

ORIGINAL ARTICLE

# Mechanism of photostabilization of poly(methyl methacrylate) films by 2-thioacetic acid benzothiazol complexes



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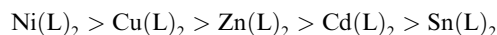
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## KEYWORDS

Photochemistry;  
Photostabilizer;  
UV absorber;  
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PMMA;  
2-Thioacetic benzothiazol  
acid

**Abstract** The photostabilization of poly(methyl methacrylate) (PMMA) films by 2-thioacetic acid benzothiazol with Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II) complexes was investigated. The PMMA films containing concentration of complexes 0.5% by weight were produced by the casting method from chloroform solvent. The photostabilization activities of these compounds were determined by monitoring the hydroxyl index with irradiation time. The changes in viscosity-average molecular weight of PMMA with irradiation time were also tracked (using benzene as a solvent). The quantum yield of the chain scission ( $\Phi_{cs}$ ) of these complexes in PMMA films was evaluated and found to range between  $3.64 \times 10^{-5}$  and  $7.44 \times 10^{-5}$ . Results obtained showed that the rate of photostabilization of PMMA in the presence of the additive followed the trend:



According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among them UV absorption, peroxide decomposer and radical scavenger for photostabilizer additives mechanisms were suggested.

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## 1. Introduction

Many polymers undergo thermal oxidative degradation during processing. Over longer periods at ambient temperature polymers also deteriorate in the solid state through autooxidation and photooxidation. In outdoor applications where the materials are exposed to UV solar radiation, the energy of this radiation is sufficient to initiate photochemical reaction leading to degradation. Plastics are commonly protected

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against such deterioration by the addition of antioxidants, light and heat stabilizers (Chmela et al., 2001; Yousif et al., 2010).

There is a great interest at present in the photo-oxidative degradation of polymeric materials because macromolecules have increasingly widespread commercial applications. Polymeric synthetic, semi synthetic and natural are degraded when exposed to the environment (Grassie and Scott, 1985). All commercial organic polymers degrade in air when exposed to sunlight as the energy of sunlight is sufficient to cause the breakdown of polymeric C–C bonds as a consequence of degradation. The resulting smaller fragments do not contribute effectively to the mechanical properties and the polymeric article because brittle. Thus the life of thermoplastics for outdoor applications becomes limited due to weathering (Andrady et al., 1988).

Almost all synthetic polymers require stabilization against the adverse effect with the development of synthetic resins it became necessary to look for ways and means to prevent, or at least reduce, the damage caused by the environmental parameters such as light, air and heat. This can be achieved through addition of special chemicals, light stabilizers or UV stabilizers, that have to be adjusted to the nature of the resin and the specific application considered. The photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of stabilizer: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) free radical scavengers, of these it is generally believed that types (c)–(e) are the most effective.

Most of stabilizers are believed to be multifunctional in their mode of operation. This view is complicated by the fact that mechanisms involved in photo-oxidation and these, in turn depend on the polymer structure and other variables, such as manufacturing, operation, processing and conditions (Harper et al., 1974).

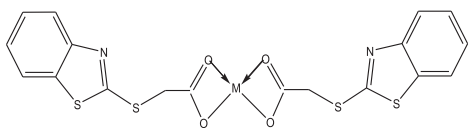
As part of our on-going research on the photostabilization of polymers, the photostabilization of PMMA was studied using 2-thioacetic benzothiazol complexes.

## 2. Experimental

### 2.1. Materials

The following complexes were all prepared by the method described by Yousif et al. (2010):

Bis(2-thioacetic acid benzothiazol) tin(II)	Sn(L) <sub>2</sub>
Bis(2-thioacetic acid benzothiazol) cadmium(II)	Cd(L) <sub>2</sub>
Bis(2-thioacetic acid benzothiazol) nickel(II)	Ni(L) <sub>2</sub>
Bis(2-thioacetic acid benzothiazol) zinc(II)	Zn(L) <sub>2</sub>
Bis(2-thioacetic acid benzothiazol) copper(II)	Cu(L) <sub>2</sub>



Where M = Sn(II), Cd(II), Ni(II), Zn(II) or Cu(II)

### 2.2. Experimental techniques

#### 2.2.1. Films preparation

Commercial PMMA supplied by Petkim Company (Turkey) was re-precipitated from chloroform solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of PMMA solution (5 g/100 ml) in chloroform were used to prepare polymer films with 40 μm thickness (measured by a micrometer type 2610 A, Germany). The prepared complexes (0.5% concentrations) were added to the films (blank). The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual chloroform solvent, film samples were further dried at room temperature for 3 h under reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

#### 2.2.2. Irradiation experiments

**2.2.2.1. Accelerated testing technique.** Accelerated weatherometer Q.U.V. tester (Q-panel, company, USA) was used for irradiation of polymers films. The accelerated weathering tester contains a stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 W each. These lamps are of the type UV-B 313 giving a spectrum range between 290 and 360 nm with a maximum at wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same.

#### 2.2.3. Photodegradation measuring methods

**2.2.3.1. Measuring the photodegradation rate of polymer films using infrared spectrophotometry.** The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000–400 cm<sup>-1</sup> using FTIR 8300 Shimadzu Spectrophotometer. The position of hydroxyl absorption is specified at 3430 cm<sup>-1</sup> (Rabek and Ranby, 1975). The progress of photodegradation during different irradiation times was followed by observing the changes in hydroxyl peak. Then hydroxyl (*I*<sub>OH</sub>) index was calculated by comparison of the FTIR absorption peak at 3430 cm<sup>-1</sup> with reference peak at 1450 cm<sup>-1</sup>, respectively. This method is called band index method which includes (Rabek and Ranby, 1975):

$$I_s = \frac{A_s}{A_r} \quad (1)$$

where *A*<sub>s</sub> is the absorbance of peak under study; *A*<sub>r</sub> the Absorbance of reference peak; *I*<sub>s</sub> is the index of group under study.

Actual absorbance, the difference between the absorbance of top peak and base line (a top peak – a base line) is calculated using the Base Line method (Rabek and Ranby, 1975).

**2.2.3.2. Determination of average molecular weight ( $\bar{M}_v$ ) using viscometry method.** The viscosity property was used to determine the average molecular weight of polymer, using the Mark–Houwink relation (Mark, 2007):

$$[\eta] = K\bar{M}_v^a \quad (2)$$

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