.1–1% into the mass of the polymers, resulting in a more or less even distribution throughout the polymer matrix. In order to concentrate the LS at the surface where they are most needed for protection, a better technology is to add light stabilizers in relatively high concentrations (2–4%) into coatings or coextruded film layers on top of the bulk polymer. Recent trends in development include the technology of chemical binding of the LS to the polymer substrate, in order to avoid losses of LS by extraction or volatilization. This can be achieved *a*) by chemical reactions of LS with functional groups already during the polymerization or polycondensation step, *b*) by radical graft polymerization of unsaturated LS molecules onto polymers, or *c*) even by photochemical grafting of special LS molecules during exposure to UV radiation.

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Chimia 47 (1993) 396

ISSN 0009–4293

Photodynamic Therapy and Photodetection of Early Cancer

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The optical properties of dyes that localize preferentially in superficial early cancer can be used to detect and treat the malignant tissue. For photodetection we use the fluorescent properties of these dyes. For photodynamic therapy (PDT) dyes are selected with high triplet yields and long triplet lifetimes that can give rise to efficient singled oxygen production which results in local phototoxicity and destruction of the neoplastic tissue.

Both PDT and photodetection are based on local changes in dye concentration in a cancer which may be either natural or induced. Several approaches are used to target malignant tumors with dyes, including attaching dyes to monoclonal antibodies, to polymers with long plasma lifetimes, and to low-density lipoproteins. One also selects particular molecular properties which cause enhanced concentrations in tumors like the use of certain tetrapyrroles or lipophilic cationic dyes. Other strategies involve application of γ-levulinic acid which interferes with the natural synthesis of heme by excess of protoporphyrin IX production, the use of liposome carriers, *etc.*

Over the past ten years, in a collaboration between the CHUV hospital in Lausanne, the Swiss Federal Institute of Technology (EPFL), the University of Lausanne, and *Ciba-Geigy* in Basel, we have developed effective clinical photodetection and photodynamic therapy. We have focused mainly on early superficial squamous cell cancers of the upper aerodigestive tract, the tracheobronchial tree and the esophagus. As an example, one may mention PDT of carcinoma *in situ* in the above mentioned parts of the body, where with a follow up between one and nine years the 15 patients treated showed no recurrence at all as checked by local biopsy. We have also developed sophisticated apparatus for endoscopic detection of early cancer by light induced fluorescence (LIF) which permits localization of sub-mm^3 superficial tumors. LIF spectroscopy is also used for non-invasive clinical pharmacokinetics of new dyes by means of a fiberoptic based optical multichannel analyzer.

PDT with the early drug *Photofrin II* is now an accepted treatment for bladder cancer in Canada. Eight new substances are undergoing PDT clinical trials at present. Furthermore, the combination of light and drugs is not only being investigated for cancer treatment but also for other diseases like psoriasis and atherosclerosis.

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