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Spectroscopic and photochemical stability of polystyrene films in the presence of metal complexes

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Abstract

Five metal complexes containing Ni(II), Cu(II), Zn(II), Cd(II) and Sn (II) metals and 4-amino-5-(pyridine-4-yl)-4*H*-1,2,4-triazole-3-thiol have been prepared for use as polystyrene photostabilizers. The additives (0.5% by weight) were mixed with polystyrene in chloroform to produce modified PS using the casting method. PS films were irradiated ($\lambda = 250–380$ nm) with a light absorption intensity of 6.02×10^{-9} ein dm^{-3} s^{-1} at room temperature. The photostabilization activity of the films was determined by monitoring various changes, such as the carbonyl index, hydroxyl index, weight loss, viscosity average molecular weight, surface morphology and quantum yield of the chain scission.

Keywords: Polystyrene films; Metal complexes; Photostabilization; 4-Amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiole; Quantum yield

1. Introduction

Polymers are organic materials composed of repeating units (low molecular weight) called monomers. Polymers are divided into natural and synthetic types. Polyester, polystyrene (PS) and polyvinyl chloride are examples of synthetic polymers [1,2]. One of the main disadvantages associated with the use of polymers is their biodegradation at high temperatures or in outdoor applications. Weathering is described as the negative effects of environment on the polymers' service life [3,4]. In recent years, polymeric materials have been widely used and the photodegradation of these materials has become an issue [5,6]. Ultraviolet (UV) radiation (280–400 nm) is less harmful to organic materials than visible (400–760 nm) and infrared (760–2500 nm) radiation [7]. A large demand for PS has been observed in various areas (*e.g.*, building construction, laboratory ware, electronics, signal lamps and packaging) due to its desirable properties (*e.g.*, clear and hard polymer) and low price [8,9]. PS is classified into isotactic, atactic and syndiotactic polystyrene, based on its structure [10–12].

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Absorption of photons by polymeric materials may lead to photodegradation that causes undesirable physical and chemical changes within the polymer structure. The presence of chromophore groups within the polymer structure is a prerequisite for the initiation of photochemical reactions [13]. Photodegradation and photooxidation of PS have been discussed and reviewed [14–16]. The main problems associated with the exposure of polymers to UV radiation are cracking, weathering and discoloration [17–20]. Therefore, researchers must identify ways to stabilize synthetic polymers against light, heat and air and heat. The photostabilization of polymers reduces or eliminates photochemical reactions within polymeric materials upon exposure to radiation [21]. Most photostabilizers act as (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) radical scavengers [22–25].

The photostability of polymers is an important property and must be high enough to increase the lifetime of polymeric materials. Therefore, many stabilizers have been developed for use as photostabilizers. Nickel and copper tetradentate Schiff base complexes were successfully used to photostabilize PS [26]. The current work investigated the use of metal complexes containing Zn(II), Cd(II), Sn(II), Ni(II) and Cu (II) and 4-amino-5-(pyridine-4-yl)-4*H*-1,2,4-triazol-3-thiol to photostabilize PS.

2. Materials and Methods

Reagents, chemicals and solvents were purchased and used without any further purification. The Fourier transform infrared (FT-IR) spectra were recorded using an FTIR.8300 Shimadzu spectrophotometer at frequencies ranging from 4000–200 cm^{-1} (Japan). The ultraviolet-visible (UV–VIS) spectra were recorded using a Shimadzu UV–vis 160 A-ultraviolet spectrophotometer at wavelengths ranging from 200–1100 nm (Japan). The morphological images were recorded using a MEIJI TECHNO Microscope.

2.1. Synthesis of metal complexes

Five metal complexes (Table 1) were prepared (Scheme 1) using a published procedure [27]. The prepared complexes were characterized using various spectroscopic techniques including FTIR, UV and NMR spectroscopy [27].

Table 1
Structure of the metal ligand complexes (ML_2) and ligand (L) used in this study.

Symbol	Name
L	4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol
NiL_2	*bis*[4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol] nickel(II)
CuL_2	*bis*[4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol] copper(II)
ZnL_2	*bis*[4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol] zinc(II)
CdL_2	*bis*[4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol] cadmium (II))
SnL_2	*bis*[4-amino-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol] tin(II)

The FTIR spectrum of the ligand (L) showed some characteristic stretching bands at 3250, 3213, 2736, 1645 and 673 cm^{-1} that were assigned to NH_2, S–H, C=N of the triazole ring and the stretching of the C-S bond, respectively. After deprotonation, the ligand was linked to the metal ion at the S atom to form a stable five membered chelate ring. The exceptional case is that the υ(C=N) of complexes was shifted to lower wave numbers compared to the ligand, indicating coordination with the ligand. The frequencies of the NH_2 bands were also shifted due to complexation. The S–H bands in the ligand completely disappeared upon complexation. Also, the C–S bands shifted to higher frequencies due to complexation between the metal ion and the ligand through sulphate. The C=N bands were shifted to lower frequencies due to complexation. In addition, the other bands, such as C=C (1590–1660 cm^{-1}) and aromatic C–H (3010–3080 cm^{-1}) bands, did not show a shift because they did not participate in complexation. New bands appeared due to the frequencies of M–S and M–N.

NMR spectral data for the ligand: ^{1}H NMR (300 MHz, DMSO-d_6; ppm) 5.30 (s, 2H, NH_2), 8.02 (d, 2H, H-3/H-5 of pyridine), 8.75 (d, 2 H, H-2/H-6 of pyridine) and 10.19 (1H, s, SH). ^{13}C NMR (75 MHz, DMSO-d_6; ppm) 121.6 (C-3/C-5 of pyridine), 132.9 (C-4 of pyridine), 147.3 (C-5 of triazole), 150.1 (C-2/C-6 of pyridine) and 167.5 (C-2 of triazole). NMR spectral data for the complexes: The ^{1}H NMR spectra of the complexes revealed singlet signals corresponding to NH_2 protons that were downshifted (*ca*. 3.31 ppm) due to coordination of metals and the ligand.

The UV electronic spectrum for the ligand showed three absorption bands at 263, 302 and 309 nm due to $\pi-\pi^*$, $\pi-\pi^*$ and n-π^* electronic transitions, respectively. The additives showed similar shifts in the electronic transition compared to the ligand. The electronic transitions of the metal *d* orbitals (*d–d* electronic transition) were observed in Ni(II) and Cu(II) complexes

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