Cobalt(II) chloride catalysed oxidative degradation of poly(ethylene oxide) by a short wavelength UV-radiation

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Abstract

Photo-oxidative degradation of poly(ethylene oxide) with small amount (1 and 3 wt.%) of cobalt (II) chloride was studied in acetonitrile solutions and in solid state. On the basis of FTIR, UV-Vis spectroscopy, GPC and viscometry measurements it was found that cobalt salt accelerates photodecomposition of PEO. DSC was applied for study of crystallinity changes in PEO and PEO + $CoCl_2$ during UV-irradiation. The structure of PEO + $CoCl_2$, mechanism of photoreactions and the influence of physical factors are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photo-oxidative degradation; Poly(ethylene oxide); Cobalt(II) chloride

1. Introduction

It is well known that the reactions induced in polymer by UV-radiation depend on many different factors including: macrochain structure, internal and external impurities, temperature, atmosphere, physical state of sample, thermal and processing history of polymer, type of radiation source, etc. In case of substances intentionally added to polymer, mechanism of photodegradation becomes very complex [1,2].

Studies of polymer photodegradation in the presence of metals or metallic compounds established that some of them have catalysing effect on polymer decomposition but not of others. Moreover, the compound accelerating degradation in one system, can retard such process in other case. Specially active in enhancing of polymer degradation are multivalent cations, which can undergo reversible photoredox reaction [3]. We have found previously that iron(III) chloride or copper(II) chloride efficiently accelerates photodegradation of such polymer as polystyrene, poly(methyl methacrylate), poly(ethylene oxide) and poly(vinyl pyrrolidone) [4–10].

Investigation of PEO is not only of academic interest. This crystalline polymer, soluble in water and in several organic solvents, is broadly used in practise: in medicine, pharmacy, cosmetics, textiles, agriculture, food and paper industry [11]. Owing to specific properties, PEO found a variety of biochemical applications (e.g. in protein immobilization, controlled release drug systems or preparation of protein rejecting surfaces) [12–14]. In combination with low molecular weight metal salts, PEO forms CT complexes, which are characterised by the ionic conductivity and can be applied as a solid polyelectrolytes in electrochemical devices [15–19]. Moreover, copolymerization or grafting of ethylene oxide with another monomers or macromolecules allows to transfer its properties to a new product, which can be modified according with needs [20–22].

Thermal, radiation and photochemical degradation of pure PEO has been investigated [1,2,23–29], however, there is much less information about the influence of metal salts added to PEO on change of its stability [4,7,8,30].

The aim of the present work was to study cobalt (II) chloride catalysed photo-oxidative degradation of poly (ethylene oxide) in solid state and in acetonitrile solution in air atmosphere.

2. Experimental

Poly(ethylene oxide) (PEO) was supplied by Aldrich; $CoCl_2·6H_2O$ – by POCh (Poland).

A low pressure mercury vapour lamp TUV 30 W (Philips, Holland) emitting mainly 253.7 nm irradiation was used. Light intensity at sample position measured by IL 1400A Radiometer (International Light, USA) equalled 1.68 mW/cm^2.
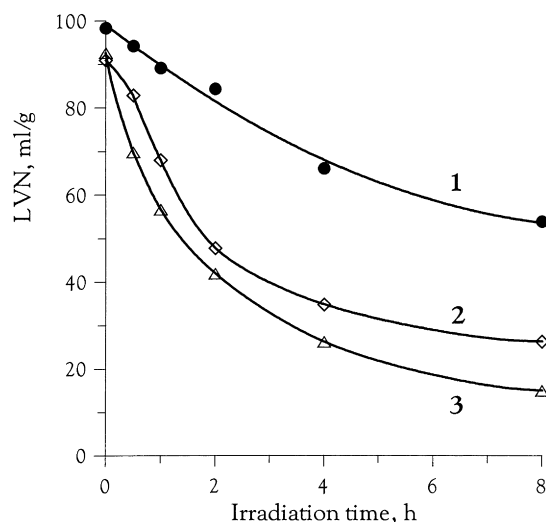
Studies of PEO photodegradation was run in 2%

Fig. 1. Changes of the limiting viscosity numbers of (1) PEO, (2) PEO + 1% CoCl$_2$ and (3) PEO + 3% CoCl$_2$ upon UV-irradiation.

acetonitrile (AN) solutions with different content of CoCl$_2$ (1–3 wt.%). Solid CoCl$_2$·6H$_2$O is pink but acetonitrile solutions of CoCl$_2$ and PEO + CoCl$_2$ are blue.

The polymer films obtained by solvent evaporation were also exposed to UV-irradiation. Thickness of films used was about 20 μm.

The course of polymer photooxidation was followed by FTIR and UV–VIS spectroscopy using Spectrum 2000 (Perkin Elmer) and UV-1601 PC Spectrophotometer (Shimadzu) respectively.

Integral intensity (i.e. surface area) of absorption bands of hydroxy/hydroperoxy, carbonyl and ether groups were calculated from IR spectra. 60 scans were done for each spectrum. Films with the same thickness were selected for comparison. In case of samples of differing thickness, integral intensities were divided by intensity of standard peak (CH$_2$ stretching at 2885 cm^{-1}).

Viscosity measurements of 1% acetonitrile solutions of PEO and PEO with CoCl$_2$ were made at 20°C using an

Ubbelohde viscometer. Limiting viscosity numbers (LVN) were calculated from Solomon–Ciuta equation [31].

Average molecular weights ($\bar{M}_w$, $\bar{M}_n$, $\bar{M}_z$) and molecular weight distribution (polydispersity index = $\bar{M}_w/\bar{M}_n$) of polymeric samples were obtained by gel permeation chromatography (GPC) with Shimadzu C-R4A Chromatopac and Ultrahydrogel column calibrated with PEO standards.

The amount of peroxide/hydroperoxide groups was estimated by an iodometric methods [32].

Differential scanning calorimetry (DSC) measurements were performed using Perkin-Elmer DSC6 thermal analysis system. The instrument was calibrated with indium standard (T_m = 156.6°C, ΔH = 28.46 J/g) [33]. The samples (3–5 mg) were heated at the rate 5°/min in the range 0°C–100°C under in inert atmosphere. Melting endotherms were recorded during the first heating run.

Degree of crystalinity (X_c, %) of the polymer was calculated using

$$X_c = \left(\frac{\Delta H_m}{\Delta H_m^0} \right) 100\% \tag{1}$$

where ΔH_m and ΔH_m^0 are the enthalpy of melting of the sample and the enthalpy of melting of a 100% pure crystalline PEO, respectively. ΔH_m^0 = 220.81 J/g [34].

3. Results

3.1. Photodegradation of PEO and PEO + CoCl$_2$ followed by viscometry and gel permeation chromatography

Changes of LVN in PEO and PEO with 1% and 3% CoCl$_2$ induced by UV-irradiation (Fig. 1) indicate that chain scission starts immediately without any induction period. It is clearly seen that the drop of LVN in PEO containing cobalt salt is faster than that in pure PEO. It leads to greater efficiency of polymer degradation in the former case. The rate of degradation (deduced from the slope of curve) in all samples is the highest in the initial stage (1 h) of exposure. Then, after 2 h UV-irradiation, the rate of degradation decreases and it has approximately equal value for all samples. PEO + 3% CoCl$_2$ degrades only slightly faster than PEO + 1% CoCl$_2$.

It is necessary to add that viscosity of linear polymers depends not only on its average molecular weight but also on its conformation. The little lower values of LVN in PEO + CoCl$_2$ than that in PEO (in undegraded samples) point out that some conformational changes occur. Probably, the addition of CoCl$_2$ to PEO causes the macromolecules, normally existing in helix form, to coil more.

Fig. 2 presents the changes of molecular weight distribution (MWD) in PEO and PEO + CoCl$_2$ after UV-irradiation. All MWD curves of photodegraded samples are shifted to lower molecular weights. The width of these curves differ depending on sample composition. MWD of pure PEO 4 h irradiated is broader than that in undegraded PEO. The
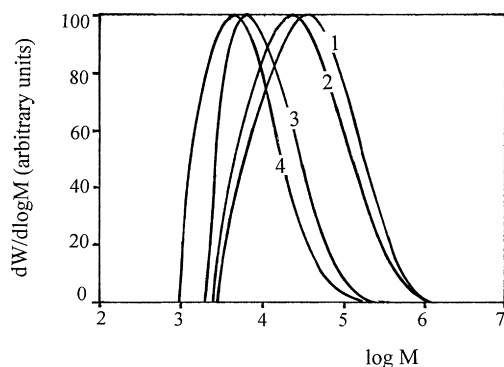

Fig. 2. Differential molecular weight distribution curves of unirradiated (1) PEO and 4 h UV-irradiated (2) PEO, (3) PEO + 1% CoCl$_2$, (4) PEO + 3% CoCl$_2$.

Table 1
Changes of average molecular weights and polydispersity in PEO and PEO with CoCl$_2$ after 4 h of UV-irradiation

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
PEO-undegraded	18 710	81 870	267 270	4.37
PEO – 4 h UV	11 250	58 260	205 040	5.18
PEO + 1% CoCl$_2$ – 4 h UV	7300	16 640	39 880	2.20
PEO + 3% CoCl$_2$ – 4 h UV	3890	9500	26 410	2.44

curves for PEO irradiated in the presence of CoCl$_2$ are narrower; it means that polymer becomes more uniform.

The number-average, weight-average and z-average molecular weights as well as polydispersity (expressed as $\bar{M}_w/\bar{M}_n$) are collected in Table 1. $\bar{M}_n$ of PEO after 4 h UV-irradiation decreases about 40% but these changes in PEO + 1% CoCl$_2$ and PEO + 3% CoCl$_2$ samples are much higher:

$\sim$ 60% and $\sim$ 80%, respectively. Taking into account $\bar{M}_w$ or $\bar{M}_z$ of comparable samples, these differences are obviously greater. Polydispersity in pure PEO increases, indicating that chain breakage occurs simultaneously with macroradical recombination. On the contrary, the polydispersity in PEO + CoCl$_2$ samples decreases after UV-irradiation. In that case, the main chain scission is predominant, moreover, the macromolecule lengths approach similar values. MWD proceeds to a most probable molecular weight distribution (i.e. Flory distribution), where $\bar{M}_w/\bar{M}_n \rightarrow 2$.

3.2. Chromophores formation in PEO and PEO + CoCl$_2$ observed using UV-Vis spectroscopy

Absorption spectra of pure PEO films (as well as solutions) do not show clear, characteristic peaks in the UV-Vis
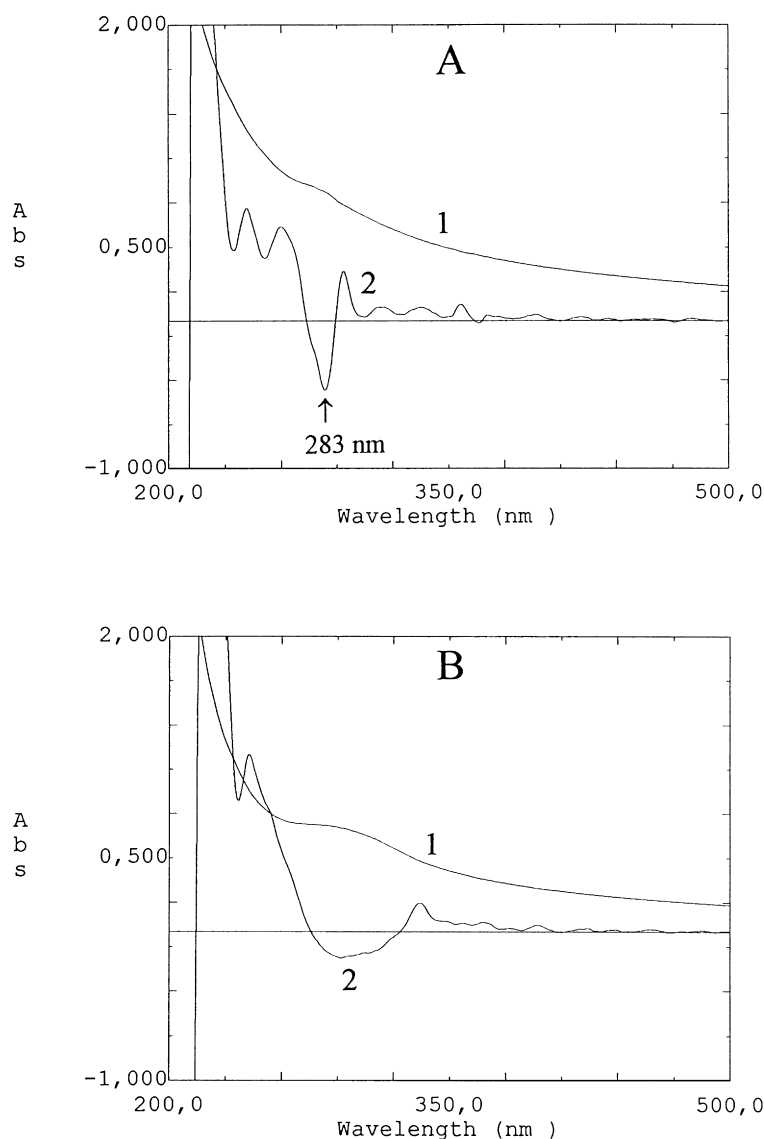

Fig. 3. Absorption spectra (1) and second order derivative spectra (2) of PEO in acetonitrile solution before (A) and after 8 h (B) of UV-irradiation (PEO concentration = 2% m/v).
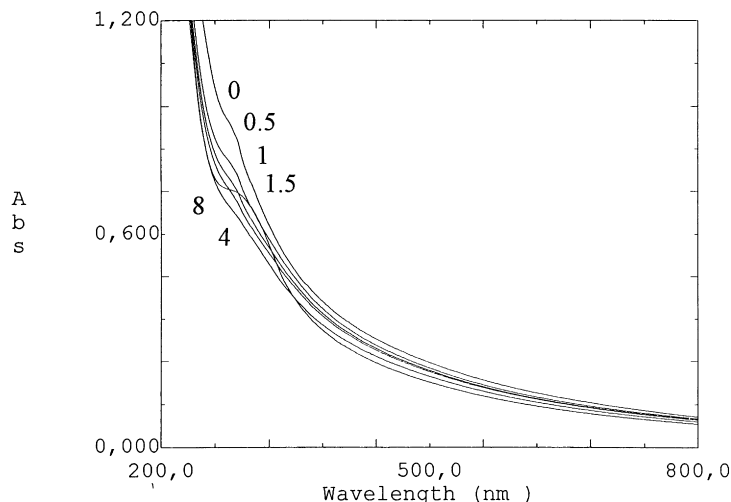
Fig. 4. Absorption spectra changes in 2% PEO solution during UV-irradiation (numbers indicate time of irradiation in hours).

region. However, first or second derivatives of absorption curve allow us to observe the traces of absorbing species. Most useful is the second derivative (Fig. 3) because minimum on the second derivative curve indicates the wavelength at which the maximum on the original absorption curve should be present. Second derivative of absorption curve points out that even pure undegraded PEO contains residue of chromophores, probably abnormal groups formed during polymerization. It is well known, that such groups are responsible for initiation of photodegradation of polymers which do not absorb UV-light.

UV-irradiation of PEO (up to 4 h) causes systematic decrease of absorption intensity in whole UV-Vis region (Fig. 4). Prolonged irradiation time (up to 8 h) leads to increase of absorption and small absorption band about 280 nm appears as a result of new oxidation products formed in PEO.

CoCl$_2$/AN solution exhibit strong charge transfer band below 300 nm and complex d–d band at 530–750 nm range with main maximum at 682 nm (Fig. 5, curve 1). Very intensive CT band was not studied because absorption exceeded 2 for the concentration applied. The insignificant decrease of the intensity of d–d bands during exposure to UV light (up to 8 h) indicates the relative photostability of CoCl$_2$/AN complexes. It is obvious because the lamp used does not emit radiation in this range.

Absorption bands observed in PEO solutions with small amount of CoCl$_2$ (1% and 3%) were similar to CoCl$_2$/AN but 530–750 nm band maxima as well as intensity ratio of branches of this band in PEO/CoCl$_2$/AN (Fig. 5, curves 2 and 3) vary somewhat from those values for pure CoCl$_2$ complex in AN. It can suggest that some changes in complex structure occur (for example, the formation of coordination bond between Co ion and oxygen atoms from PEO).
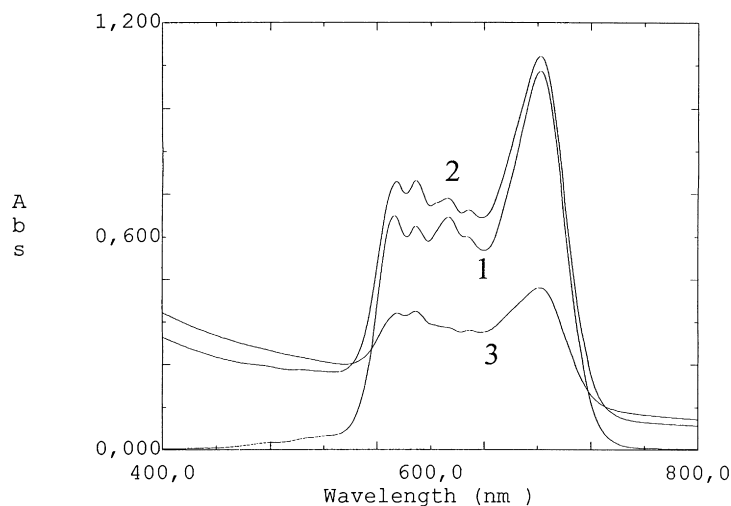

Fig. 5. Absorption spectra of unirradiated CoCl$_2$/AN (1) ($C_m = 1.26 \times 10^{-3}$ mol/l), (2) PEO + 3% CoCl$_2$ and (3) PEO + 1% CoCl$_2$ solutions (PEO concentration = % m/v).
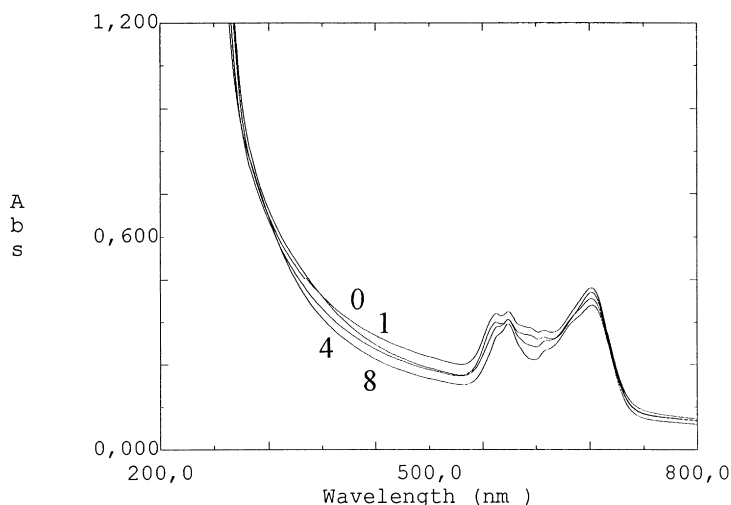
Fig. 6. Absorption spectra changes in solution of PEO + 1% CoCl$_2$ during UV-irradiation (numbers indicate time of irradiation in hours).

Absorption changes in exposed PEO solutions with CoCl$_2$ are different than that in pure PEO (Fig. 6). The absorbance at 282 nm was chosen for comparison of the behavior of these samples upon UV-irradiation. The plot of ΔA(282 nm) versus irradiation time (Fig. 7A) shows that absorbance of PEO solutions with 1% and 3% CoCl$_2$ increases in the first stage of exposure, and then it decreases after 2 h. It can be explained by initial formation of chromophores, which are, however, unstable and undergo photolysis during prolonged irradiation. It means that at the beginning, formation of chromophores in PEO with CoCl$_2$ prevails over the destruction of abnormal absorbing groups present in PEO, in contrast to the behaviour of PEO in the absence of CoCl$_2$.

Such accelerating effect of CoCl$_2$ was not observed in polymer films (Fig. 7B). These films show only very small changes of the absorbance during UV-irradiation but the trend of these changes is different from that observed in AN solutions (Fig. 7A). Films of PEO and PEO + 1% and 3% CoCl$_2$ were very thin but even in thicker films the absorbance changes are very small if films are irradiated always on the same side. UV-irradiation acts only on the surface of solid samples and can not penetrate very deep into polymer. Thus, from Fig. 7, it can be concluded that the effect of small amount of Co salt as well as UV-irradiation on oxidative degradation of PEO films is negligible compared to PEO solutions.

As was mentioned earlier, CoCl$_2$ is relatively photostable and changes of absorption at 682 nm during UV-irradiation in AN solution are very small (Fig. 8, curve 1). However, in the presence of PEO these changes are faster (Fig. 8, curve 2). It points out that PEO also has destabilising influence on cobalt complex in acetonitrile solution. It is necessary to remind that the structure of Co complex in AN can change in the presence of polymer as was suggested by viscometric results.

3.3. Photooxidation of PEO and PEO + CoCl$_2$ monitored by FTIR spectroscopy and iodometric analysis

Notable changes in the IR spectra at 3100–3600 and 1700–1760 cm^{-1} region indicate that carbonyl and hydroxy/hydroperoxy groups are formed during UV-irradiation of PEO and PEO with cobalt salt. An example of such changes in PEO + 3% CoCl$_2$ in carbonyl region is shown in Fig. 9. The variation of spectroscopic parameters of studied bands such as intensity, peak maxima, band widths and range observed for UV-irradiated PEO proves that mixture of different photooxidation products is created.

Variation of hydroxy/hydroperoxy group amount in irradiated pure PEO are irregular (Fig. 10). In PEO containing 1% and 3% CoCl$_2$ an initial increase of [OH/OOH] is followed by fast drop after longer irradiation time (>2 h).

Changes of carbonyl groups concentration plotted versus irradiation time (Fig. 11) clearly show that PEO photooxidation is accelerated by the presence of CoCl$_2$. This trend is observed for samples irradiated in solid state as well as in solution but the effect of cobalt salt is much higher in the latter case.

Detailed analysis of IR spectra allows also to monitor photodegradation processes in PEO. The decrease of the intensity of peaks characteristic for ether groups (at 1145, 1115 and 1061 cm^{-1}) [35] confirms the occurrence of chain scission. For comparison of the course of this reaction in PEO and PEO with cobalt salt, the most intensive peak at 1115 cm^{-1} was chosen (Fig. 12). Significant decrease of absorbance at 1115 cm^{-1} was observed in PEO films containing 1% and 3% CoCl$_2$ after 2–4 h of UV-irradiation, contrary to negligible changes in pure PEO. It confirms the results obtained by viscometry measurements.

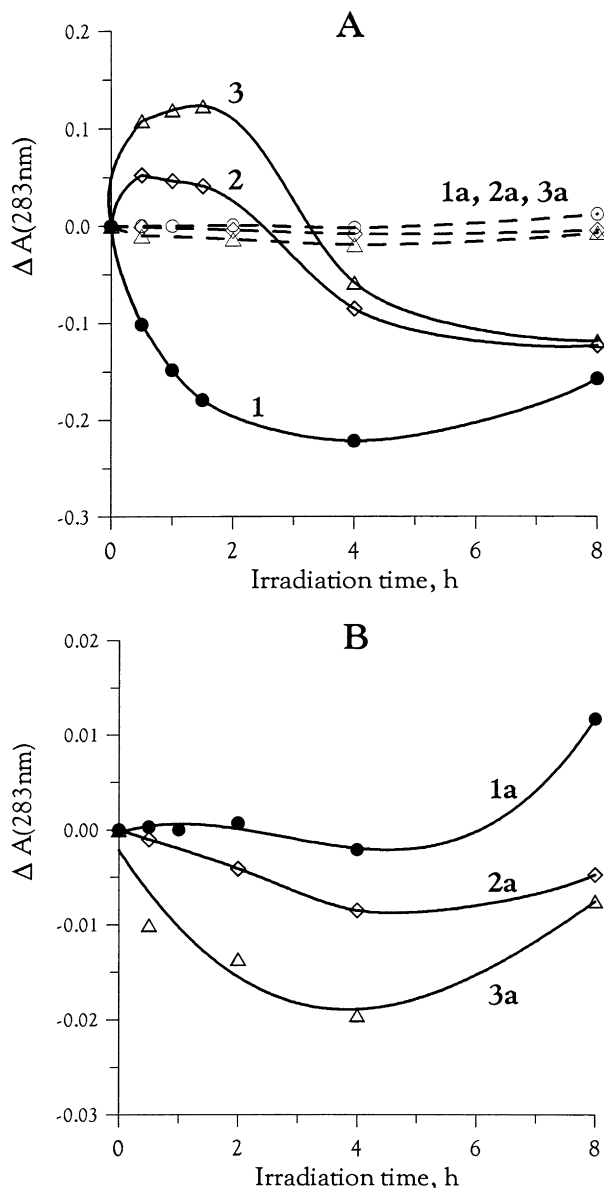Total concentration of peroxides (hydroperoxides and

A

B

Fig. 7. Changes of the absorbance at 283 nm in (1) PEO, (2) PEO + 1% CoCl$_2$, (3) PEO + 3% CoCl$_2$ in acetonitrile solutions (A) and in films (B).

Fig. 8. Changes of the absorbance at 682 nm in (1) CoCl$_2$ and (2) PEO + 1% CoCl$_2$ solutions.

3.4. Changes of crystallinity in PEO and PEO + CoCl$_2$ determined by DSC.

Temperatures characterising the melting of PEO crystallities, maximal melting rate, fusion enthalpy and degree of crystallinity are given in Table 3. Temperature of polymer melting does not change significantly during photodegradation of PEO and PEO + CoCl$_2$. The most useful parameter for such small changes is the onset temperature of the melting (T_o) determined as the intersection between the tangent to the maximum rising slope of the peak and the extrapolated sample baseline.

Small decrease of T_o in all degraded samples can be caused by disturbances in the regular packing of PEO after UV-irradiation. The slight narrowing of the melting peak, observed in majority of samples, indicates that sizes of crystallities are a little more uniform after UV-irradiation.

One can see significant increase of fusion enthalpy and degree of crystallinity caused in PEO by UV-irradiation. The changes observed in PEO degraded in the presence of CoCl$_2$ are higher than that in pure PEO. Prolonging exposure time causes further increase of degree of crystallinity except for PEO + 1% CoCl$_2$ sample. The rate of melting in all degraded samples is higher than that in PEO undegraded. The increase of degree of crystallinity was observed also during thermal degradation of PEO [26,27].

There are a few reasons of the increase of degree of crystallinity during UV-irradiation. It is known that in semi-crystalline polymer like PEO, photo-oxidative degradation starts in the amorphous phase because of easy diffusion of oxygen to the unordered macrochains. The access of oxygen to tightly packed, rigid crystalline regions is restricted and this phase remains unchanged for a relatively long time during UV-irradiation. One also considers the possibility

internal peroxides) formed during PEO irradiation, evaluated by iodometric method, is collected in Table 2. It is seen that the amount of peroxide group in PEO increases with irradiation time (up to 2 h) whereas in PEO + 1% CoCl$_2$ the increase of [POOP + POOH] is much faster in the first period (5–10 min) of UV-irradiation. Then, after reaching a maximum, the amount of these groups decreases because of their photolysis. It is in accordance with data from IR (Fig. 10), where the maximum of hydroxyl peak in kinetic curve appears a little later, i.e. after 1 h. It means that photoproducts monitored by IR in 3100–3600 cm^{-1} region after longer irradiation time are composed mainly of hydroxy groups. It is necessary to add that even small content of –OOH or –COOC– is responsible for the formation of free radicals initiating polymer degradation.
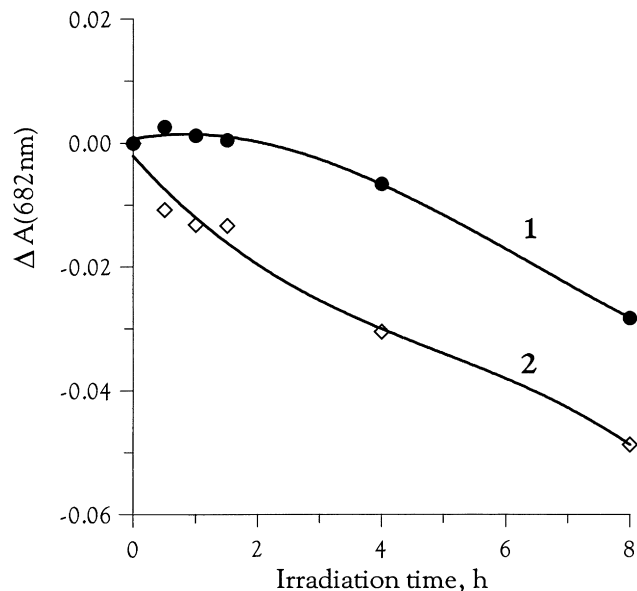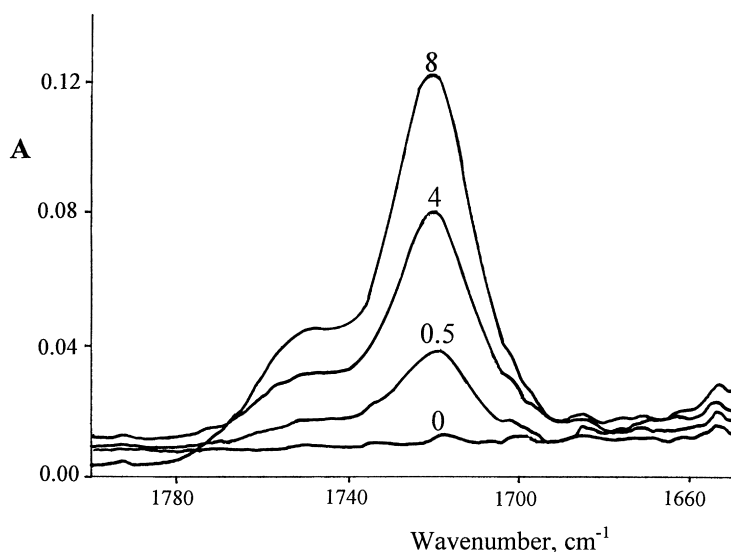
Fig. 9. FT-IR spectra of PEO + 3% CoCl$_2$ before and after UV-irradiation (numbers indicate time of irradiation in hours).

of delocalization of excitation energy through the crystal lattice. Fast degradation of amorphous phase leads to formation of low molecular weight products which can diffuse out decreasing the mass of amorphous polymer. Hence, the ratio of crystalline to amorphous fraction increases. The second reason of increase of crystallinity is probably the reordering of broken, shorter macrochains. Such degraded macromolecules have higher mobility facilitating the formation of well-ordered structures. We also suggest that during UV exposure very small crystallities are reordered and replaced by slowly growing larger crystallities, similarly as during crystals storage and maturing.

Effectiveness of CoCl$_2$ action on the degradation of PEO is the highest in sample with 3% of this salt: after 4 h of UV-irradiation the degree of crystallinity increases twice that of the unirradiated PEO.
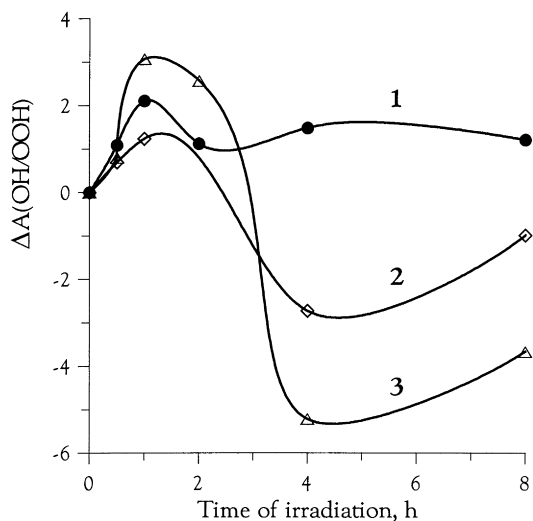
Fig. 10. Kinetics of OH/OOH group formation in films of (1) PEO, (2) PEO + 1% CoCl$_2$, (3) PEO + 3% CoCl$_2$ during UV-irradiation.

The results of changes of crystallinity caused by UV-irradiation in PEO and PEO + CoCl$_2$ differs from data obtained earlier [7], where we established that crystalline phase in high molecular weight PEO ($\bar{M}_n \approx 10\,000$, $\bar{M}_w \approx 30\,000$) in the absence and in the presence of CuCl$_2$ is also destroyed upon UV-irradiation. It seems that the photochemical changes observed there for PEO + CuCl$_2$ were more efficient and faster than phototransformation observed in PEO and PEO + CoCl$_2$ in this work. However, direct comparison of both the systems is difficult. Not only different salt in different amount were used but also the PEOs were different. In the present study we used PEO with about 5 times lower average molecular weight. It suggests that the susceptibility of semicrystalline polymer to UV-light depends on the initial molecular weight. It is not surprising because one can imagine that much more chain scission must take place in polymer with shorter chains than in polymer with longer chains to obtain the same degree of degradation.

4. Discussion

4.1. Structure of PEO with CoCl$_2$

PEO is a polar polymer in which *trans–trans–gauche* conformation is dominant [36,37]. In solid state PEO forms single helix. It was revealed that metal ions are coordinated by oxygen atoms from PEO [38–44]. Such coordination complexes are created easily because of the privileged spacing of oxygen atoms in macrochains [43]. In our case, the amount of CoCl$_2$ in PEO is small but even such quantity can induce the strong, specific molecular interactions and change the polymer conformation, which is observable as a decrease of LVN.

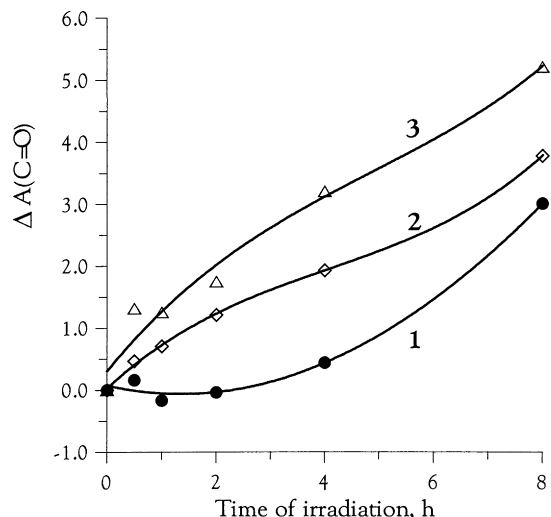The conformation of PEO containing metal salt is also

Fig. 11. Kinetics of C = O group formation in solution of (1) PEO, (2) PEO + 1% CoCl$_2$, (3) PEO + 3% CoCl$_2$ during UV-irradiation.

Table 2
Changes of peroxy/hydroperoxy groups concentration in PEO and PEO + CoCl$_2$ samples during UV-irradiation

Irradiation time (min)	Δ[POOP + POOH] $\times 10^4$ (mol/l per 1g of polymer)		
	PEO	PEO + 1% CoCl$_2$	PEO + 3% CoCl$_2$
5	2.67	5.16	1.18
10	2.96	7.94	2.33
120	5.89	3.00	1.28
240	4.20	1.63	2.78

dependent on the molar ratio of components. In typical complex structures, metal ions were coordinated by three or four nearest oxygen atoms. PEO wraps around cation when higher amount of metal salt is added. Moreover, a different conformation of PEO for amorphous phase than crystalline phase can be expected. Ion association (pairing and clustering) in completely amorphous PEO (in melt) was suggested [45].

Divalent cobalt with electronic configuration (Ar)3d^7 mostly occurs in high spin octahedral and tetragonal symmetry [46–48]. Sometimes these two configurations are in equilibrium because of the small stability difference between octahedral and tetrahedral Co(II) complexes [47]. Another structure such as five coordinate or square species are formed more rarely. Solid CoCl$_2$·6H$_2$O has octahedral structure but dissolving this salt in AN causes change to
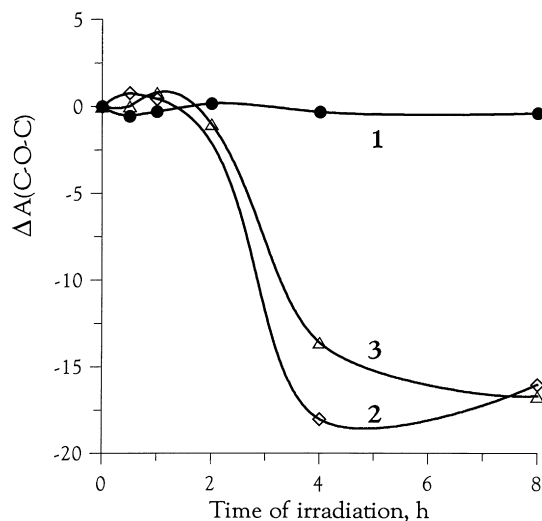
tetrahedral complex. Tetrahedral structure remains after mixing of CoCl$_2$/AN with PEO/AN solutions, which was confirmed by electronic spectra. However, small changes observed in UV-Vis absorption spectra suggest that some reorganisation in coordination sphere takes place, for example, AN ligands (as weakly solvating metal cations) can be replaced by oxygen atoms from PEO macrochains:

$$[CoL_n] + X \longrightarrow [CoL_{n-1}X] + L \qquad (2)$$
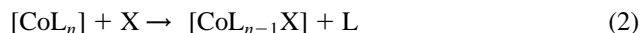
where L is Cl$^-$ or AN ligand, X the PEO ligand, and n the coordination number.

It seems probable, that in this study we have the mixture of complexes with different composition (with following ligands: Cl$^-$, AN, PEO and maybe H$_2$O) distributed in PEO matrix.

Main transition occurring in complexes, in which the donor is oxidizable metal ion (as Co^{2+}) is metal-to-ligand charge transfer (MLCT) [49]

$$[Co(II)L_n] \xrightarrow{h\nu} [Co(III)L_{n-1}]L^- \qquad (3)$$
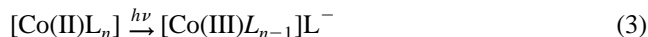
UV-irradiation may also cause isomerisation of complexes:

$$cis\text{-}CoL_nX_m \xrightarrow{h\nu} trans\text{-}CoL_nX_m \qquad (4)$$
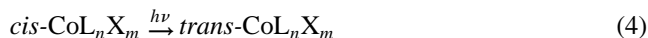
4.2. Mechanism of photo-oxidative degradation of PEO + CoCl$_2$

The primary photochemical reaction is breaking of macrochains. In pure PEO, main chain scission arises at weak chemical bonds. Not only structural defects (hydroperoxides, carbonyls, tail-to-tail structures etc.) are responsible for initiation of photochemical processes in PEO but also the energy of UV irradiation (for instance, $E \approx 400$ kJ/mol at $\lambda = 300$ nm) is enough to cause the random breaking of PEO chains. Bond dissociation energy of C–O and C–C in PEO chains equals 335 and 369 J/mol, respectively [50].

Formed in primary process, macroradicals react readily with atmospheric oxygen and various oxidation products appear (mainly hydroperoxides and carbonyls). Peroxide and hydroperoxide groups do not accumulate in polymer and so they undergo further fast photolysis. Mobile, active hydroxy/hydroperoxy radicals again initiate polymer destruction [1,2]. Macroradicals formed by chain scission

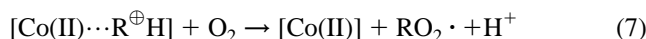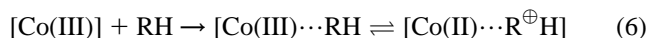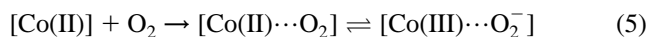Fig. 12. Changes of ether group concentration in films of (1) PEO, (2) PEO + 1% CoCl$_2$, (3) PEO + 3% CoCl$_2$ during UV-irradiation.

Table 3
Changes of thermal parameters and crystallinity of PEO and PEO + CoCl$_2$ induced by UV-irradiation; estimated from DSC. T_o: onset temperature of melting, T_{max}: temperature in maximum of melting peak, ΔH_m: enthalpy of melting, X_c: crystallinity degree

Sample	Temp. range (°C)	T_o (°C)	T_{max} (°C)	ΔH_m (J/g)	X_c (%)
PEO – undegraded	54.9–67.6	61.6	65.8	107.7	48.8
PEO – 2 h UV	56.2–67.7	60.8	65.9	136.5	61.8
PEO – 4 h UV	55.8–66.7	60.1	65.0	139.9	63.4
PEO – 8 h UV	58.6–66.1	61.3	64.3	121.2	54.9
PEO + 1% CoCl$_2$ – 2 h UV	52.0–65.3	58.3	63.3	141.1	63.9
PEO + 1% CoCl$_2$ – 4 h UV	53.0–62.2	58.1	64.4	135.0	61.2
PEO + 1% CoCl$_2$ – 8 h UV	37.3–62.7	38.4	58.8	130.8	59.2
PEO + 3% CoCl$_2$ – 2 h UV	54.5–65.2	60.4	64.6	152.6	69.2
PEO + 3% CoCl$_2$ – 4 h UV	54.7–64.8	59.7	62.9	214.4	97.1
PEO + 3% CoCl$_2$ – 8 h UV	52.1–63.9	57.1	61.8	134.5	60.9

may also depolymerize evolving monomer (ehylene oxide), ethylene, formaldehyde or acetaldehyde [30].
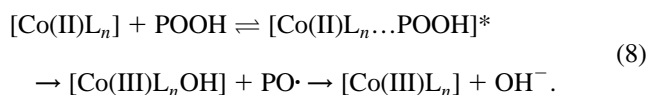
Our results indicate that the addition of CoCl$_2$ enhanced photodegradation of PEO. The decrease of viscosity and average molecular weights is significantly larger in photo-degraded PEO + CoCl$_2$ than that in pure UV-irradiated PEO. However, there are no considerable effect of CoCl$_2$ amount on the rate of PEO photodegradation.

This accelerating effect can be explained by catalytic action of cobalt salt. The mechanism, proposed for catalytic oxidation of hydrocarbons (RH) [51], is shown below:

$$[\text{Co(II)}] + \text{O}_2 \rightarrow [\text{Co(II)}\cdots\text{O}_2] \rightleftharpoons [\text{Co(III)}\cdots\text{O}_2^-] \qquad (5)$$

$$[\text{Co(III)}] + \text{RH} \rightarrow [\text{Co(III)}\cdots\text{RH}] \rightleftharpoons [\text{Co(II)}\cdots\text{R}^{\oplus}\text{H}] \qquad (6)$$

$$[\text{Co(II)}\cdots\text{R}^{\oplus}\text{H}] + \text{O}_2 \rightarrow [\text{Co(II)}] + \text{RO}_2\cdot + \text{H}^+ \qquad (7)$$

It seems reasonable to consider similar action in case of CoCl$_2$/PEO system.

Transition metal ions are capable of catalysing hydroper-oxide decomposition, which act as new sources of radicals initiating polymer degradation.

$$[\text{Co(II)L}_n] + \text{POOH} \rightleftharpoons [\text{Co(II)L}_n\ldots\text{POOH}]^*$$
$$\rightarrow [\text{Co(III)L}_n\text{OH}] + \text{PO}\cdot \rightarrow [\text{Co(III)L}_n] + \text{OH}^-. \qquad (8)$$

The Co(III) cation, formed during oxidation in the presence of air, is relatively unstable in simple compounds [47] and its reduction by chloride anion is possible:

$$[\text{Co(III)}] + \text{Cl}^- \rightarrow [\text{Co(II)}] + \text{Cl}\cdot. \qquad (9)$$
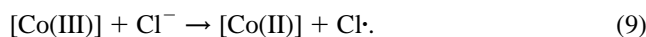
Created this way, chlorine atoms as very reactive species can abstract hydrogen atoms from PEO macromolecules. Then, polymer degradation cycle is repeated. Besides Cl ·, another active agent – chlororadical anion (Cl$_2$ ·$^-$) can be formed during UV-irradiation of chloride metals [7].

Photoredox reaction between CoCl$_2$ and photodegraded PEO molecules can not be also excluded. Furthermore, oxidation of Co(II) by molecular oxygen leads to formation of binuclear peroxobridged species type [47,52]:

$$\text{L}_n - \text{Co} - \text{O} - \text{O} - \text{Co} - \text{L}_n \qquad (10)$$
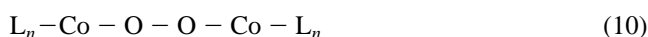
Such bridges, chain or cyclic, were described as intermediate products of catalytic oxidation of organic compounds [47].

There are no spectral evidences that halogenation of PEO chains occurs (the lack of C–Cl stretching vibrations in IR spectra), probably beacause of very low amount of formed Cl atoms, which are rather used as initiator of polymer degradation.

It is necessary to mention, that in the studied samples photocrosslinking does not occur (insoluble gel is not formed in any case). It means that termination by macro-radicals recombination gives only linear polymer. Probably, termination occurs also via macroradical disproportionation with hydrogen atom transfer.

It was recently demonstrated that transition metal salts react with end or pendant double bonds in polymers [53]. In our case, double bonds are created rather at chain ends resulting disproportionation and such reaction with CoCl$_2$ can take place in degraded PEO.

4.3. The influence of physical state of PEO on its photo-oxidative degradation

Photo-oxidative degradation of PEO and PEO + CoCl$_2$ in acetonitrile solution is much faster than that in PEO film with the same cobalt salt content. It was revealed by UV-Vis and FT-IR spectroscopy. The differences of chromophore and oxidation product (C=O and OH/OOH) concentration are much higher when UV irradiation of PEO and PEO + CoCl$_2$ is carried out in AN solutions. This fact can be explained as follows.

Dissolution of PEO causes the change of its helix confor-mation, typical for solid state. In solutions, rigid ordered lattice disappeared and PEO exists in form when random coil fragments are separated by helical segments [54]. In diluted solutions the interactions between macromolecules are weaker because they are separated from each other by many solvent molecules. Then, in solution PEO structure

become more loose than that in solid state and diffusion of oxygen to macrochains is facilitated. This is the main reason of acceleration of PEO photo-oxidation in solution compared to rate in solid state samples.

Photo-oxidative degradation of polymers in solutions is more homogenous process than that in solid state. In solution, oxidation products are uniformly distributed in all polymer volume, mainly owing to higher mobility of macrochains but also owing to vigorous mixing. In solid films these products are mainly concentrated at the surface layer and protect further polymer degradation inside of sample i.e. they act as UV-light screeners.

PEO films are more opaque than PEO solution. Hence, in solid samples the incident light is dissipated and it can be also the reason of slower photo-oxidative degradation in solid state. In transparent polymer solution more light energy is absorbed by chromophores at the same dose.

Moreover, cage effects hamper polymer reactions in solid state. If macroradicals are trapped in the matrix with restricted mobility of macromolecules, the probability of recombination in the same place, when radicals were created, is very high. However, a second opposing fact should be considered. Rigid matrix also stabilises the excited states of macromolecules, thus it prolongs lifetime of these states and increases the probability of chemical reaction [2]. Experimental results indicate that in our case the former effect is dominant.

5. Conclusions

The following conclusions may be drawn:

- PEO and Co(II) chloride forms charge transfer complexes with tetrahedral symmetry. These complexes are distributed in PEO matrix.
- 1% and 3% $CoCl_2$ accelerate photodegradation of PEO. It was revealed by faster decrease of limiting viscosity numbers and average molecular weights in PEO containing $CoCl_2$ than that in pure PEO during UV-irradiation. It is confirmed by IR data.
- Presence of $CoCl_2$ leads to formation of photounstable chromophores in PEO during the first stages of degradation.
- PEO photooxidation is also accelerated by small amount of $CoCl_2$ (1%–3%). It was demonstrated by changes of carbonyl groups detected by IR. Carbonyl groups in PEO are formed at the cost of photolysis of hydroperoxide groups formed at the beginning of UV-irradiation.
- UV-irradiation causes increase of the crystallinity of PEO. These changes are more efficient in the presence of cobalt salt.
- The course of PEO photo-oxidative degradation strongly depends on the physical state of polymer: all photoreactions in acetonitrile solutions are much faster and more efficient than that observed in PEO solid state.

- Destabilising effect of PEO on the photostability of cobalt salt occurred simultaneously.

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