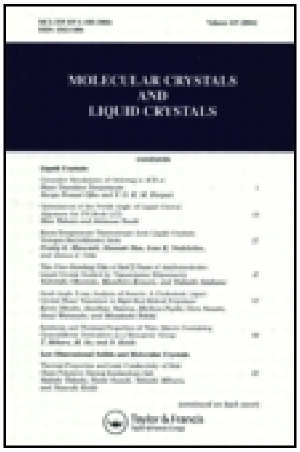

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Photoreactions of Metal Compounds, Pigments and Dyes in the Ageing of Polymeric Materials

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Photoreactions of Metal Compounds, Pigments and Dyes in the Ageing of Polymeric Materials

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Many inorganic pigments, organic dyes and other additives introduced to polymer matrix influence its photochemical stability. Some of them accelerate polymer decomposition in the ageing, others - exhibit stabilising effect. The photochemistry of these compounds depends on their chemical structure. General mechanism of polymer photodegradation as well as photoreactions occurring in metal compounds (such as transition metal halides, metal oxides, ferrocene, Fenton reagent) and organic dyes is revised.

Keywords: photodegradation, ageing, metal compounds, dyes, pigments, polymers.

INTRODUCTION

Owing to excellent properties of polymers the production of plastics increases rapidly since many years. The contemporary knowledge of polymerisation mechanisms allows to produce the new type of polymeric materials with precisely desired properties.

However, in cases of polymers a lot of factors influence on their behaviour. Not only chemical structure and conditions of uses but also average molecular weight, molecular weight distribution, macromolecules conformations, physical state of sample, morphology, tacticity, crystallinity, polarity, chain branching or crosslinking and structural defects (for example head-to head structures) determine final polymer properties [1,2].

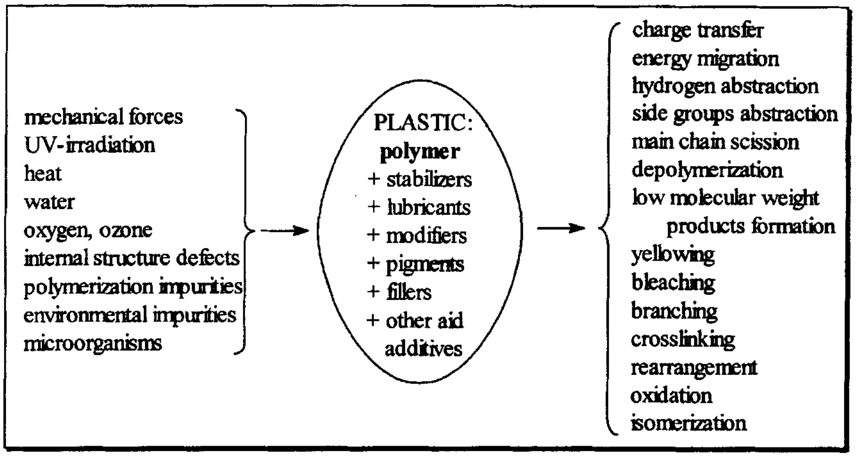
Moreover, polymer properties can be modified in a broad range by addition of special substances such as plasticizers, fillers, pigments, dyes, thermal and photostabilizers, flame retardants, compounds improving mechanical properties, etc. All these compounds can influence the course of photoreactions during plastic ageing. Resulting of intensive scientific research focused on studies of degradation and stabilisation of polymers, the new products are characterised by a long lifetime [3,4]. The modern, sophisticated, techniques developed recently help in studies of polymer degradation [5-9].

Photochemical properties of polymers are specially sensitive to the traces of active impurities and aid agents introduced into polymer bulk (often in large amount). Substances having chromophore groups (even in small concentration) act as initiators or sensitizers and accelerate polymer photodegradation [10-14]. Energy of light absorbed by small molecules can be transferred to macrochains and can induce phototransformations even in very resistant polymers. In case of turbid samples, light energy is reflected or dissipated and photoeffect may be smaller than that in transparent species containing small amount of absorbing groups. However, typical light absorbers specially added to polymers act as photostabilizers owing to their screening effect. In pigmented plastic, mechanisms of reactions caused by UV-irradiation or visible light are more complicated because of the high inhomogenity of samples. In such complex mixture as plastic, the synergistic or antagonistic effect of individual components takes place.

In this work, some photoreactions occurring in chosen organic and inorganic compounds applied in plastics production are presented and the influence of these substances on photo-oxidative degradation of polymers is discussed.

1. PRINCIPLES OF POLYMERS DEGRADATION

Main reactions occurring in polymers containing different additives under environmental conditions are listed in Scheme1:



SCHEME 1. Factors influencing plastics deterioration and main processes occurring in the polymer ageing.

Degradation of polymers is initiated by heat, light, mechanical forces, internal or external impurities [10-14]. Free radicals or/and active ions are formed after an induction period. If macromolecules absorb UV-irradiation, random breaking of weak chemical bonds takes place. Once initiated reaction involves secondary processes by free radicals (or ionic) mechanism. Alkyl macroradicals react rapidly with atmospheric oxygen giving peroxy macroradicals, which can abstract hydrogen atoms from neighbouring macromolecules and form hydroperoxides. The transfer or migration of energy leads to activation of other parts of macromolecules, which were not directly attacked by initiating agents. In chain propagation step, different functional groups (such as hydroxyl, hydroperoxy, carbonyl and unsaturated groups) are created in macromolecules. Carbonyl groups undergo Norrish type I and II reactions leading to the reduction of polymer molecular weight. Sometimes, opposite reactions occur simultaneously, for example: chain scission and crosslinking, yellowing and bleaching, cyclization and ring opening reactions. Termination occurs mainly by bimolecular recombination or disproportionation of macroradicals.

2. PHOTOCHEMISTRY OF METAL COMPOUNDS

Polymers are in contact with metallic parts of reactors and processing installations. Plastic cables used in electrotechnique are in contact with copper wires. Moreover, typical fillers and inorganic pigments can be contaminated by metal ions. Thus, the influence of metal ions on polymer degradation must be taken into account.

$$
\begin{array}{l}
MX \xrightarrow{h\nu} M^{\cdot} + X^{\cdot} \\
X^{\cdot} + PH \longrightarrow P^{\cdot} + HX \\
MX \xrightarrow{h\nu} (MX)^{*} \\
(MX)^{*} + PH \longrightarrow MX + (PH)^{*} \\
(PH)^{*} \longrightarrow P^{\cdot} + H^{\cdot} \\
M^{n+} + POOH \rightleftharpoons [M^{n+}.....POOH] \rightleftharpoons M^{(n+1)+} + PO^{\cdot} + OH^{-} \\
M^{(n+1)+} + POOH \rightleftharpoons [M^{(n+1)+}.....POOH] \rightleftharpoons M^{n+} + POO^{\cdot} + H^{+} \\
MX_2 + PH \longrightarrow MX + P^{\cdot} + HX \\
MX + PH \longrightarrow M + P^{\cdot} + HX \\
M^{n+} + O_2 \longrightarrow [M^{n+}.....O_2] \\
[M^{n+}.....O_2] + PH \longrightarrow M^{n+} + P^{\cdot} + HO_2^{\cdot} \\
M^{n+} + O_2 \longrightarrow M^{(n+1)+} + O_2^{\cdot -}
\end{array}
$$

SCHEME 2. Photoreactions of transition metal compounds (where X is halogen).

Transition metal ions (M^{n+}) mostly catalyse photochemical degradation (as well as thermal degradation) of polymers. This is caused by their photolysis with formation free radicals, polymer photosensybilization, decomposition of peroxides, direct reactions with macromolecules, formation of active complexes with oxygen and superoxide radical-anions (Scheme 2) [15-20].

Photochemistry of iron salt [21-26] is presented in Scheme 3 and 4. Iron (III) chloride forms different complexes in water solution. These complexes show reversible photochromic effect due to the rapid electron exchange between iron ions (Scheme 3). Chlorine radicals formed in $FeCl_3$ photolysis act as an initiator in polymer degradation.

$$
\begin{gathered}
2FeCl_3 \rightleftharpoons (FeCl_2^{+}.....FeCl_4^{-}) \\
(FeCl_2^{+}...FeCl_4^{-}) \xrightarrow{h\nu} (FeCl_2^{\cdot+}...FeCl_3^{-}) + Cl^{\cdot} \\
(FeCl_2^{\cdot+}...FeCl_3^{-}) \xrightarrow{dark} FeCl^{\cdot+} + FeCl_4^{-} \\
FeCl^{\cdot+} + Cl^{\cdot} \xrightarrow{dark} FeCl_2^{+} \\
FeCl_4^{-} \xrightarrow{h\nu} FeCl_2 + Cl^{-} + Cl^{\cdot} \\
FeCl^{\cdot+} + O_2 \longrightarrow FeCl^{2+} + O_2^{\cdot-} \\
FeCl^{2+} + Cl^{-} \longrightarrow FeCl_2^{+} \\
FeCl_2^{+} + FeCl_4^{\cdot} \longrightarrow (FeCl_2^{+}.....FeCl_4^{-})
\end{gathered}
$$

SCHEME 3. Photochemistry of iron (III) chloride.

Iron (II) ions absorb UV-irradiation and produce free electrons. In the presence of water traces, hydrogen atoms can be formed (Scheme 4).

$$
\begin{gathered}
Fe^{2+} \xrightarrow{h\nu} (Fe^{2+})^{*} \\
(Fe^{2+})^{*} \longrightarrow Fe^{3+} + e^{-} \\
(Fe^{2+})^{*} + H_3O^{+} \longrightarrow Fe^{3+} + H_2O + H^{\cdot} \\
FeCl_2 + O_2 \longrightarrow FeCl_2^{+} + O_2^{\cdot-} \\
FeCl_2^{+} + Cl^{-} \longrightarrow FeCl_3
\end{gathered}
$$

SCHEME 4. Photochemistry of iron (II) in water.

Ferrocene - dicyclopentadienyliron(II), (Cp_2Fe) is also degradation accelerating agent, which easily forms electron-donor acceptor complexes with halogen compounds such as CCl_4 [10,13,27] and undergoes photoreactions shown in Scheme 5. Trichlororadicals ($^{\cdot}CCl_3$) are able to initiate polymerization of vinyl compounds. Ferrocene and iron-arene salts initiate also polymerization of pyrrole (C_4H_5N) in halogenated compounds. Similar photochemistry exhibit another iron metallocenes Cp_2M (where M = Ru or Os) [28].

$$\begin{aligned}
&Cp_2Fe + CCl_4 \rightleftharpoons (Cp_2Fe)^+(CCl_4)^-\\
&(Cp_2Fe)^+(CCl_4)^- \xrightarrow{h\nu} Cp_2Fe^+Cl^- + {}^{\cdot}CCl_3\\
&Cp_2Fe^+Cl^- + 2CCl_4 \xrightarrow{h\nu} FeCl_3 + 2CpCl_3\\
&2CpFe^+Cl^- \xrightarrow{h\nu} Cp_2Fe + FeCl_2 + 2Cp^{\cdot}\\
&Cp_2Fe^+Cl^- + FeCl_2 \rightleftharpoons FeCl_3 + Cp_2Fe\\
&Cp_2Fe^+Cl^- + FeCl_3 \rightleftharpoons Cp_2Fe{+}FeCl_4^-
\end{aligned}$$

SCHEME 5. Photoreactions of ferrocene in tetrachlorocarbon.

The mixture of iron salt with hydrogen peroxide (Fenton reagent), in which exothermic oxidation of Fe(II) to Fe(III) occurs, is a source of various radicals and ions (Scheme 6). These products are efficient initiators of polymer degradation, which is additionally accelerated by UV-irradiation [13,25]

$$\begin{aligned}
&Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO^{\cdot}\\
&HO^{\cdot} + H_2O_2 \longrightarrow HO_2^{\cdot} + H_2O\\
&HO_2^{\cdot} + H_2O_2 \longrightarrow HO^{\cdot} + H_2O + O_2\\
&HO^{\cdot} + Fe^{2+} \longrightarrow Fe^{3+} + OH^-\\
&HO_2^{\cdot} + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + O_2\\
&Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^{\cdot}\\
&HO^- + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot}\\
&HO_2^{\cdot} + Fe^{2+} \longrightarrow HO_2^{\cdot -} + Fe^{3+}
\end{aligned}$$

SCHEME 6. Fenton reactions.

3. PHOTOCHEMISTRY OF PIGMENTS

Another type of metal compounds influencing polymer degradation are inorganic pigments for example TiO_2 (titanium white) or ZnO (zinc white).

TiO_2, which exists in two different crystalline forms (anatase and rutile), has an interesting photochemical properties (Scheme 7) [3,10,13,14]. The anatase is less stable and it catalyses photodegradation of polyethylene, polyamides, poly(vinyl chloride), contrary to rutile, which hampers photodecomposition of these polymers. TiO_2 behaves as semiconductor. It was suggested that electron-hole (e^--p^+) pairs are formed on the pigment surface. The positive hole reacts with hydroxyl groups giving hydroxy radicals. Moreover, TiO_2 causes catalytic decomposition of hydroperoxides formed in degraded polymers.

$$\boxed{\begin{gathered}
TiO_2 \xrightarrow{h\nu} e^- + h^+ \\
h^+ + Ti^{4+}OH^- \longrightarrow Ti^{4+} + HO^{\cdot} \\
e- + Ti^{4+} \longrightarrow Ti^{3+} \\
Ti^{3+} + O_2 \longrightarrow Ti^{4+} + O_2^{\cdot -} \\
TiO_2 + O_2 \xrightarrow{h\nu} TiO_2^{\cdot +} + O_2^{\cdot -} \\
TiO_2^{\cdot +} + O_2^{\cdot -} \longrightarrow TiO_2 + {}^1O_2 \\
TiO_2 \xrightarrow{h\nu} TiO_2{}^* \\
TiO_2{}^* + POOH \longrightarrow TiO_2 + PO^{\cdot} + HO^{\cdot}
\end{gathered}}$$

SCHEME 7. Photochemistry of titanium dioxide.

Similarly to TiO_2, also zinc oxide accelerates photooxidative degradation of polymers. Photochemical reactions of ZnO (Scheme 8) are also very complex [3,13,14]. Active radicals and ions formed in these processes can diffuse to polymer matrix and react with macromolecules.

$$\boxed{\begin{gathered}
ZnO \xrightarrow{h\nu} e^- + p^+ \\
p^+ + ZnO \longrightarrow Zn^+ + O \\
p^+ + Zn^+ \longrightarrow Zn^{2+} \\
e^- + Zn^+ \longrightarrow Zn \\
e^- + O_2 \longrightarrow O_2^{\cdot -} \\
e^- + O \longrightarrow O^{\cdot -} \\
O_2 + O^{\cdot -} \longrightarrow O_3^{\cdot -} \\
2O_2^{\cdot -} + H_2O \rightleftharpoons 2HO_2^{\cdot} + 2OH^- \\
2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2
\end{gathered}}$$

SCHEME 8. Photochemistry of zinc oxide.

4. PHOTOCHEMISTRY OF ORGANIC DYES

The organic dyes containing chromophore groups are widely used in industry for colouring of polymeric materials. Such compounds, in excited states, can react with macromolecules and cause main chain scission. They often sensitise macromolecules, which subsequently undergo unwanted reactions. The photochemistry of dyes is related to their structure, pH and medium used. (Scheme 9)[10,13,29,30].

$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^*$ (singlet or triplet)
$\mathrm{D}^* \longrightarrow \mathrm{D}^{\cdot +} + e^-$ (semioxidized radical kation)
$\mathrm{D}^* + e^- \longrightarrow \mathrm{D}^{\cdot -}$ (semireduced radical anion)
$\mathrm{D}^* + \mathrm{PH} \longrightarrow \mathrm{DH}^{\cdot} + \mathrm{P}^{\cdot}$
$\mathrm{DH}^{\cdot} \rightleftharpoons \mathrm{D}^{\cdot -} + \mathrm{H}^+$
$\mathrm{D}^* + \mathrm{HD} \longrightarrow \mathrm{D}^{\cdot -} + \mathrm{HD}^{\cdot +}$
(where PH - polymer, HD - electron donor)

SCHEME 9. Radicals formed from photoactivated dyes.

Oxygen generally suppresses above reactions because of quenching of dye excited states (Scheme 10). Formation of singlet oxygen was observed in eosin, fluorescein, Rose Bengal, crystal violet and rhodamine G. In organic solvents, dye molecule may forms semireduced radical, which subsequently abstracts hydrogen atom to give the *leuco-form* of dye. $\mathrm{DH_2}$ is also formed by a disproportionation of DH·.

$\mathrm{D}^* + \mathrm{O_2} \longrightarrow \mathrm{D} + {}^1\mathrm{O_2}$
$\mathrm{D}^* + \mathrm{O_2} \longrightarrow \mathrm{X} + \mathrm{HO_2^{\cdot}}$ (or $\mathrm{O_2^{\cdot -}}$)
$\mathrm{D}^* + \mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{D} + \mathrm{R}^{\cdot} + \mathrm{HO_2^{\cdot}}$
$\mathrm{DH_2}^* + \mathrm{H_2O} + \mathrm{O_2} \longrightarrow \mathrm{DH}^{\cdot} + \mathrm{HO}^{\cdot} + \mathrm{H_2O_2}$
$\mathrm{DH}^{\cdot} + \mathrm{DH}^{\cdot} \longrightarrow \mathrm{D} + \mathrm{DH_2}$
$\mathrm{DH_2}$ - reduced form of dye (leuco)

SCHEME 10. Reactions of photoexcited dyes with oxygen.

Photochemistry of dyes is dependent on solvent used. Examples of dye photoreactions occurring in the presence of $\mathrm{CCl_4}$ are shown in Scheme 11:

$$\begin{array}{l}
\mathrm{DH} \xrightarrow{h\nu} \mathrm{DH}^{*} \\
\mathrm{DH}^{*} + \mathrm{CCl_4} \longrightarrow \mathrm{DH}^{\cdot +} + \mathrm{CCl_4^{\cdot -}} \\
\mathrm{DH}^{\cdot +} + \mathrm{CCl_4^{\cdot -}} \longrightarrow \mathrm{D}^{+} + \mathrm{H}^{\cdot} + \mathrm{CCl_3^{\cdot}} + \mathrm{Cl}^{-} \\
\mathrm{PH} + \mathrm{CCl_3^{\cdot}} \longrightarrow \mathrm{CHCl_3} + \mathrm{P}^{\cdot} \\
\mathrm{P}^{\cdot} + \mathrm{O_2} \longrightarrow \mathrm{PO_2^{\cdot}}
\end{array}$$

SCHEME 11. Photoreactions of dye in the presence of tetrachlorocarbon.

If dyes added to polymer matrix reflects light or loses the absorbed energy in harmless way (for example in fluorescence or phosphorescence processes), it acts as stabiliser. Such protective action was observed in case of carotenoids [31-34]. Excited β-carotene molecules use their energy for *cis-trans* isomerization and macromolecules in matrix remain unchanged. This phenomenon can be utilised in protection of natural polymers (such as proteins) against UV-radiation. [33-34]. Moreover, carotenoids deactivate singlet oxygen by physical or chemical quenching [10].

Thermal and photochemical stability of organic dyes is limited. Coloured plastics undergo bleaching upon light (or heat) because of dyes photolysis, thus the using of very effective stabiliser is needed.

Photochemistry of dyes is also studied in aspect of their application as initiators in photopolymerization processes (photocuring) [35-39].

It is necessary to mention, that recently, the role of organic dyes increases comparing to inorganic pigments containing heavy metals, which are dangerous for environment.

CONCLUSIONS

Substances added to polymers undergo photolysis (or thermal decay) during plastics storage and using (specially in outdoor applications) and initiate or accelerate polymer decomposition. Activity of inorganic pigments is connected with possibility of electron transfer. Free radicals and ions formed during UV-irradiation of compounds present in polymer matrix are a main source of initiation species. Moreover, the kind of solvent and atmosphere influence significantly the course of polymer decomposition.

Some type of modifiers show protection effect on photooxidative degradation. There are mainly substances, which use absorbed energy in physical or chemical processes, which do not cause the changes in polymer structure.

Degradation products formed during plastic ageing can be harmful for people, specially in case of plastics having contact with food (packaging materials). Pollution of soil (during plastic waste composting) or rivers (by introduction of contamination with sewer) is also danger for environment purity.

References

[1.]D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam 1990

[2.]Bodor, *Structural Investigation of Polymers*, Akademiai Kiado, Budapest 1991.

[3.]J. F. Rabek, *Photostabilization of Polymers*, Elsevier Applied Science, London, 1990.

[4.]H. Zweifel, *Stabilization of Polymeric Materials*, Springer-Verlag, Berlin 1998.

[5.]J. F. Rabek, *Experimental Methods in Polymer Degradation*, John Wiley & Sons Ltd, Chichester 1980.

[6.]T. R. Crompton, *The Analysis of Plastics*, Pergamon Series in Analytical Chemistry, vol. 8, Pergamon Press, Oxford 1984;

[7.]W. Przygocki, *Metody fizyczne badań polimerów*, PWN, Warszawa 1990.

[8.]T. R. Crompton, *Practical Polymer Analysis*, Plenum Press, New York 1993.

[9.]*Polymer Characterization*, edited by B. J. Hunt, M. I. James, Blackie Academic & Professional, London 1993.

[10.]B. Rånby, J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, John Wiley and Sons, London 1975.

[11.]J. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge 1987.

[12.]J. F. Rabek, *Photodegradation of Polymers. Physical Characteristics and Applications*, Springer Verlag, 1996.

[13.]J. F. Rabek, *Polymer Photodegradation. Mechanisms and Experimental Methods*, Chapman & Hall, London 1995.

[14.]*Current Trends in Polymer Photochemistry*, edited by N. S. Allen, M. Edge, I. q R. Bellobono, E. Selli, Ellis Horwood, N. York 1995.

[15.]J. F. Rabek, *Photochem. Photobiol.*, 7, 5 (1968).

[16.]B. Ranby, J. F. Rabek, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 35, 243 (1979).

[17.]Z. Osawa, *Polym. Deg. Stab.*, **20**, 203 (1988).

[18.]H. Kaczmarek, J. F. Rabek, *Angew. Makromol. Chem.*, **247**, 111 (1997).

[19.]H. Kaczmarek, *J. Photochem. Photobiol., A: Chemistry*, **95**, 61 (1996).

[20.]H. Kaczmarek, A. Kamińska, L. A. Linden, J. F. Rabek, *Polymer*, **37**, 4061 (1996).

[21.]J. F. Rabek, J. Lucki, B. J. Qu, W. F. Shi, *Macromolecules*, **24**, 836 (1991).

[22.]E. D. Owen, S. R. Brooks, *Polym. Photochem.*, **6**, 21 (1985).

[23.]T. V. Pokholok, G. B. Pariysky, N. I. Zaitseva, D. Ya. Toptygin, *Eur. Polym. J.*, **20**, 609 (1984).

[24.]J. F. Rabek, L. A. Linden, *Polym. Deg. Stab.*, **37**, 33 (1992).

[25.]L-A. Linden, J. F. Rabek, H. Kaczmarek, A. Kamińska, M. Scoponi, *Coord. Chem. Rev.*, **125**, 195 (1993).

[26.]A. Kamińska, H. Kaczmarek, G. Modrzyńska, *Polish J. Chem.*, **69**, 865 (1995).

[27.]J. F. Rabek, J. Lucki, M. Zuber, B. J. Qu, W. F. Shi, *J.M.S.-Pure Appl. Chem.*, **A29**, 297 (1992).

[28.]P. Bergamini, S. Di Martino, A. Maldotti, S. Sostero, O. Traverso, *J. Organometallic Chem.*, **365**, 341 (1989).

[29.]N. S. Allen, *Polym. Deg. Stab.*, **44**, 357 (1994).

[30.]A. Kamińska, M. Świątek, H. Kaczmarek, *Polish J. Chem.*, **71**, 1479 (1997).

[31.]M. Nowakowska, *Makromol. Chem.*, **181**, 1021 (1980).

[32.]J. F. Rabek, D. Lala, *J. Polym. Sci.: Polym. Letters Ed.*, **18**, 427 (1980).

[33.]A. Kamińska, A. Sionkowska, *Polimery*, **39**, 758 (1994).

[34.]A. Kamińska, A. Sionkowska, *J. Photochem. Photobiol., A: Chemistry*, **96**, 123 (1996).

[35.]J. Pączkowski, *Monomeryczne i polimeryczne pochodne różu bengalskiego*, ATR, Bydgoszcz 1988.

[36.]q B. Pączkowska, J. Pączkowski, D. C. Neckers, *Polimery*, **39**, 527 (1994).

[37.]Z. Kucybała, J. Pączkowski, *Polymer*, 34, 1558 (1993).

[38.]J. Pączkowski, Z. Kucybała, *Macromolecules*, **28**, 269 (1995).

[39.]J. Pączkowski, M. Pietrzak, Z. Kucybała, *Macromolecules*, **29**, 269, 5057 (1996).