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Changes of poly(ethylene oxide) photostability by doping with nickel(II) chloride

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Abstract

The influence of small addition of nickel(II) chloride on photooxidative degradation of poly(ethylene oxide) (PEO) in solution and in solid state has been investigated. Gel permeation chromatography, viscometry, differential scanning calorimetry, infrared and UV–Vis absorption spectroscopy has been used in these studies. It was found that nickel salt accelerates photodegradation and photooxidation of PEO. Photoinduced changes of PEO crystallinity and influence of macrochains conformation on the efficiency of photodecomposition has also been discussed. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Poly(ethylene oxide); Nickel(II) chloride; Photodegradation; Photooxidation

1. Introduction

Poly(ethylene oxide) (PEO) is a commercially available polymer with a simple chemical structure and specific properties. It is built from flexible, linear macrochains consisting from elements with different electronegativity: carbon and oxygen (–CH_2–CH_2–O–). In crystalline solid state PEO exists mainly in form of regular helix but in solution it can change its conformation to a random coil with statistically placed residual helix segments [1–4]. PEO found application in different branches of industry, cosmetics, pharmacy, medicine (for example it is typically used as surfactant, lubricant, textile size, hydraulic fluid, water-soluble packaging film). Moreover, original concepts of copolymerization of ethylene oxide with different monomers and various modification of PEO allow to obtain new materials with excellent optical, conducting, amphiphilic and other properties having miscellaneous applications [5–8].

Very interesting feature of PEO is it ability to form coordination complexes with different metal cations in which oxygen atoms play a ligand role [9–13]. The loops of PEO helix behave similarly to cyclic ethers (known as crown ethers) [7,14]. They are able to trap cations and owing to high flexibility of macrochains, the size of loop can be fitted to ion diameter. Such complexes are ionic conductors and can be applied as polyelectrolytes in electronic apparatus.

However, PEO is characterised by the low thermal and photochemical stability, it is also known as a biodegradable polymer. Photochemical reactions of PEO complexes furnish a number of intermediates with different reactivity. Recently, one found that PEO photostability is drastically reduced by introduction of small amount of transition metal salt such as $FeCl_3$, $CuCl_2$ or $CoCl_2$ [12,13,15–18].

The aim of the present work was to study the influence of few percentage addition of $NiCl_2$ on photochemical reactions of PEO in solid state and in acetonitrile solution.

2. Experimental details

PEO (Aldrich) was purified by dissolution in distilled water and centrifugation from slightly turbid, insoluble contaminations. Completely clear solution was cast to Petrie's plate and evaporated to dryness. Before use polymer was dried in vacuum at room temperature.

Acetonitrile (ACN) (pure per analysis, Fluka) was the solvent and unhydrous $NiCl_2$ (POCh, Gliwice, Poland) was a doped substance. PEO containing 1, 2 or 3% of nickel salt in ACN (1% m/v) was used for preparation of thin polymer films. Solutions were poured out directly onto CaF_2 spectrophotometric windows (for IR) or onto quartz plates (for UV–Vis).

Then, after solvent evaporation, polymeric samples were dried in a vacuum to a constant weight. Obtained thin films

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were exposed upon low-pressure mercury lamp (TUV 30 W, Philips, Holland) emitting mainly 253.6 nm radiation. The intensity of incident light, measured by IL1400A Radiometer (International Light, USA), was 2.58–2.80 mW/cm^2. Simultaneously, some experiments were carried out in ACN solutions (1% or 2% m/v). Polymeric solutions during UV-irradiation were mixed by magnetic stiffer.

The course of polymer degradation was monitored by viscometry measurements in ACN (1% m/v) at 20°C using a quartz Ubbelohde viscometer. Limiting viscosity numbers (LVN), η were calculated from Solomon–Ciuta equation [19,20]:

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

where η_{sp} and η_{rel} are specific and relative viscosity; c the solution concentration (g/dl).

The average number of chain scission was obtained from LVN of sample before and after UV-irradiation [20]:

$$S = \left(\frac{\eta_0}{\eta_t}\right)^{1/\alpha} - 1$$

where η_0 and η_t are LVN of polymer before and after t time of irradiation and α is a constant in Mark–Houwink equation ($\alpha = 0.61$ [15]).

Photochemical changes in polymer structure were recorded by infrared and electronic absorption spectroscopy using FTIR Genesis II Spectrophotometer (Mattson, USA) and PC 1600 Spectrometer (Shimadzu, Japan), respectively. The kinetic curves of photooxidation and chromophore formation process in PEO were plotted on the base of absorbance changes versus irradiation time (after normalisation to the same sample thickness).

Average molecular weights ($\bar{M}_{\mathrm{w}}$, $\bar{M}_{\mathrm{n}}$, $\bar{M}_{\mathrm{z}}$) and molecular weight distribution of polymeric samples were obtained by gel permeation chromatography (GPC) using Shimadzu C-R4A Chromatopac equipped with refractive index detector and ultrahydrogel column calibrated with narrowly distributed PEO standards.

Changes of PEO crystallinity during UV-irradiation were checked by differential scanning calorimetry (DSC). A Perkin Elmer DCS7 was used with an empty pan as reference. The calorimeter was fitted with an Intracooler and controlled by an IBM compatible PC, runnig Perkin Elmer thermal analysis software (1991 revision). The temperature and energy scales were calibrated effectively using the manufacturer's instruction, with water and indium as standards, applying different temperature calibrations for each scanning rate. The energy scale calibration did not change with scanning rate. All data were measured at a scanning rate of 10°C/min. Degree of polymer crystallinity (X_{c}, %) was calculated from the ratio of the enthalpy of melting of the sample studied (ΔH_{m}) and the enthalpy of melting of a 100% pure crystalline PEO ($\Delta H^0_{\mathrm{m}} = 220.81$ J/g [21]):

$$X_{\mathrm{c}} = \frac{\Delta H_{\mathrm{m}}}{\Delta H^0_{\mathrm{m}}} 100\%$$

3. Results and discussion

The changes of molecular weight from GPC analysis show that PEO is a photochemically unstable polymer. $\bar{M}_{\mathrm{n}}$, $\bar{M}_{\mathrm{w}}$, $\bar{M}_{\mathrm{z}}$ in pure PEO decrease about 17–27% after 2 h and 23–40% after 4 h UV-irradiation, respectively. Simultaneously, the polydispersity index rises from 4.37 to 5.18 in this period of exposure (Table 1).

In PEO doped by $NiCl_2$ all average molecular weights decreases much faster — the drop exceeds 80–90% after 2–4 h UV-irradiation and $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ reaches value ~10, independently of the amount of salt introduced. Such significant changes of polydispesrity indicate that besides of chain-breaking, recombination of macroradicals leading to a longer, linear chains also occurs. The photobranching and photocrosslinking in PEO does not occur neither in pure polymer nor in the presence of nickel salt.

Above results are evidence that main chain scission in PEO is efficiently accelerated by the presence of nickel(II) chloride. We can conclude, that in this case either homolytic bond-cleavage reactions at weak points in the polymer chains (typical for pure PEO) or degradation photoinitiated by free radicals coming from nickel(II) chloride can take place.

Resulting of addition of $NiCl_2$ to polymer solution slight decrease of LVN of undegraded PEO is observed (Fig. 1). It is caused by binding of the salt molecules to polymer chains and their aggregation. We suppose that pseudo-crown structure are formed in some fragments of PEO chains. More extended chains are transformed to a random coils but Ni

Table 1
Changes of average molecular weights and polydispersity ($\bar{M}_{\mathrm{w}}/\bar{M}_n$) in PEO and PEO with $NiCl_2$ after UV-irradiation

Sample	$\bar{M}_{\mathrm{n}}$	$\Delta\bar{M}_{\mathrm{n}}$, %	$\bar{M}_{\mathrm{w}}$	$\Delta\bar{M}_{\mathrm{w}}$, %	$\bar{M}_{\mathrm{z}}$	$\Delta\bar{M}_{\mathrm{z}}$, %	$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$
PEG - undegraded	18710	–	81870	–	267270	–	4.37
PEO - 2 h UV	13600	27.3	67730	17.3	220100	17.7	4.98
PEO - 4 h UV	11250	39.9	58260	28.8	205040	23.3	5.18
PEO + 1% $NiCl_2$ - 2 h UV	2660	85.8	26460	6.7	73490	72.5	9.95
PEO + 1% $NiCl_2$ - 4 h UV	1350	92.8	16170	80.2	47170	82.3	11.98
PEO + 3% $NiCl_2$ - 2 h UV	1120	94.0	11530	85.9	33330	87.5	10.30
PEO + 3% $NiCl_2$ - 4 h UV	1270	93.2	12480	84.7	37325	86.0	9.83

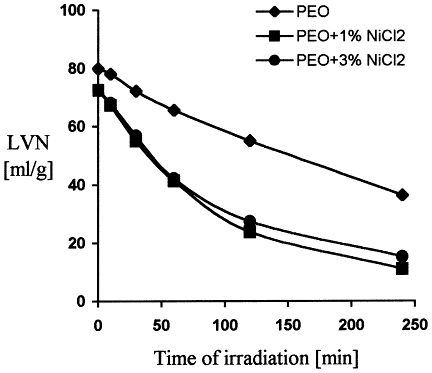


Fig. 1. Changes of the limiting viscosity numbers of PEO and PEO doped by $NiCl_2$ during UV-irradiation ($\lambda = 254$ nm, PEO concentration = 1% m/v).

cations can be entrapped in some loops of host polymer. Probable conformations of PEO are shown in Scheme 1.

The viscometry measurements allows the calculation of the changes of limiting viscosity numbers and the average number of main chain scission in PEO caused by UV-irradiation. These results are presented in Fig. 1 and Table 2. The changes of LVN in pure PEO are slower and less efficient than those in PEO with 1–3% $NiCl_2$, but kinetic curves in Fig. 1 could suggest that accelerating effect of nickel salt is not so high as was concluded on the base of GPC results. It is necessary to remember that about LVN values decide not only real chain length (related to polymerisation degree) but also its conformation depending on circumstances, solvent and interactions between macromolecules. As was mentioned above, these interactions are strongly changed by introduction of metal salts to polymer solution. Moreover, changes of chemical structure resulting of photooxidative degradation of PEO also significantly influence both short-range and long-range interactions influencing shape and size of macromolecules.

However, calculated numbers of chain scission per molecule (Table 2) again confirm very efficient action of $NiCl_2$ in PEO photodegradation. S values of PEO + (1–3%) $NiCl_2$ are about three times higher that in case of pure PEO already after short time of UV-irradiation (10–30 min).

Table 2
Number of chain scission (**S**) per molecule in PEO and PEO doped by $NiCl_2$ during UV-irradiation

Sample	Time of irradiation				
	10 min	30 min	1 h	2 h	4 h
PEO	0.04	0.18	0.38	0.84	2.64
PEO + 1% $NiCl_2$	0.13	0.57	1.49	5.19	20.86
PEO + 3% $NiCl_2$	0.11	0.49	1.44	3.89	11.92

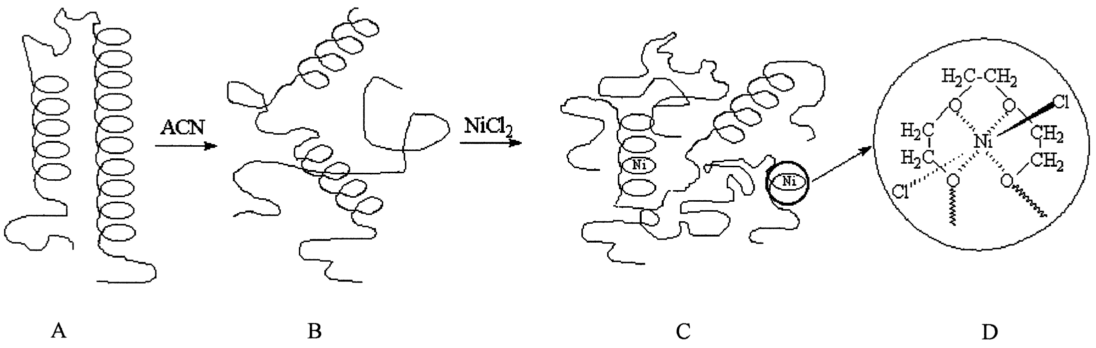
These differences in *S* values increases with prolongation exposure time. After 1–4 h UV-irradiation, numbers of chain scission in PEO + $NiCl_2$ are ~4 to 8 times larger than in PEO alone at the same time.

Photooxidation of PEO + $NiCl_2$ in acetonitrile solutions as well as in thin films was monitored by FTIR. An example IR absorption changes for PEO + $NiCl_2$ is shown in Figs. 2 and 3. Formation of broad absorption bands in 1600–1800 cm^{-1} and 3100–3700 cm^{-1} range can be attributed to carbonyl and hydroxyl/hydroperoxide groups, respectively. Carbonyl band has maximum at 1721 cm^{-1} with the shoulders at 1748 and 1648 cm^{-1}, hydroxyl band is centred at 3500 cm^{-1}. Moreover, significant changes are observed in ether stretching range (1000–1260 cm^{-1}).

It is seen in Fig. 4 that in pure PEO photooxidation starts after 2 h induction period and absorbance changes reach plateau already after 4 h UV-irradiation. Induction period of photooxidation is shorter in PEO doped by $NiCl_2$ (in sample with 3% of salt, it equals 20 min but in PEO containing 1% salt is not detectable). Simultaneously, the efficiency of carbonyl group formation is much higher in PEO + $NiCl_2$.

Enhancing of PEO photooxidation by $NiCl_2$ is observed not only in solution but also in solid state (Fig. 3). Spectra of undoped PEO film do not show any changes in carbonyl and hydroxyl region up to 8 h UV-irradiation. $\Delta A(C{=}O)$ in PEO + $NiCl_2$ films is measurable after 20 min of induction period and then quickly increases. C=O absorbance does not change significantly in these samples after exposure time longer than 4 h.

Unexpectedly, the effect of 1% addition is more significant that caused by 3% of salt in solution as well as in solid state. The reason of this phenomenon is probably



Scheme 1. Conformations of PEO in solid state (A), in acetonitrile solution (B) and in the presence $NiCl_2$ (C); possible structure of PEO + $NiCl_2$ complex (D).

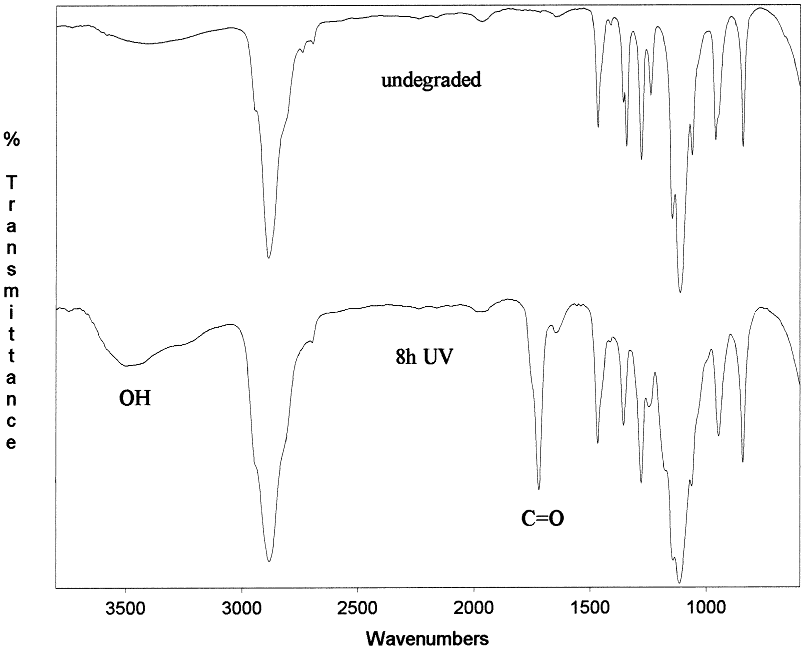


Fig. 2. FTIR spectra of PEO + 1% $NiCl_2$: undegraded and after 8 h UV-irradiation (UV-irradiation was carried out in 2% ACN solution, spectra were taken from films).

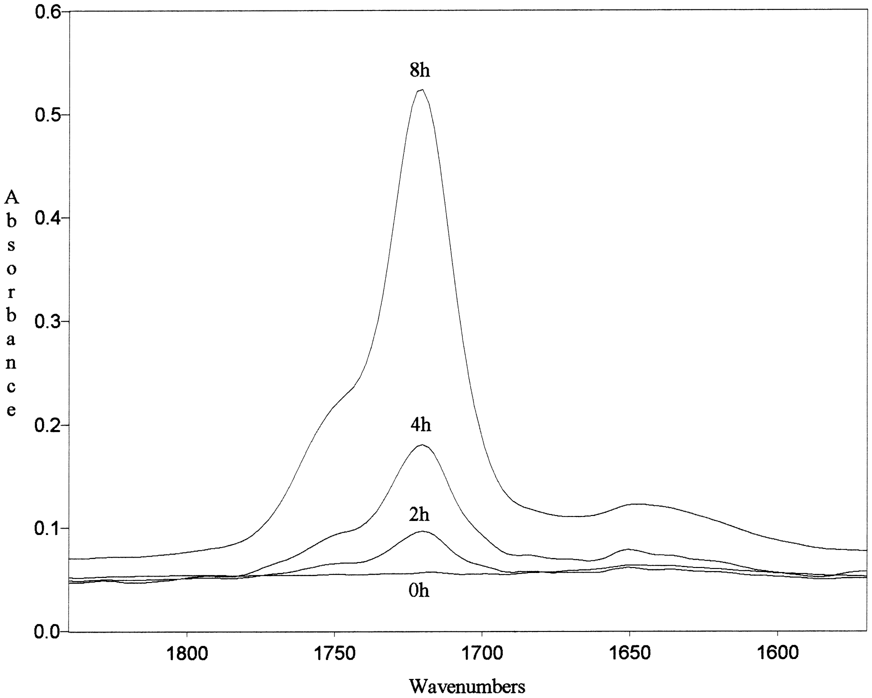


Fig. 3. Changes of FTIR spectra in carbonyl region for PEO + 1%$NiCl_2$ during UV-irradiation (numbers indicate the time of irradiation in hours).

different degree of dispersion of inorganic compound in PEO macrochains and different degree of coordination bonding in samples varying composition. In samples with 3% $NiCl_2$ aggregation is probably larger than in sample with 1% of this salt, therefore, the access of oxygen is impeded.

Changes of absorbance due to hydroxyl/hydroperoxide groups observed during UV-radiation of samples in solution and in solid films are irregular. It means that competitive reactions of formation and decay of OH/OOH groups in PEO occurs. It is not surprising because hydroperoxides are very photounstable groups and as a result of their decay, further

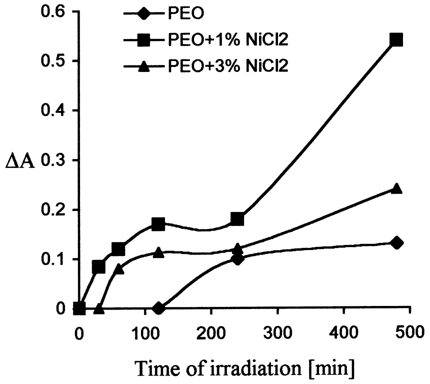


Fig. 4. Kinetics of carbonyl group formation during photooxidation of PEO and PEO doped by $NiCl_2$ in acetonitrile solution (concentration of PEO = 2% m/v).

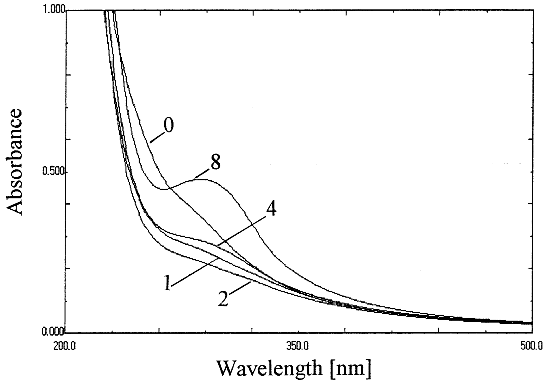


Fig. 6. Changes of UV–Vis absorption spectra of 2% PEO solution in ACN caused by UV-irradiation (numbers indicate the time of irradiation in hours).

reactions take place. Such secondary reactions lead mainly to creation of carbonyl groups detected in PEO. However, here also variations of absorbance for polymer containing 1–3% $NiCl_2$ prove the accelerating effect of salt on PEO photooxidative degradation, in which OH and OOH groups participates. It is generally accepted, that transition metal salts enhance hydroperoxide decomposition and supply free radical initiating species.

Concentration of photooxidation products containing carbonyl groups (proportional to absorbance) in polymer solution (Fig. 4) is a few times higher than that in solid state (Fig. 5). Similar effect was observed during photooxidative degradation of the same type of PEO doped by $CoCl_2$ [18]. It can be explained by the different structures of PEO chains in both physical states. In solid state, the crystalline very dense network dominates the amorphous phase of PEO (Scheme 1). Then, the flexibility of chains is hampered by such rigid structures and the diffusion of oxygen is more difficult (oxygen molecules can penetrate only disordered regions). In solution, only residual ordered segments can be statistically distributed inside macrochains but generally, crystalline structure does not exist. Thus, all photoreactions in polymeric solution are facilitated and occurs in whole volume in contrast to photoprocesses in films which take place only in thin surface layer.

Studies of UV–Vis absorption spectra provide additional data about photochemical transformations of PEO and PEO + $NiCl_2$ and also about the structure of samples. UV-irradiation of PEO and PEO doped by nickel salt in ACN solution leads firstly (after 1–2 h) to the decrease of absorbance in 200–350 nm range (Fig. 6). It is caused by significant degradation of PEO. Next, after 4–8 h UV-irradiation, a systematic increase in whole UV–Vis region with formation of absorption band with maximum at 286 nm is observed. It results from the formation of new oxidation and degradation products such as carbonyl groups and double bonds. The kinetic curves in Fig. 7 illustrate the influence of nickel salt on chromophore formation in PEO during UV-irradiation. In all spectra, the minimum absorbance at 286 nm occurs after 2 h of exposure, however, the decrease observed in PEO + $NiCl_2$ is much higher than that in pure PEO. Also formation of new degradation products containing chromophores is faster in the presence of nickel salt.

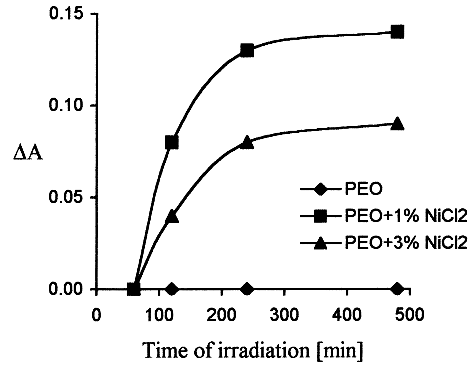


Fig. 5. Kinetics of carbonyl group formation during photooxidation of films of PEO and PEO + $NiCl_2$.

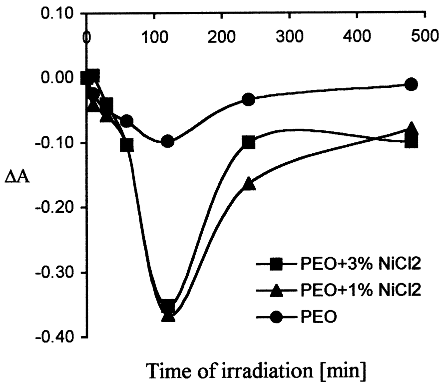


Fig. 7. Changes of absorbance at 286 nm in PEO and PEO with $NiCl_2$ addition vs. irradiation time (UV-irradiation was carried out in 2% ACN solution).

Table 3
Changes of onset temperature of melting (T_0), temperature in maximum of melting peak (T_{max}), enthalpy of melting (H_m) and crystallinity degree (X_c) in PEO and PEO with $NiCl_2$ addition caused by UV-irradiation (obtained from DSC)

Sample	Time of UV-irradition (h)	T_0 (°C)	T_{max} (°C)	ΔH_m (J/g)	X_c (%)	ΔX_c[a] (%)
PEO (undegraded)	–	53.59	60.37	133.87	60.6	–
PEO	2	56.58	61.76	155.13	70.3	9.7
PEO	4	56.54	61.49	159.59	72.3	11.7
PEO	8	55.31	60.64	160.35	72.6	12.0
PEO + 1% $NiCl_2$	2	54.11	58.98	163.10	73.9	13.0
PEO + 1% $NiCl_2$	4	53.27	58.30	159.17	72.1	11.5
PEO + 1% $NiCl_2$	8	52.62	58.08	155.00	70.2	9.6
PEO + 3% $NiCl_2$	2	52.57	57.79	157.38	71.3	10.7
PEO + 3% $NiCl_2$	4	52.10	55.70	153.05	69.3	8.7
PEO + 3% $NiCl_2$	8	51.81	55.19	147.94	67.0	6.4

[a] Changes of crystallinity degree after UV irradiation: $\Delta X_c = X_c(t) - X_c(0)$; (0 and t in parenthesis refer to irradiation time).

The crystallinity changes caused in PEO and PEO + $NiCl_2$ by UV-radiation were monitored by DSC. Distinct melting peak appears at 52–66°C range in all samples. The temperature of the melting start (onset) and temperature at the maximum of peak in pure PEO slightly increases in the first period of light exposure (Table 3). Simultaneously in this sample, the increase of enthalpy of melting and crystallinity degree is observed, which is simple a evidence of consumption of amorphous fraction of PEO.

In PEO with 1–3% $NiCl_2$, the T_0 and T_{max} temperatures show opposite trends — they slightly decrease during UV-irradiation. The changes of crystallinity degree (ΔX_c, %) in PEO containing 1% or 3% $NiCl_2$ after 2 h of irradiation are higher than the relative changes in PEO alone. However, prolonged irradiation time (4–8 h) causes smaller differences in doped PEO than that in pure PEO.

These changes can be explained as follow: At the beginning of exposure the amorphous phase undergoes efficient decomposition (it is observed as a rise in X_c) and then, after higher doses of irradiation also crystalline areas are destroyed (it is demonstrated by a drop in X_c).

3.1. What is the reason of such action of $NiCl_2$ during UV-irradiation of PEO?

It is known that UV-irradiation causes the excitation of PEO as well as $NiCl_2$ molecules. In case of excitation of complexes by radiation corresponding to d–d transition wavelength, the main reactions are ligand substitution or compound isomerisation, therefore, in case of excitation by wavelength in CT range, the redox process is dominant. However, there are known to be a lot of exceptions from this rule [22,23].

The way of deactivation of excited states, which are generally not long-lived, depends on many factors: the nature of the compound, circumstances, temperature, the presence of quenching or deactivating additives, the wavelength of exciting light, etc. The loss of energy occurs by physical process (energy transfer, photoluminescence) or in chemical reactions (breaking of chemical bonds with free radical generation, electron transfer). The concurrence of these reactions in complex systems should be considered.

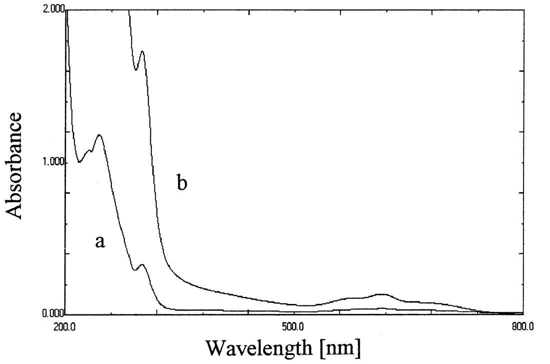


Fig. 8. UV–Vis absorption spectra of $NiCl_2$ and PEO + 1% $NiCl_2$ in ACN solution (concentration of $NiCl_2$ = 0.063% mlv, concentration of PEO = 2% m/v).

Although the study of structure of PEO + $NiCl_2$ complexes was not our aim, we should remember that small amount of coordination bonds between Ni(II) and oxygen atoms from PEO exist in our system. Thus, typical photoreactions characteristic for CT complexes can occur.

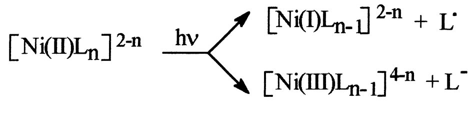
Ni^{2+} is the most popular and stable oxidation state among possible states of nickel (+1 to +4). Coordination number of nickel complexes varies from 4 to 6. Its compounds favour planar square, tetrahedral or octahedral structure. Electronic spectra (Fig. 8) and blue–green colour of $NiCl_2$ and PEO + $NiCl_2$ in acetonitrile solutions suggest that these complexes have similar octahedral symmetry [24–27].

Small changes in electronic spectra of $NiCl_2$ and $NiCl_2$ doped to PEO suggest that some ligands in coordination sphere of Ni(II) can be substituted:

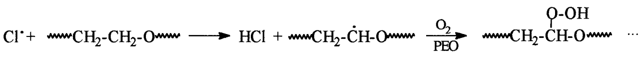
$$[NiL_n] + X \rightarrow [NiL_{n-1}X] + L$$

where $L = Cl^-$, CH_3CN, H_2O (from atmospheric moisture), X = PEO and n-the coordination number. Similarly in PEO + $NiBr_2$ complexes it was found that the nickel central ion is surrounded by both oxygen and bromide nearest neighbours [27].

Nickel(II) chloride can, upon UV-irradiation, undergo photoreduction to Ni(I) or photooxidation to Ni(III):



If $L^\bullet$ is chlorine atom, which is very active, the initiation of PEO degradation by hydrogen atom abstraction occurs:



$$Cl^{\cdot} + \sim CH_2\text{-}CH_2\text{-}O\sim \longrightarrow HCl + \sim CH_2\text{-}\dot{C}H\text{-}O\sim \xrightarrow[PEO]{O_2} \sim CH_2\text{-}\overset{O\text{-}OH}{CH}\text{-}O\sim \cdots$$

Carbon atom adjacent to the oxygen atom is very susceptible to radical attack and hydroperoxides are quickly formed in this position resulting in secondary reactions in the presence of atmospheric oxygen. The secondary reactions occurring in PEO + $NiCl_2$ system are certainly similar to mechanism proposed generally for free radical photooxidative degradation of polymers described elsewhere [15,18,28,29]. We can only remind that finally mixture of photodegradation products is formed in UV-irradiated PEO and some of them induces cleavage of PEO chains (for example, carbonyl groups undergoing Norrish reactions). It is obvious from our results that formation of photoproducts in PEO is efficiently accelerated by nickel salt. It is worthy adding that besides chlorine atoms, chlorine radical anions ($Cl_2^{\bullet-}$) formed during nickel(II) photolysis

$$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-}$$

can also initiate PEO degradation. Moreover, probably typical catalytic action of nickel salt also influences the photoreaction in PEO.

4. Conclusions

Summarising our result we can conclude that addition of small amount of $NiCl_2$ to PEO significantly enhances its photooxidative degradation.

The decrease of photochemical stability in PEO doping by $NiCl_2$ results from several factors:

1. Photoinduced generation of free chlorine atoms and $Cl_2^{\bullet-}$ radical anions acting as initiators of PEO degradation;
2. The weakness of ether linkages in PEO resulting in the ionic interactions of nickel salt;
3. Possibility of formation of small amount of CT complex between PEO and $NiCl_2$ with lower photochemical stability;
4. Catalytic action of $NiCl_2$ on PEO decomposition;
5. Enhancing decay of peroxides photogenerated in macrochains with formation of active radicals and ions;
6. Photoredox reactions in PEO-$NiCl_2$ system and influence of their products on PEO photostability;
7. Disturbances in helical structure of PEO caused by the presence of $NiCl_2$;
8. Facilitation of oxygen diffusion to PEO bulk caused by photodestruction of the crystalline phase.

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References

[1] H.G. Elias, An introduction to Polymer Science, VCH, Weinheim, 1997.
[2] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Elsevier Applied Science, London, 1987.
[3] H.F. Mark, N.G. Gaylord, N.M. Bikales (Eds.), Encyclopedia of Polymer Science arid Technology, Vol. 6, Wiley, New York, 1967, p. 103.
[4] F.M. Gray, Homopolymer Hosts, in: Solid Polymer Electrolytes, Chapter 2, VCH, Weinheim, 1991.
[5] M.L. Hallensleben, F. Lucarelli, Polym. Bull. 37 (1996) 759–765.
[6] D. Taton, E. Cloutet, Y. Gnanou, Macromol. Chem. Phys. 199 (1998) 2501.
[7] B. Fabre, J. Simonet, Coord. Chem. Rev. 178-180 (1998) 1211.
[8] G. Dreezen, Z. Fang, G. Goeninckx, Polymer 40 (1999) 5907.
[9] G.G. Camerom, M.D. Ingram, M.Y. Qureshi, H.M. Gearing, L. Costa, G. Camino, Eur. Polym. J. 25 (1989) 779.
[10] P. V Wright, J. Macromol Sci.-Chem. A 26 (1989) 519.
[11] H. Honda, K. Ono, Macromolecules 23 (1990) 4950.
[12] J. F Rabek, J. Lucki, B.J. Qu, W.F. Shi, Macromolecules 24 (1991) 836.
[13] J.F. Rabek, L.A. Linden, H. Kaczmarek, B.J. Qu, W.F. Shi, Polym. Deg. Stab. 37 (1992) 33.
[14] Y. Kobuke, K. Kokubo, M. Munakata, J. Am. Chem. Soc. 117 (1995) 12751.
[15] H. Kaczmarek, A. Kamińska, L.A. Linden, J. F Rabek, Polymer 37 (1996) 4061.
[16] H. Kaczmarek, Photochem. Photobiol. A: Chem. 95 (1996) 61.
[17] H. Kaczmarek, J.F. Rabek, Angew. Makromol. Chem. 247 (1997) 111.
[18] A. Kamińska, H. Kaczmarek, J. Kowalonek, Polymer 40 (1999) 5781.
[19] O.F. Solomon, I.A. Ciuta, J. Appl. Polym. Sci. 6 (1962) 683.
[20] J. F Rabek, Experimental Methods in Polymer Chemistry, Wiley, Chichester, 1980.
[21] W. Braun, K.-H. Hellwege, W. Knappe, Kolid-Z. U. Z. Polymere 215 (1967) 10.
[22] A.I. Krukov, S.J. Kuczmin, Osnovyfotochimii koordinacjonnych coedinienrj, Naukova Dumka, Kijev, 1990.
[23] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.
[24] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1988.
[25] G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, Vol. 5, pp. 1–300.
[26] R.B King (Ed.), Encyclopedia of Inorganic Chemistry, Vol. 5, Wiley, Chichester, 1994, pp. 2384–2444.
[27] R.J. Latham, R.G. Linford, A.J. Pymenburg, J. Chem. Soc., Faraday Trans. 89 (1993) 349.
[28] J.F. Rabek, Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers, Wiley, Chichester, 1987.
[29] J.F. Rabek, Poymer Photodegradation, Chapman and Hall, London, 1995.