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Photo-oxidative degradation of poly(ethylene oxide)–copper chloride complexes

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Poly(ethylene oxide) (PEO) forms with $CuCl_2$ a complex in acetonitrile (AN) solution as well as in solid phase (after evaporation of solvent). During u.v. or visible light irradiation it has been observed that a rapid photo-oxidative degradation of the PEO–$CuCl_2$ complex in AN is caused by free $Cl^{\cdot}$ and/or $Cl_2^{\cdot -}$ radicals (formed from the photolysis of $CuCl_2$). With increasing degradation processes, there is also a pronounced change in the morphology of PEO–$CuCl_2$ complexes. They lose their capability to form spherulites. This results from changes in molecular weight and dispersity that affect crystallization conditions. Both wide angle X-ray spectroscopy and differential scanning calorimetry show that photodegraded PEO molecules are almost amorphous. Low-molecular fractions are formed as a result of chain scission processes. Photodegradation processes in AN solution do not cause crosslinking or formation of a gel fraction. Copyright © 1996 Elsevier Science Ltd.

(Keywords: photo-oxidative degradation; poly(ethylene oxide); copper complexes)

INTRODUCTION

Intensive studies on the behaviour and properties of polymer–metal salt complexes have been carried out[1–6]. The great interest in investigation of such complexes is connected with their potential applications in industry and medicine. Since a number of polymer–metal salt complexes exhibit ionic conductivity[7–9], they can be used in advanced electrochemical devices such as high energy batteries, electrochromic displays, electrochromic windows, solid-state photochromic cells and sensors[10].

The characteristic feature of polymeric complexes is the formation of a single thermoplastic phase with a strong elevated glass transition temperature (T_g)[11,12]. Moreover, such complexes are more flame resistant than the polymeric ligands alone[13]. Some of them also exhibit a high degree of crystallinity and hence restrict ionic mobility; there have been attempts in the past to introduce salts that prevent crystallization of the material[14–17].

One of the most important polymers capable of binding different cations is poly(ethylene oxide) [poly(oxy-1,2-ethanediyl); PEO]. This semicrystalline, water-soluble material forms coordination complexes with metal ions such as: Hg(II)[18], Fe(III)[19,20], Cu(II)[21,22], Mo(VI)[23] and alkali metals[3,24,25]. The flexibility of PEO chains allows them to encircle the metal ions and to adjust the ionic radius. A favourable conformation is achieved, resulting in the chain folding, and this is accompanied with an entropy decrease.

It is also possible to grow conducting polymers such as polypyrrole on or within PEO complexes with $FeCl_3$[26,27] and $CuCl_2$[22].

Surface photodegradation of PEO plays a tremendous role in the application of this polymer as a polymeric biomaterial in dentistry. Changing of the surface properties provides a site for bacterial attachment and proliferation. Adherent bacteria are covered by a biofilm, which supports bacterial growth while protecting them from antibodies, phagocytes and antibiotics. Infection of vascular grafts, for instance, are usually associated with *Pseudomonas aeruginosa*, *Eschericha coli*, *Staphylococcus aureus* and *S. epidermis*[28].

Inorganic metal salts can have a disadvantageous influence on polymer stability and cause unexpected changes in their properties during ageing. It is know that metal salts act as catalysts in polymer thermal oxidation[13] as well as sensitizers or initiators of photo-oxidative degradation of PEO host[20,21,29]. It was concluded that the catalytic effect of metal compounds on polymer degradation depends on the metal ion valency and bonding character (covalent or ionic) between a metal centre and anions and ligands[30]. The higher valency of the metal ion and the more ionic the character of complex bonding, the greater the catalytic activity will be.

Several electronic transitions during u.v. irradiation of polymeric complexes appear[31]. In the case of

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PEO–$CuCl_2$, the ligand-to-metal charge-transfer is most favourable. U.v. irradiation of this system leads to the reduction of Cu(II) to Cu(I) and chlorine radical formation, which undergoes secondary reactions[21]. PEO–$CuCl_2$ complexes have extended absorption in the visible range (they are intensely yellow) and they are, therefore, also sensitive on long wavelength irradiation. Results of our investigation on the mechanism of photo-oxidative degradation of PEO–$CuCl_2$ complexes are reported in this paper.

EXPERIMENTAL

High molecular weight PEO (WSRN 750), kindly supplied by Union Carbide, was used in this study. All complexes were prepared by dissolving both the polymer and anhydrous $CuCl_2$ (Aldrich) in acetonitrile (AN) in a suitable ratio (9/1 or 7/3).

Two types of lamps were used as irradiation source:

1. High pressure mercury lamp HPK 125 W (Philips, The Netherlands); emission range: 254–578 nm; radiation intensity at the position of sample—12.5 mW cm^{-2};
2. Halolux E 27 lamp, 250 W (Osram, Germany); emitted visible light above 400 nm; light intensity—482.7 μW cm^{-2}.

The radiation intensity was determined directly by using the Photometer IL 1400 A (International Light, Inc., USA).

Viscosity measurements of 1 wt% PEO or PEO–$CuCl_2$ complexes were performed in AN at 20 ± 0.1°C using a modified quartz Ubbelohde viscometer[32,33]. The limiting viscosity number $[\eta]$ was calculated from the Solomon–Ciuta equation[34]:

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

where η_{sp} and η_{rel} are the specific viscosity and relative viscosity, respectively, and c is the polymer concentration. The average number of chain scissions (S) was calculated according to the equation[33]:

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

where $[\eta]_0$ and $[\eta]_t$ are the limiting viscosity numbers of PEO (PEO–$CuCl_2$) before and after irradiation, and α is a constant in the Mark–Houwink–Sakurada equation. Because of discrepant data for K and α in the Mark–Houwink–Sakurada equation in the literature, their values were verified by viscosity measurement of three monodispersive PEO fractions in the range of molecular weight 34 400–450 000. It was found that, in AN at 20°C, $K = 0.175$ ml g^{-1} and $\alpha = 0.61$.

Changes in the molecular weight (MW) and molecular weight distribution (MWD) (polydispersity index M_w/M_n) were obtained by gel permeation chromatography (g.p.c.) with a Shimadzu C-R4A Chromatograph and Ultrahydrogel column calibrated with PEO standards.

^{1}H n.m.r. spectra were obtained with a Gemini 200 Varian Spectrometer (200 MHz) in $CDCl_3$ solutions; 1024 scans were made for each sample.

Wide angle X-ray diffraction (WAXD) was performed on a diffractometer type HZG 4/A-2 (Germany) (CuK_α tube, Ni filter, $\lambda = 1.542$ Å). The scattering patterns were recorded in the reflection mode as a function of the scattering angle 2Θ from 4 to 54° with the step size 0.02°.

Differential scanning calorimetry (d.s.c.) measurements were obtained with a Perkin-Elmer DSC4 thermal analysis system with a standard heating and cooling rate of 10° min^{-1}. Samples of 3 mg were run in a nitrogen atmosphere over the range 25–100°C. Indium ($T_m = 156.6$°C) was used for temperature calibration.

Polarized optical micrographs were made with a Nikon polarizing microscope type Optiphot-2 (Japan).

RESULTS AND DISCUSSION

When $CuCl_2$ is dissolved in aprotic solvents it gives rise to a series of chlorocopper (II) complexes[35,36]. AN forms solvated di-, tri- and tetra-chlorocopper complexes: $CuCl_3(AN)^-$, $CuCl_2(AN)_2$, $CuCl(AN)_3^+$, $Cu(AN)_4^{2+}$. These complexes in AN, a strong π-acceptor, represent an interesting photocatalytic system[37] working under visible light. Chlorocopper (II) complexes have intense charge-transfer (CT) absorption bands with maxima at 223, 262, 306 and 461 mm[21]. The intensity and position of these bands depend on the copper(II) and chloride ratio[28]. Irradiation of the system, in the region of the lowest spin-allowed CT excited state, results in the photoreduction of the Cu(II) metal centre to Cu(I)[38], and $Cl^\cdot$ radical formation, which presence has been evidenced by pulsed laser flash photolysis[39,40] and the electron spin resonance spin-trapping technique[41]:

$$[CuCl_n]^{2-n} \xrightleftharpoons[AN]{h\nu} [CuCl_{n-1}]^{2-n} + Cl^\cdot \tag{3}$$

Formation of $Cl^\cdot$ occurs with quantum yields of about 10^{-1}–10^{-2}, depending on the [Cu(II)]/[Cl^-] ratio[42]. The active transient is actually a $Cl_2^{\cdot -}$ radical ion which is formed by the association of $Cl^\cdot$ with Cl^- present in solution[36]:

$$Cl^\cdot + Cl^- \rightarrow Cl_2^{\cdot -} \tag{4}$$

This chloro radical anion is a powerful oxidizing ($E_0 = 2.3$ V)[43] and chlorinating agent[44].

Irradiation of PEO–$CuCl_2$ (at ratios of 9/1 and 7/3) in AN solution with u.v. (*Figure 1*) or visible light (*Figure 2*) causes a rapid change of the solution viscosity, which results from the chain scission processes. The calculated number of chain scission (S) for both types of irradiation is shown in *Figures 3* and *4* as indicated. These plots show some curvature, which can be the result of an expansion of the chain reaction, typical for further stadia of photo-oxidative processes.

As has been previously suggested[21] the $Cl^\cdot$ and/or $Cl_2^{\cdot -}$ radicals may abstract hydrogen atom from the PEO molecule (abbreviated here as PH) according to the mechanism:

$$PH + Cl^\cdot \rightarrow P^\cdot + HCl \tag{5}$$

$$PH + Cl_2^{\cdot -} \rightarrow P^\cdot + HCl + Cl^- \tag{6}$$

In the presence of oxygen (air), the photo-oxidative reactions in which PEO alkyl radical ($P^\cdot$) is involved, may occur according to *Scheme 1*.

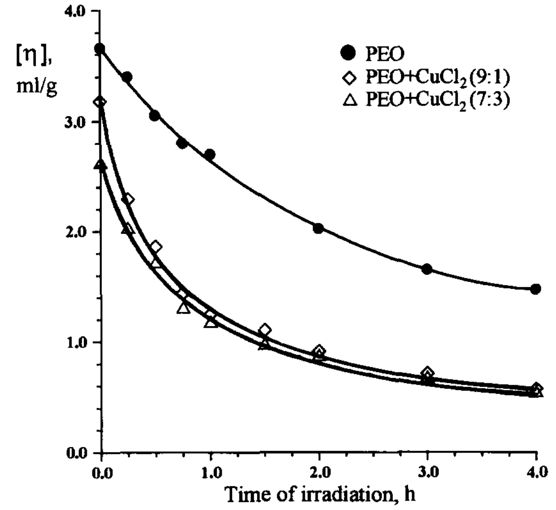


Figure 1 Changes of the limiting viscosity number [η] of PEO and PEO–$CuCl_2$ complexes during u.v. irradiation

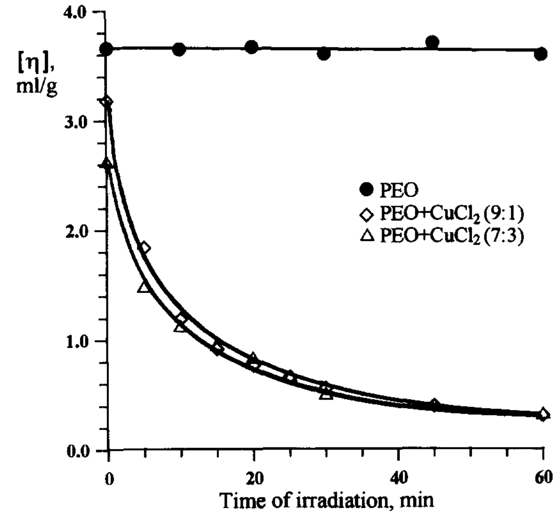


Figure 2 Changes of the limiting viscosity number [η] of PEO and PEO–$CuCl_2$ complexes during visible light irradiation

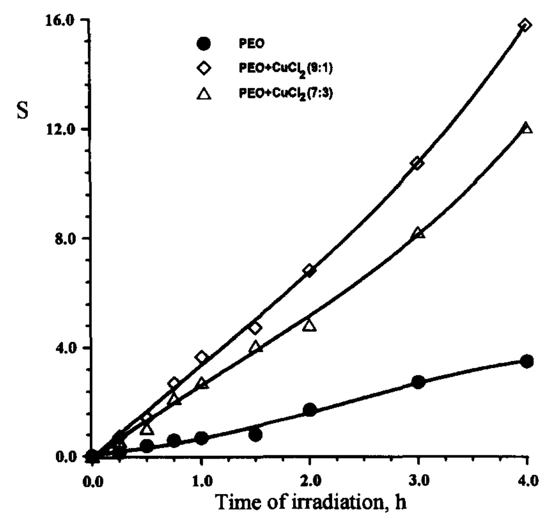


Figure 3 Number of chain scissions (S) per molecule in PEO and PEO–$CuCl_2$ complexes during u.v. irradiation

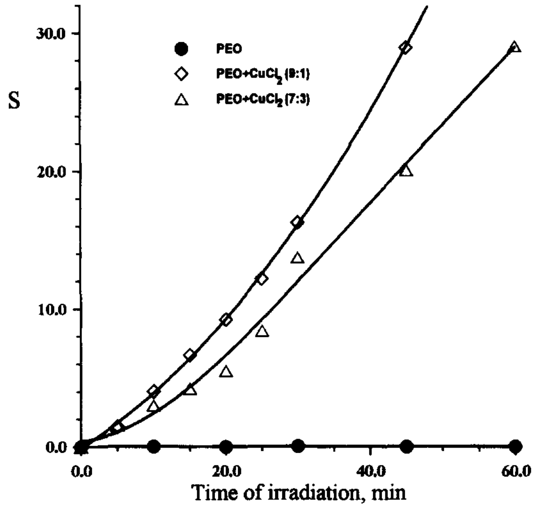


Figure 4 Number of chain scissions (S) per molecule in PEO and PEO–$CuCl_2$ complexes during visible light irradiation

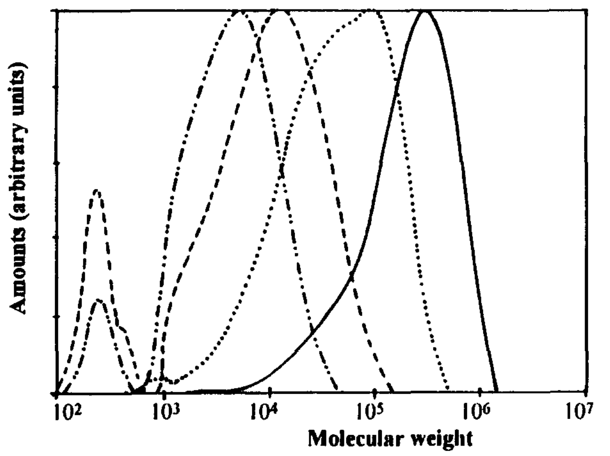


Figure 5 Differential molecular weight (MW) distribution curves (g.p.c.) of: (——) PEO before irradiation and (· · ·) PEO, (– – –) PEO–$CuCl_2$ (7/3) and (· – – · ·) PEO–$CuCl_2$ (9/1) after 2 h u.v. irradiation

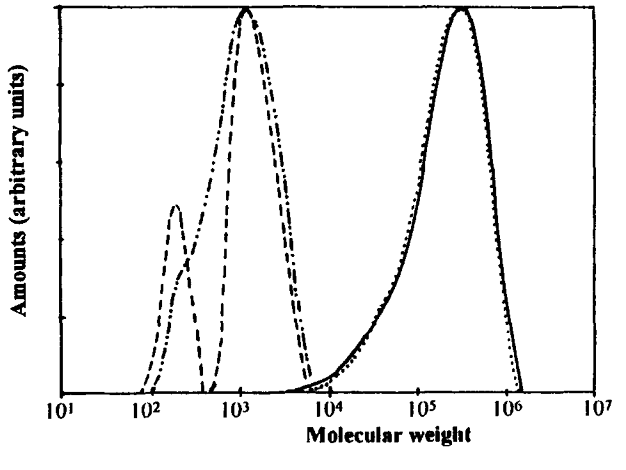


Figure 6 Differential molecular weight (MW) distribution curves (g.p.c.) of: (——) PEO before irradiation and (· · ·) PEO, (– – –) PEO–$CuCl_2$ (7/3) and (· – – · ·) PEO–$CuCl_2$ (9/1) after 2 h visible light irradiation

Table 1 The changes of molecular weight and its distribution in pure PEO and PEO–$CuCl_2$ complexes after 2 h u.v. irradiation ($\lambda > 254$ nm): main high molecular weight fraction (I) and oligomers fraction (II)

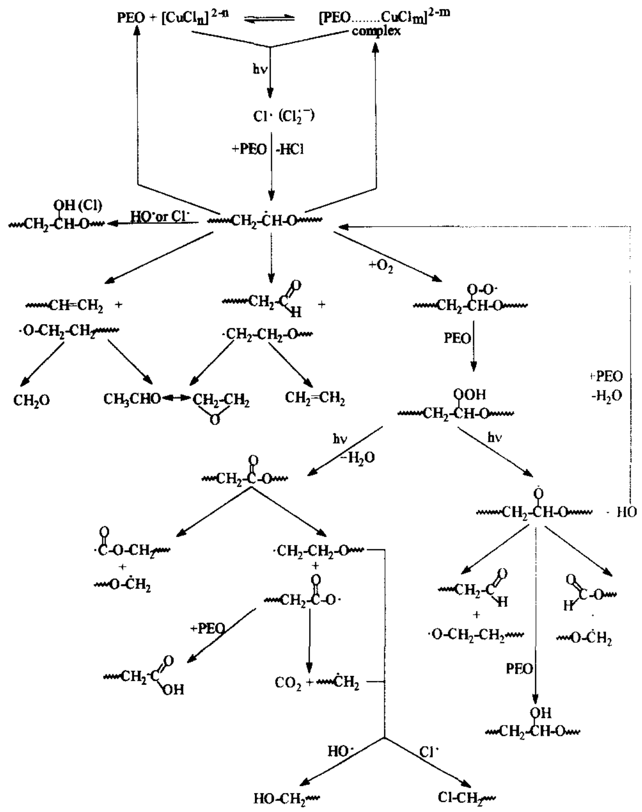
Sample	Number of peak	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
PEO[a]	I	104 970	292 400	483 930	2.79
PEO	I	20 380	74 150	149 700	3.64
	II	800	830	870	1.04
PEO + $CuCl_2$	I	3 290	6 500	11 920	1.99
(9/1)	II	240	260	290	1.08
PEO + $CuCl_2$	I	6 130	17 410	37 710	2.84
(7/3)	II	230	260	290	1.13

[a] Sample unirradiated

Table 2 The changes of molecular weight and its distribution in pure PEO and PEO–$CuCl_2$ complexes after 2 h visible light exposition ($\lambda > 400$ nm): main high molecular weight fraction (I) and oligomers fraction (II)

Sample	Number of peak	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
PEO[a]	I	104 970	292 440	483 930	2.79
PEO + $CuCl_2$	I	8 900	13 500	24 850	1.52
(9/1)	II	690	850	900	1.23
PEO + $CuCl_2$	I	1 495	2 020	2 800	1.35
(7/3)	II	200	220	250	1.10

[a] Sample unirradiated



Scheme 1

As a result of the β-chain scission process, the MW and MWD of PEO changes rapidly (*Figures 5* and *6*). These results show the differences in MWD for PEO–$CuCl_2$ (9/1 and 7/3) samples and u.v. or visible light radiation. It is a very interesting fact that visible light is more effective than u.v. irradiation. Visible light does not cause a change of viscosity (*Figure 2*) and MW (*Figure 6*) of pure PEO whereas u.v. radiation causes a rapid change of viscosity (*Figure 1*) and MW (*Figure 5*). This can be explained by the fact that chlorocopper(II) complexes are very sensitive towards visible light irradiation, which causes formation of $Cl^{\cdot}$ ($Cl_2^{\cdot -}$) radicals with high efficiency.

The MWD curves (*Figures 5* and *6*) show the formation of two fractions of degraded PEO: oligomers (10^2–10^3) and strongly degraded molecules (10^3–10^5) with different polydispersity M_w/M_n (*Tables 1* and *2*). There is also evident difference in the MWD, depending on the type of irradiation source used.

The free radical oxidative degradation of PEO alkyl radicals ($P^{\cdot}$) leads to the formation of many oxygenated products (*Scheme 1*). In particular, the presence of carbonyl compounds (mainly aldehydes) can be easily detected by Fourier transform i.r. spectroscopy[20,33,45] as a broad band centred at about 1720 cm^{-1}. Aldehyde formation in PEO may result from a disproportionation reaction (*Scheme 1*). The 3446 and 3590 cm^{-1} bands can be attributed to the formation of OH/OOH groups, respectively. Formation of a weak band at 1610 cm^{-1} belongs to the unsaturated groups formation. Intensities of these newly formed absorption bands depend on the irradiation conditions, type of radiation source (u.v. or vis.) and time of irradiation; however, there is no observable effect caused by the changing PEO–$CuCl_2$ ratio from 9/1 to 7/3.

The ^1H n.m.r. spectroscopy confirms formation of some of these groups. New weak signals appeared within the ranges 0.8–2.7 ppm (CH_3 and/or $=CH_2$) and 4–5.5 ppm (OH) and at 8.1 ppm (CHO). A signal at 9.7 ppm (COOH)[45] has not been found, because $CuCl_2$ may cause photochemical decarboxylation of the COOH group[46]. Photo-oxidative processes of PEO

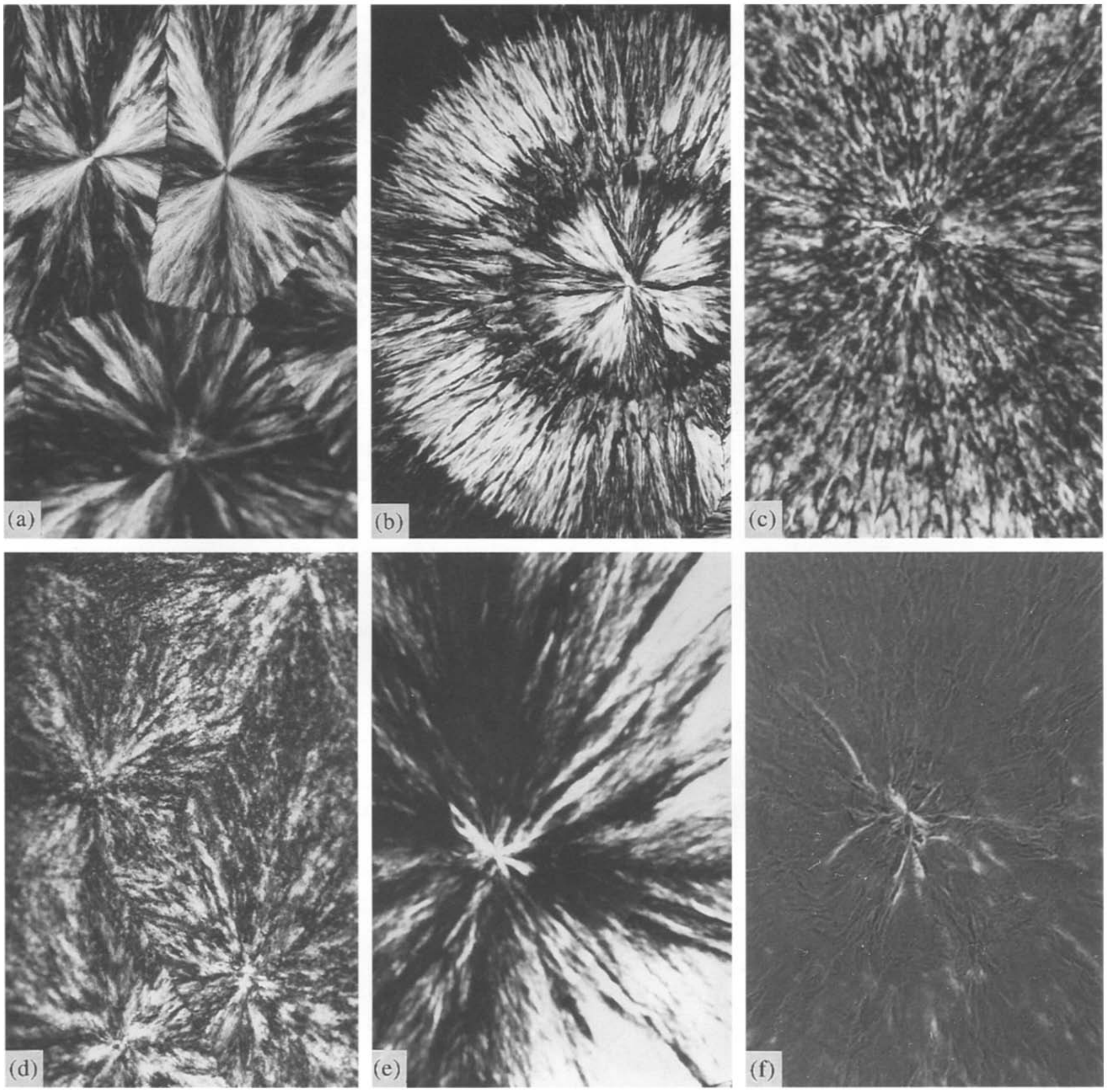


Figure 7 Photomicrographs (×250) of: (a) PEO–$CuCl_2$ (9/1) complex before irradiation; (b) and (c) after 1 h and 2 h u.v. irradiation, respectively; (d) PEO–$CuCl_2$ (7/3) complex before irradiation; and (e) and (f) after 1 and 2 h u.v. irradiation, respectively

in AN are specially enhanced, because oxygen is highly soluble in AN[47]. *Scheme 1* shows mechanisms of formation of oxygenated products in PEO. Detailed interpretation of these reactions have been given elsewhere[33,45,48].

The good coordination properties of PEO for many salts are due to the optimal spacing of the heteroatom in the –(CH_2CH_2O)– chain unit where the C–O bond length is 0.143 nm. When this geometry is changed, as in –(CH_2O)– and –$(CH_2CH_2CH_2O)$–, the polymers have poor complexing properties for metal cations because of the incorrect spacing between oxygen atoms. This highlights the point that a simple increase in polarity is insufficient to ensure good complexing characteristics[49]. The PEO in the crystalline solid state has a helical structure consisting of a succession of nearly *trans*, *trans* and *gauche* forms about the C–O, O–C and C–C bonds, respectively[18,50–53].

The solid PEO–metal salt complexes have multiphase structure which are more complicated in complexes with di- or multi-valent cations than in alkali metal complexes. The degree of crystallinity of the different complexes depends on both cation and anion type, as well as on the ratio of PEO to metal salt. Furthermore, several crystalline phases may coexist, e.g. pure crystalline PEO and polycrystalline PEO–salt complexes. The amorphous phase consists of PEO with the dissolved salt at high content in the last. The structure of PEO–metal salts complexes depend not only on the salt concentration, but also on temperature and water (moisture) present and is very sensitive to the method of preparation. The solvent (water) can be even

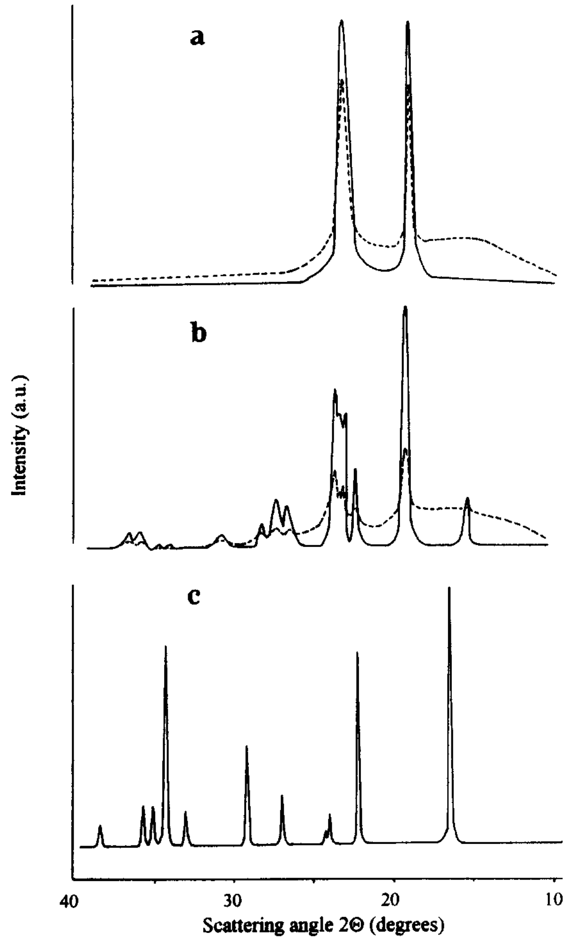


Figure 8 WAXD patterns of: (a) PEO and (b) PEO–$CuCl_2$ (9/1) complexes (——) before irradiation and after (– – –) 2 h u.v. irradiation, respectively; (c) $CuCl_2 \cdot 2H_2O$

coordinated in the PEO–metal salt complexes. The effects mentioned above vary from one PEO-metal salt complex to another, increasing the difficulties in characterization.

The structure of PEO–$CuCl_2$ complexes has been previously discussed[21]. For this research we chose two ratios of PEO–$CuCl_2$ (9/1 and 7/3) by analogy with our previous study of PEO–$FeCl_3$[19]. The PEO–$CuCl_2$ complexes (obtained from solvent evaporation) are crystalline, giving a typical spherulitic structure with different patterns, depending on the PEO–$CuCl_2$ ratio (*Figures 7a* and *d*). It was observed that the spherical symmetry of the PEO spherulites in PEO–$CuCl_2$ complexes is distorted during photo-oxidative degradation process (*Figure 7*). Polygonal morphology with a typical Maltese cross disappears.

The products of PEO–$CuCl_2$ photo-oxidative degradation in AN, after evaporation of the solvent, are mixtures of highly viscous liquids in which somewhere remain crystals of the solid structure (images of samples under a polarizing microscope are very inhomogeneous). Highly degraded PEO molecules with $CuCl_2$ form liquid complexes, which contain mainly an amorphous phase of PEO. This conclusion is also confirmed by the WAXD patterns (*Figure 8*) used to determine changes in the PEO crystallinity. Two crystalline reflection peaks for pure PEO at 2Θ, equal to about 19°12′ and 23°23′ (suggesting a helical structure of this polymer in the solid state) (*Figure 8a*), decreased during photo-oxidative degradation. A broad band formed, resulting from the amorphous phase of low-MW PEO. The WAXD pattern for PEO–$CuCl_2$ (9/1) complex (*Figure 8b*) shows the presence of a crystalline form of PEO in a $CuCl_2$ complex. However, it does not show any peak characteristic of the diffraction pattern of crystalline

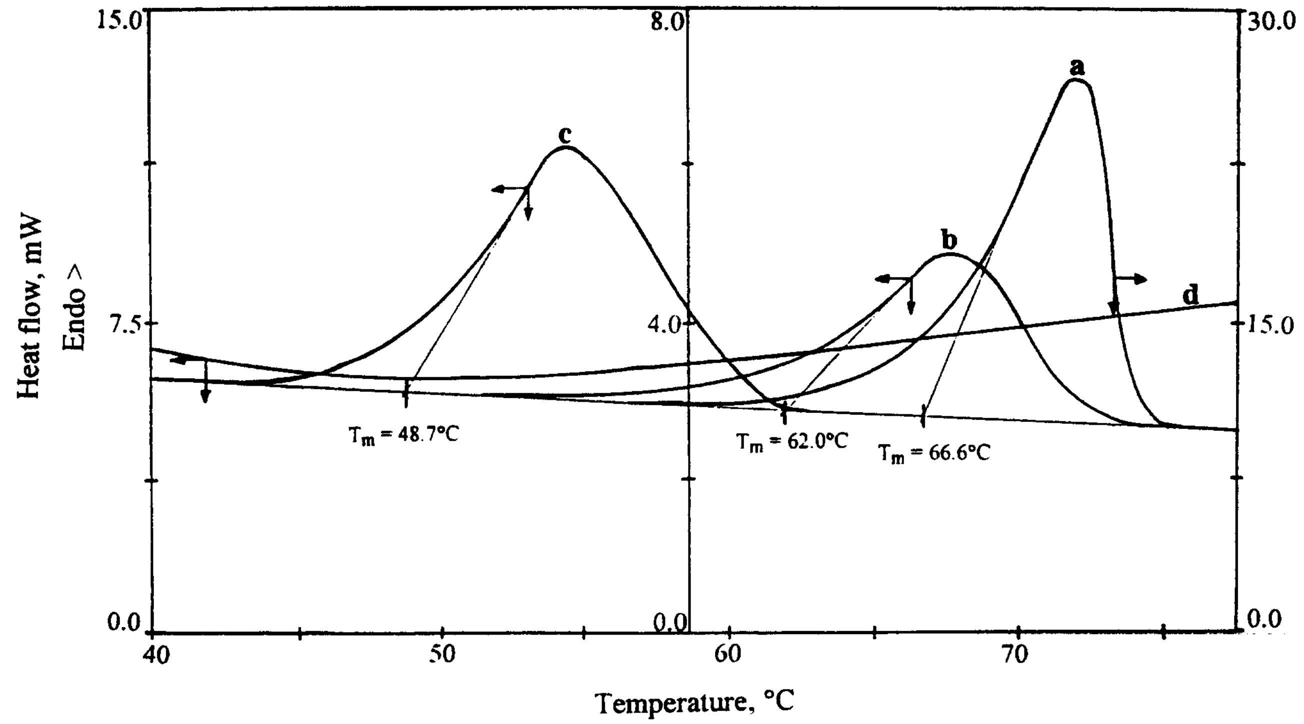


Figure 9 D.s.c. curves of: (a) PEO and (b) PEO–$CuCl_2$ (9/1) complex before irradiation, (c) PEO–$CuCl_2$ (9/1) complex after 1 h u.v. irradiation and (d) PEO–$CuCl_2$ (9/1) complex after 2 h visible light irradiation

$CuCl_2$ (*Figure 8c*). This evidence suggests that the $CuCl_2$ molecules were randomly distributed throughout the polymer to give essentially a single phase system with no evidence of cluster formation, as observed in ionomeric systems. After u.v. irradiation the crystalline pattern of the PEO–$CuCl_2$ complex partially disappears and a broad band from the amorphous phase of PEO is formed (*Figure 8b*).

The d.s.c. measurements show that there is no appreciable increase in the glass transition temperature (T_g) of PEO–$CuCl_2$ complexes ($T_g = -72$°C) in comparison to pure PEO ($T_g = -76$°C)[54]. The PEO–$CuCl_2$ behaviour differs from that of the other metal salts, e.g. $CoCl_2$, $ZnCl_2$ and $FeCl_3$, which exhibit T_g at considerably higher temperatures than the T_g of the parent polymer[11,54]. These results indicate that $CuCl_2$ is attached to the PEO molecule as a side group rather than as a crosslinking two chains group[21]. Stiffening of the flexible polymer chain, due to the interaction between ions, gives higher T_g for the complex than for pure PEO and decreases the ion mobility. It is well established[55] that compatible molecules of lower T_g depress the T_g of the system, whereas the effect of inorganic fillers dispersed as a second phase is minimal[56–58]. The effect of the incorporation of ions on the T_g of polymers has been reviewed elsewhere[59]. The d.s.c. results for PEO and the PEO–$CuCl_2$ complex (9/1) show the presence of a crystalline phase in the later (*Figure 9*). The melting temperature (T_m) of the PEO–$CuCl_2$ complex ($T_m = 62$°C) lies a few degrees lower than for pure PEO ($T_m = 66.6$°C). After u.v. irradiation of the PEO–$CuCl_2$ complex, the T_m is shifted to 48.7°C. This indicates that the crystalline phase still exists in u.v. irradiated sample. After visible light irradiation, the PEO–$CuCl_2$ sample exists in a highly viscous liquid form and does not show the presence of any crystalline phase (T_m does not exist) (*Figure 9*).

The u.v. and visible light irradiated samples of PEO–$CuCl_2$ (7/3) complexes only exist as highly viscous liquids and do not show the presence of a crystalline phase; all are amorphous. This implies that the PEO is highly degraded.

CONCLUSIONS

The photo-oxidative degradation of PEO–$CuCl_2$ complexes in AN solution shows a rapid formation of low-MW fractions as a result of chain scission processes. With the increasing degradation process, there is also a pronounced change in the morphology of PEO–$CuCl_2$ complexes casted from AN solution. They lose their capability to form spherulites. This results from changes in MW and polydispersity, which affects crystallization conditions. The $CuCl_2$ acts as a photo-initiator, which in AN solution under u.v. or visible light irradiation, produces very active $Cl^{\cdot}$ and $Cl_2^{\cdot -}$ radicals. These abstract hydrogen atom from methylene (CH_2) groups in PEO and produce polymer alkyl radicals which further participate in oxidative degradation of PEO macromolecules.

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