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Mechanism of photoinitiated degradation of poly(ethylene oxide) by copper complexes in acetonitrile [1]

Halina Kaczmarek

Nicolaus Copernicus University, Faculty of Chemistry, Gagarina 7, 87-100 Toruń, Poland

Abstract

The photodegradation of the complexes of poly(ethylene oxide) with copper(II) chloride in acetonitrile solutions was studied using UV–Vis, FT–IR spectroscopy and viscosity measurements. PEO–$CuCl_2$ complexes decompose much faster than pure PEO, which was revealed by a great decrease of molecular weight of PEO and a large amount of oxidized products. The mechanism of photooxidative degradation of investigated complexes is discussed.

Keywords: Photoinitated degradation; Poly(ethylene oxide); Copper complexes; Acetonitrile

1. Introduction

Polymers containing oxygen bridges in the main chain, such as poly(ethylene oxide) (PEO), are susceptible to light, although pure polyethers should not absorb the irradiation at wavelengths shorter than 200 nm [1–3]. The photoreactions of such polymers are induced or sensitized by structural defects, impurities, residues of catalysts or other additives deliberately added which absorb light of longer wavelengths [4–6]. In practice, pure PEO is applied very seldom, but modifying substances introduced into the polymer bulk can dramatically change its photostability.

PEO is known as a polymer forming coordination complexes with inorganic salts [7–12]. It is a polymer having a fiber repeat period of 0.712 nm and trans–trans–trans conformation [13]. The normal structure is 7/2 helix; that is, seven ethylene oxide repeat units with two turns in the fiber period of 1.93 nm. The good coordination properties of PEO are due to the optimal spacing of the oxygen in the chain unit [7]. The size and shape of the external space in the PEO helix allows small ions or molecules to be bound [12]. However, the helix structure of PEO is often destroyed when complex formation occurs. PEO is a highly crystalline polymer, but its structure in complexes can be changed. PEO complexes form folded-chain lamellae and well-defined spherulites or less-ordered, amorphous structures, depending on its method of preparation, type and amount of salt used, the degree of ions and polymer solvatation by solvent [12,14–15].

One of the most important cations interacting with PEO is the Cu(II) ion. The photosensivity of copper complexes with organic systems may lead to many phototransformations of organic molecules; for example, isomerisation, substitution, oxidation, and double-bond migration [16,17]. Moreover, copper complexes can participate in many types of redox reactions with organic compounds [17,18].

The aim of this work was to investigate photodegradation processes of PEO complexes with copper(II) chloride in acetonitrile (ACN) solution and to determine the reaction mechanisms.

2. Experimental details

A sample of commercial poly(ethylene oxide), type WSRN 750 (Union Carbide), was used in this study. PEO–$CuCl_2$ complexes were prepared by dissolving separately 5% polymer and anhydrous copper(II) chloride in acetonitrile (analytical grade). These two solutions were mixed together at different ratios and shaken for 15 min.

A high-pressure mercury lamp (HPK 125W UV, Philips), emitting radiation from 254 to 578 nm, was applied as a light source. The distance between the lamp and the surface of polymer solution was 10 cm; the light intensity at this position measured with a IL1400A Radiometer was 12.5 mW cm^{-2}. All irradiations were performed in the presence of air, at room temperature.

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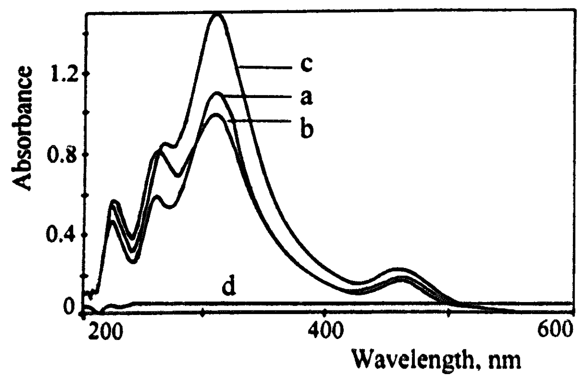


Fig. 1. UV-Vis absorption spectra of $[CuCl_n]^{2-n}$ (4.6×10^{-4} M) (curve (a)), PEO–$CuCl_2$ (4.5×10^{-4} M) 9:1 (curve (b)), PEO–$CuCl_2$ (5.8×10^{-4} M) 7:3 (curve (c)) and pure PEO (curve (d)).

UV–Vis and IR spectra were recorded with an UV-160A spectrometer (Shimadzu, Japan) and a Perkin–Elmer 1650 FT–IR spectrometer, respectively. Films for IR spectroscopy were cast on NaCl plates.

Viscosity measurements were performed in acetonitrile at 20 ± 0.1 °C using a modified quartz Ubbelohde viscometer. The limiting viscosity number $[\eta]$ was calculated from the Solomon–Ciuta equation:

$$[\eta]=\frac{\sqrt{2}}{c}(\eta_{sp}-\ln\eta_{rel})^{1/2} \tag{1}$$

where η_{sp} and η_{rel} are the specific viscosity and relative viscosity, respectively, and c is the polymer concentration. Number of chain scissions per molecule (S) was estimated from the relation:

$$S=\left(\frac{[\eta]_0}{[\eta]_t}\right)^{1/a}-1 \tag{2}$$

where $[\eta]_0$ and $[\eta]_t$ are the limiting viscosity numbers of PEO before and after irradiation, and a is a constant in the Mark–Houwink equation.

3. Results and discussion

The chloride complexes of copper(II) formed in acetonitrile solution

$$Cu^{2+}+nCl^- \rightleftharpoons [CuCl_n]^{2-n} \tag{3}$$

have intense ultraviolet charge-transfer absorption bands with maxima at 223, 262, 305 and 461 nm (Fig. 1, curve (a)). It was reported that the intensity and position of these bands depend on the copper(II) and chloride ratio [19]. The absorption spectrum of $[CuCl_n]^{2-n}$ indicates that the mixture of complexes consists of $CuCl_4^{2-}$, $CuCl_3^-$, $CuCl_2$ and $CuCl^+$. The equilibrium where the cuprous chloride serves as an electron donor for the chlorine atom is possible:

$$[Cl_{n-1}{}^-Cu^{2+}Cl^- \longleftrightarrow Cl_{n-1}^-Cu^+Cl^\bullet] \tag{4}$$

The mixing of PEO with $[CuCl_n]^{2-n}$ in acetonitrile solution causes a slight shift of all CT absorption bands, and changes in the ratio of their intensity (Fig. 1, curves (b) and (c)). It indicates that some Cl^- ligands are replaced by oxygen atoms from PEO. The color of the complexes depends on the amount of $CuCl_2$ introduced: it is yellow in solutions containing 10% of $CuCl_2$ and is much darker in complexes with 30% of copper salt.

UV irradiation of $[CuCl_n]^{2-n}$ and PEO–$CuCl_2$ complexes (9:1, 7:3) causes significant changes in the UV absorption spectra. An example of these changes is shown in Fig. 2. The band at 458 nm decreases, but peaks at 227 and 264 nm increase with irradiation time. The peak centered at 308 nm decreases during the first 15 min of exposure and then continuously increases, with development of shoulders at 300 and 326 nm. It means that the composition of complexes is changed during UV irradiation.

It was reported [17,19], that copper(II) complexes in nonsolvating media such as acetonitrile undergo reversible photolysis:

$$[CuCl_n]^{2-n} \underset{ACN}{\overset{h\nu}{\rightleftharpoons}} [CuCl_{n-1}]^{2-n}+Cl^\bullet \tag{5}$$

Particularly active chlorine atoms, formed in reaction (5), can then induce secondary reactions in a polymer, for example, abstract the hydrogen atom from PEO macromolecule:

$$PH+Cl^\bullet \longrightarrow P^\bullet+HCl \tag{6}$$

Ether macroradicals ($P^\bullet$) will react with copper(II) chloride complexes, changing their composition because of the redox process

$$P^\bullet+[CuCl_n]^{2-n} \longrightarrow PCl+[CuCl_{n-1}]^{1-n} \tag{7}$$

The limiting viscosity numbers of nondegraded PEO–$CuCl_2$ complexes are lower than the $[\eta]$ of pure nonirradiated PEO (Table 1). It suggests that the Cu^{2+} ion only interacts with one chain, which causes an increased coiling-up of the chains. Similar viscosimetric results were obtained for poly(methacrylic acid)–copper (II) complexes [20,21].

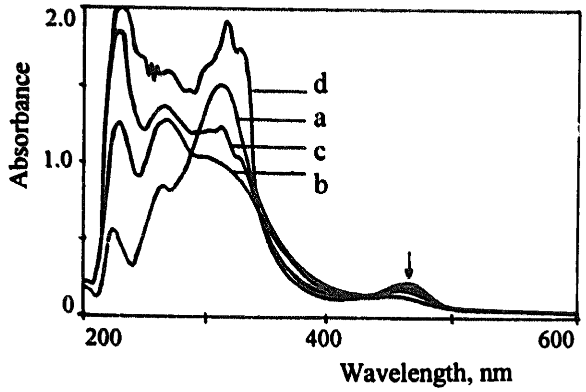
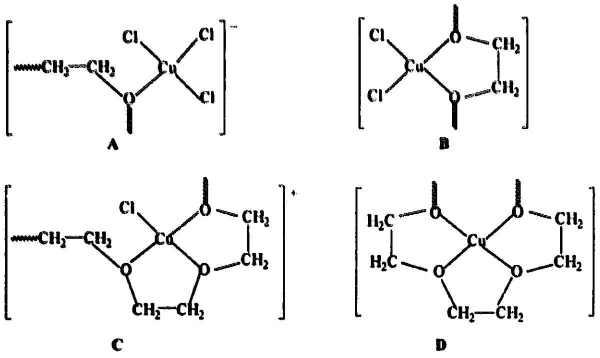


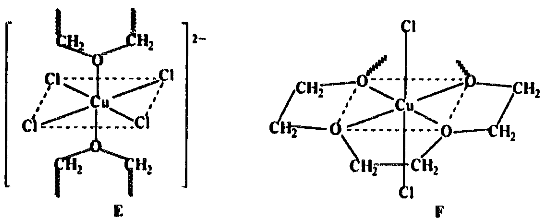
Fig. 2. UV–Vis absorption spectra of PEO–$CuCl_2$ (7:3) complexes before irradiation (curve (a)) and after 15 min (curve (b)), 1 h (curve (c)) and 3 h (curve (d)) of UV irradiation.

Table 1
Changes of the limiting viscosity numbers and numbers of chain scission per molecule for PEO and PEO–$CuCl_2$ (9:1, 7:3) complexes during UV irradiation

Time of irradiation (h)	PEO		PEO + $CuCl_2$ (9:1)		PEO + $CuCl_2$ (7:3)	
	$[\eta]$ (dl g^{-1})	*S*	$[\eta]$ (dl g^{-1})	*S*	$[\eta]$ (dl g^{-1})	*S*
0	3.66	–	3.18	–	2.63	–
0.25	3.40	0.16	2.29	0.93	2.03	0.68
0.50	3.05	0.44	1.86	1.92	1.72	1.34
0.75	2.80	0.71	1.44	3.88	1.31	3.03
1.00	2.70	0.84	1.25	5.47	1.18	3.97
1.50	2.58	1.01	1.10	7.35	0.98	6.20
2.00	2.02	2.28	0.91	11.21	0.90	7.54
3.00	1.65	3.92	0.71	19.06	0.68	13.96
4.00	1.47	5.20	0.57	30.12	0.55	21.87



Scheme 1.



Scheme 2.

Thus, taking the common coordination number of copper equal to four, some of the probable structures of PEO–$CuCl_2$ complexes with square planar or flattened tetrahedral configurations are shown in Scheme 1.

The formation of five-member rings resulting from the coordination of Cu(II) by between two and four adjacent oxygen atoms (structures B, C, D) is usually favorable because of their stability. Moreover, Cu(II) complexes exist also in the octahedral ligand field, distorted by the Jahn–Teller effect. In this case, the central metal ion is coordinated by six ligands; four placed closer to the Cu(II) in the equatorial *x*–*y* plane, and the other two further along the *z* axis (Scheme 2).

Viscosity measurements also provide evidence for high nonstability of PEO in complexes upon UV irradiation (Table 1). The $[\eta]$ values of PEO–$CuCl_2$ decrease with irradiation time much faster than the $[\eta]$ of pure PEO. The greatest changes are observed during the first hour of photodegradation. However, there are no significant variations between the $[\eta]$ of PEO complexes with 10 and 30% of $CuCl_2$. Similarly, the calculated numbers of chain scission (*S*) clearly indicate that degradation leading to a great molecular-weight decrease is more efficient in PEO–$CuCl_2$ complexes than in PEO. The *S* value of irradiated PEO–$CuCl_2$ complexes with a 9:1 ratio changes with irradiation time even faster than the *S* of PEO–$CuCl_2$ complexes with a 7:3 ratio.

The degradation process is accompanied by oxidation, which is monitored by IR spectroscopy. The FT–IR spectra of pure PEO and PEO–$CuCl_2$ (9:1) complexes before and after UV irradiation are shown in Fig. 3. In spite of the presence of low amounts of hydroxyl groups in pure unirradiated PEO, its photooxidation progresses very slowly. In contrast to pure PEO, PEO–$CuCl_2$ complexes undergo fast photooxidation. Strong bands in the carbonyl and hydroxyl regions are formed after 1 and 2 h of UV irradiation of PEO–$CuCl_2$ complexes with 9:1 and 7:3 weight ratios. The band

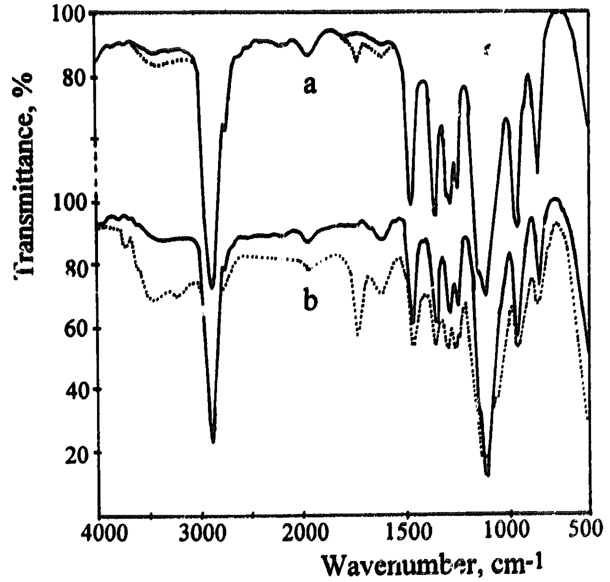
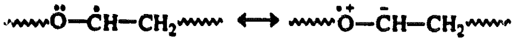


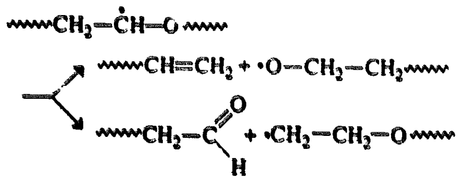
Fig. 3. FT-IR spectra of PEO (curves (a)) and PEO–$CuCl_2$ (9:1) complexes (curves (b)) before irradiation (solid lines) and after 2 h of UV irradiation (dotted lines)

centered at 1723 cm^{-1} is attributed to the mixture of carbonyl groups (ketones, aldehydes and esters). In addition, the appearance of the band at 1610 cm^{-1} indicates the formation of unsaturated end-bonds in PEO macromolecules. The complex broad band within the 3050–3700 cm^{-1} range is due to hydroxy and hydroperoxide groups, which cannot be distinguished by this method. There are some differences in the composition of this band depending on the polymer–salt ratio. PEO–$CuCl_2$ (9:1) complex after 2 h of UV irradiation shows clear maxima at 3220, 3446 (associated with OH/OOH) and 3590 cm^{-1} (free OH groups), where the 3446 cm^{-1} branch is the most intense, while the PEO–$CuCl_2$ (7:3) complex reveals components at 3087, 3189 and 3450 cm^{-1}, where the peak at 3189 cm^{-1} is the highest in the hydroxyl region. Simultaneously, changes in the region of the antisymmetric C–O–C band (1000–1200 cm^{-1}) were observed. A small decrease of the band centered at 1108 cm^{-1} with its significant broadening confirms the previous observation of degradation processes (breaking of ether bonds) with the formation of new types of oxidized groups.

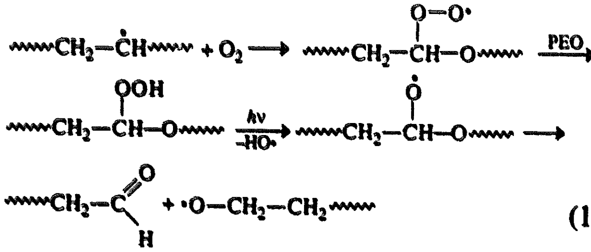
The mechanism of photooxidative degradation can be explained as follows. According to reaction (6), cleavage of a relatively weak C–H bond, because of the vicinity of ether linkage, leads to the formation of free radicals of the type $-O-\dot{C}H-CH_2-$ which can be stabilized by resonance [23]


$$\sim\ddot{O}-\dot{C}H-CH_2\sim \longleftrightarrow \sim\overset{\cdot +}{O}-\overset{-}{C}H-CH_2\sim \quad (9)$$

The ether radicals, once produced, can participate in a variety of chemical reactions, mainly chain scission (reactions (10) and (11)) and oxidation by atmospheric oxygen (reaction (12))

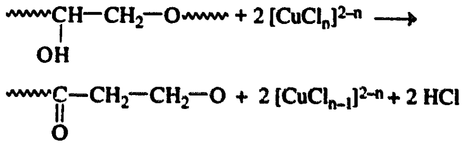

(10)

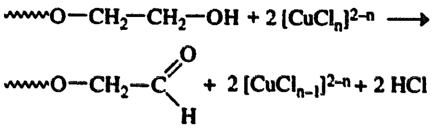
(11)


(12)

Each free radical formed in the reactions described above can abstract a hydrogen atom from the next PEO macromolecule or recombine with another radical, giving an inactive product. Moreover, oxidized products of PEO containing C=O, C=C, OH and OOH groups absorb irradiation at a longer wavelength; consequently, they induce the subsequent photodegradation of the polymer.

The influence of the oxidative properties of Cu(II) must be taken into account. $CuCl_2$ upon UV irradiation may oxidize alcohols to carbonyl compounds [16]


$$\sim\underset{OH}{CH}-CH_2-O\sim + 2\,[CuCl_n]^{2-n} \longrightarrow \sim\underset{O}{\overset{}{\underset{\|}{C}}}-CH_2-CH_2-O + 2\,[CuCl_{n-1}]^{2-n} + 2\,HCl \quad (13)$$


$$\sim O-CH_2-CH_2-OH + 2\,[CuCl_n]^{2-n} \longrightarrow \sim O-CH_2-CHO + 2\,[CuCl_{n-1}]^{2-n} + 2\,HCl \quad (14)$$

It explains the fast development of the IR carbonyl band of PEO–$CuCl_2$ complexes.

Photoxidized polymeric products, in the presence of $CuCl_2$ and CuCl salts, may also form complexes, which can degrade with the generation of active radicals and ions

$$Cu^{2+} + POOH \rightleftharpoons [Cu^{2+}...HOOP] \rightleftharpoons Cu^{+} + POO^{\cdot} + H^{+} \quad (15)$$

$$Cu^{+} + POOH \rightleftharpoons [Cu^{+}...HOOP] \rightleftharpoons Cu^{2+} + PO^{\cdot} + OH^{-} \quad (16)$$

The reaction of substitution or addition of chlorine atoms to the double bond in photodegraded PEO–$CuCl_2$ complexes cannot be excluded; therefore, there is no evidence of the presence of chlorinated derivatives in the IR spectra, probably because of their very low concentration.

Finally, the influence of the solvent on the photoprocesses investigated must be mentioned. ACN may bond to Cu(II) ions through the nitrogen donor atom. Moreover, the triple carbon–nitrogen bonds in ACN are sensitive to highly energetic UV irradiation, particularly in the presence of copper ions. This problem will be investigated further.

4. Conclusions

It was found that PEO–$CuCl_2$ complexes formed in ACN solution are very unstable to polychromatic UV irradiation. The photodegradation of PEO in complexes is initiated by chlorine radicals formed during photolysis of $[CuCl_n]^{2-n}$. The hydrogen abstraction from the PEO macromolecule by Cl atoms, main chain scission, and oxidation leading to the formation of hydroxy, hydroperoxide and carbonyl groups as well as end double bonds are further secondary processes. The structural change of irradiated PEO monitored by UV–Vis and IR spectroscopy clearly indicates that $[CuCl_n]^{2-n}$ markedly accelerates photoprocesses in this polymer.

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