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Influence of water on the photodegradation of poly(ethylene oxide)

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Abstract

The UV-light degradation of polyethylene oxide (PEO) in aqueous solution was investigated operating under long wavelengths ($\lambda > 300$ nm) at 20 °C in different pH conditions varying from 2.3 to 12.0 and at two different concentrations. Thermo-oxidation experiments on PEO aqueous solution at 50 °C are also reported and compared to photo-oxidation results. The formation of oxidation products was followed by infrared analysis of deposits obtained by evaporation of aliquots of irradiated polymer solution. Photo-oxidation led to formates and esters but a third product was also identified, formic acid ions formed by partial hydrolysis of formates. The degradation of PEO in water led to the acidification of the aquatic medium. Size exclusion chromatography (SEC) was used to monitor the changes in molar weight and intrinsic viscosity with irradiation time. It was shown that the photo-oxidation produced a dramatic decrease of the average molar weights which is more important in acidic medium. Total organic carbon (TOC) measurements of the aged aqueous solutions showed that the mineralization of PEO could not be achieved in these photo-oxidative conditions.

Keywords: Photodegradation; Water; Poly(ethylene oxide); SEC

1. Introduction

Water-soluble polymers are produced in large volumes and are widely used in a variety of industrial and consumer products. These polymers find use in polymeric surfactant, pigment dispersants, mining oil drilling, detergents, etc. After use, depending on their characteristics and particular applications, water-soluble polymers are discarded into solid waste disposal systems or as dilute aqueous solutions and they are potential contributors to environmental problems [1]. Their photochemical degradation in aqueous solution gives insight of their impact on environment in outdoor conditions. The knowledge of their degradation is then of prime importance to evaluate their fate and their long term behaviour.

Among polyethers, PEO with PVME are the only one that are readily soluble in water [2]. PEO is biocompatible, biodegradable, non-ionic and a water-soluble polymer of considerable industrial significance. PEO finds applications in many different branches of industry, cosmetics, pharmacy and medicine. For example it is typically used as a surfactant, lubricant, textile size, hydraulic fluid, and water-soluble packaging film [3–6].

Poly(ethylene oxide) (PEO) has a simple chemical structure. It is built from flexible linear macrochains consisting of elements with different electronegativity, carbon and oxygen ($-CH_2-CH_2-O-$). In the crystalline solid state, PEO exists mainly in the form of a regular helix. The characterisation of the spatial configuration of PEO shows an arrangement with *trans* ($O-CH_2$), *gauche* (CH_2-CH_2) and *trans* ($O-CH_2$) conformations [7,8]. In aqueous solution PEO conformation shifts to a random coil with statically placed residual helix segments [2,4,9,10], the helix structure being conserved. According to experimental and theoretical studies realised on water–PEO systems [4,11–13], hydrogen bonding plays an important role in the interactions between PEO and water. PEO in water adopts the local conformations ($-O-C-C-O-$ dihedral sequences) *tgt*, *tgg*, *ttt*,…etc. (with $t = trans$ and $g = gauche$). The conformations *tgt* and *ttg* are favoured under low concentration and low temperature conditions whereas the population

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of the hydrophobic conformers increases with concentration and temperature. These two conformers exhibit a substantial hydrophilic character while the rest are essentially hydrophobic. Hydrogen bonds play an important role in the preferential conformation *tgt* characterised by O–C–C–O– dihedral angle of 85.4°.

This study of photo-oxidation of PEO is part of a general study of water-soluble polymers carried out in our laboratory [14,15]. The mechanism of photo-oxidation of PEO in the solid state has already been studied under irradiation at long wavelengths ($\lambda > 300$ nm, 35 °C) in presence of oxygen [14]. This previous study has shown that PEO is very sensitive to oxidation. Hydroperoxides (POOH) are formed as primary products within a classical chain oxidation reaction that involves hydrogen abstraction which occurs on methylene groups in α-position of the oxygen atom. These primary hydroperoxides readily decompose to form macroalkoxy radicals $PO^{\bullet}$ and hydroxyl radical $^{\bullet}OH$. In photo-oxidative conditions, the main route of decomposition of macroalkoxy radicals is a β-scission, which generates formates in a 5/1 ratio against chain esters. In contrast, in conditions of thermo-oxidation, the situation is different. The hydroxy radicals $^{\bullet}OH$ formed by decomposition of the hydroperoxides mainly react with the macroalkoxy radicals in a cage reaction, producing esters. A same amount of esters and formates is then observed.

A first approach of the photodegradation of PEO in aqueous solution has been carried out [15]. Irradiation of PEO aqueous solutions leads to the formation of macromolecular esters, formate end groups and a third photoproduct was identified, $HCOO^-$. The main difference observed between the photoproducts formed in photo-oxidation conditions either in solid state or in aqueous solution concerns the formation of formic acid ions ($HCOO^-$) released in solution. A strong influence of the pH of aqueous solution was observed on the photochemical behaviour of PEO, which could not have been explained. The chemical structure of the polymer cannot explain the influence of pH on the mechanism of oxidation, and the importance of radical or ionic reactions occurring in water was still questionable.

The present paper is mainly focused on the influence of pH of the aquatic medium on the mechanism of photo-oxidation of PEO; a specific attention is being paid to the analysis of photoproducts and to the characterisation of the rate of photo-oxidation. Photo-oxidation experiments were carried out in different pH conditions. The modifications of the chemical structure of the polymer were followed by IR spectrometry and by SEC analysis in order to characterise the changes of molar weight distribution and the evolution of the viscosity of the solution. The aqueous solutions were also characterised by measuring the variations of pH during irradiation. The influence of the pH on the stability of the photoproducts was also studied. Moreover, an evaluation of the possibility to achieve the mineralization of PEO in photo-oxidation conditions was also carried out by measuring the Total Organic Carbon (TOC) concentration of the irradiated solution.

2. Experimental

2.1. Materials

Poly(ethylene oxide) was obtained from Scientific Polymer Products and used without further purification. Average molar weight of the polymer was 100 000 g mol^{-1}. PEO solutions of 5 wt.% and 0.5 wt.% (respectively, 50 gm mL^{-1} and 5 mg mL^{-1}) were prepared by dissolving PEO into a distilled and deionized water with mild stirring overnight at room temperature. The pH value was measured with an ORION pH meter to ±0.1 pH unit. Dissolution of PEO in deionized ultrapure water (at concentration of 50 mg mL^{-1} or 5 mg mL^{-1}) results in a solution with a pH value of 8.4. Solutions in acidic or basic medium (pH = 2.3 or 3.1 and 12.0) were, respectively, obtained by adding drops of diluted $HClO_4$ or NaOH ($HClO_4$ was chosen to acidify the aqueous solution because ClO_4^- is photochemically stable contrary to Cl^-). No buffer was used in order to avoid making the system too complex by adding too many species.

2.2. Irradiation

Irradiations of PEO in solid state (as films) were carried out in a SEPAP 14/24 unit. This apparatus has been designed for the study of polymer photodegradation in artificial ageing corresponding to medium accelerated conditions [14,16].

Irradiation of PEO aqueous solutions was carried out in an elliptical chamber which is equipped with one medium-pressure mercury lamp (Mazda MA 400) in a vertical position at one focal axis of the chamber [15]. Wavelengths below 300 nm are filtered by a glass envelope. The aqueous solution of PEO was irradiated in a Pyrex reactor cooled by water circulation. The temperature of the solution was maintained at 15 °C in order to avoid water evaporation. This reactor was placed at the second focal axis of the chamber. The solutions were continuously stirred with a magnetic stirrer and a Teflon bar.

Thermo-oxidation experiments were carried out at 50 °C in a 100-mL round bottom flask equipped with reflux condenser. This temperature was chosen to keep the aqueous solution at a temperature below the cloud point temperature (CPT = 100 °C) [17,18]. The reactor was therefore placed into an oil bath.

2.3. Chemical characterisations

PEO solutions of 5 wt.% concentration were chosen in order to follow the chemical modifications of the irradiated solutions by IR analysis of deposits on CaF_2 windows. Thin deposits of oxidized samples of PEO obtained by evaporation of aliquots of irradiated aqueous solution of PEO were analysed in transmission mode before infrared analysis. The samples were dried at room temperature for 24 h. In the manuscript, the figures of FTIR spectra are limited to the range 4000–1000 cm^{-1} due to the opacity of the CaF_2 plate between 1000 cm^{-1} and 400 cm^{-1}. Infrared spectra were recorded with a Nicolet FTIR 760 spectrometer, working with OMNIC software.